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Molecular Engineering of Liquid Crystalline Polymers

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This chapter reviews the molecular engineering of main chain and side chain liquid crystalline polymers. Several factors influencing the phase transitions of liquid crystalline polymers are critically discussed. These include thermodynamics of phase transitions, isomorphism of liquid crystals, "rigidity" of rod-like mesogens and chemical heterogeneity of main chain liquid crystalline copolymers. The use of polyetherification and copolyetherification and of living cationic polymerization and copolymerization in the manipulation of phase transitions of liquid crystalline polymers is extensively discussed. This review also discusses several novel architectures such as liquid crystalline dendrimers and cyclic oligomers, liquid crystalline polymers containing crown ethers and polypodants, electron donor-acceptor complexes of discotic liquid crystalline polymers, as well as, self-assemblying supramolecular liquid crystalline polymers.

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CONTENTS

14.1 INTRODUCTION AND HISTORICAL REVIEW

Liquid crystals were discovered in 1888 by the Austrian botanist Reinitzer[1] who observed that cholesteryl benzoate exhibits two melting points. The first melting at 145.5 °C transforms the crystal phase into an anisotropic, turbid liquid which "melts" into an isotropic, clear liquid at 178.8 °C. This anisotropic liquid was first named by Lehmann in 1889 " flowing crystals", then "crystalline liquid" and finally "liquid crystal" in 1900.[2] The first synthetic nematic liquid crystals were prepared by Gattermann in 1890.[3] The first smectic liquid crystals were synthesized by Vorländer in 1902.[4]

The fifty-eight discussion organized by the Faraday Society on the 24th and 25th of April, 1933 was devoted to "Liquid Crystals and Anisotropic Melts",[5] thus recognizing the general scientific interest in the field of liquid crystals. The proceedings of this meeting are still providing a comprehensive entry to this field. In our opinion, the most valuable monographs describing the dependence between the molecular structure and the properties of thermotropic liquid crystals remain the book published by Gray in 1962 and his subsequent reviews.[6a,b,c,d] The history of the entire field of liquid crystals was described by Kelker.[7,8] A systematic description of the molecular structure-properties development during the first one hundred years of liquid crystal chemistry was published by Demus.[9] Additional monographs which can introduce the reader to the field of both thermotropic and lyotropic liquid crystals[10-13] and provide basic information also on its history,[7,8,11] classification[14] and identification of various mesomorphic textures,[15,16] are available.

To our knowledge, the idea of performing chemical reactions in anisotropic liquids belongs to Svedberg who reported his first experimental data in 1916.[17-20] In his publications Svedberg showed that the rate of decomposition of picric acid, trinitroresorcinol and pyrogallol, increases slightly with increasing temperature when the reaction is performed in the nematic phase of *p*-azoxyphenetole, jumps at the clearing point and continuous steeply upwards in the isotropic liquid. In addition, the reaction rate exhibits a distinct change when the nematic phase is under the increasing influence of a magnetic field. Regardless of the accuracy of these results, they suggest that an anisotropic phase can play the role of a "catalyst" in a certain reaction. Reactions and interactions in liquid crystalline media were recently reviewed.[21]

As early as 1922 Lehmann[22] recognized that some of the properties exhibited by liquid crystals may have analogies to those of the living state. At the Faraday Discussions from 1933[23,24] it was clearly recognized that the mobility and structural order of biological and synthetic liquid crystals furnish an ideal medium for catalytic action and that the living cell is actually a liquid crystal.

A significant citation from Bernal made at the Faraday Society meeting in 1933 is as follows:[24]

"Rinne was not the first to see that liquid crystals had a bearing on biological problems, but I think that he had glimpsed at the fundamental rôle that they played, and understood the essential nature of the properties that enabled to do so.

The biologically important liquid crystals are plainly two or more component systems. At least one must be a substance tending to para-crystallinity and another will in general be water. This variable permeability of liquid crystals enables them to be as effective for chemical reactions as true liquids or gels as against the relative impenetrability of solid crystals. On the other hand, liquid crystals possess internal structure lacking in liquids, and directional properties not found in gels. These two properties have far-reaching consequences. In the first place, a liquid crystal in a cell through its own structure becomes a proto organ for mechanical or electrical activity, and when associated in specialized cells in higher animals gives rise to true organs, such as muscle and nerve. Secondly, and probably more fundamentally, the oriented molecules in liquid crystals furnish an ideal *medium for catalytic action, particularly of the complex type needed to account for growth and reproduction. Lastly, a liquid crystal has the possibility of its own structure, singular lines, rods and cones, etc. Such structures belong to the liquid crystal as a unit and not to its molecules which may be replaced by others without destroying them, and they persist in spite of the complete fluidity of the substance. These are just the properties to be required for a degree of organization between that of the continuous substance, liquid or crystalline solid and even the simplest living cell*".

Today, it is well accepted that many of the low molar mass and polymeric biological derivatives exhibit liquid crystalline phases.[25-37] Although the elucidation of the role of liquid crystalline phases in various biological processes is in an early stage of development, it should be quite instructive to recall the following statement: "*Liquid crystals stand between the isotropic liquid phase and the strongly organized state. Life stands between complete disorder, which is death and complete rigidity which is death again*".[25]

Onsager in 1933[38] and Flory in 1956[39] predicted that rigid rod-like macromolecules should display liquid crystallinity. However, the first main chain thermotropic liquid crystalline polymer was reported in open literature only in 1975.[40] This publication is independent from the flexible spacer concept publication of deGennes[41] in the same year. However, patents on thermotropic main chain liquid crystalline polymers were published in 1973.[42] Publications dealing with the driving force behind the development of main chain thermotropic liquid crystalline polymers and various historical variants of these developments are available.[43-49]

Although the field of thermotropic side chain liquid crystalline polymers is older than that of thermotropic main chain liquid crystalline polymers, systematic investigations in this field started only after Ringsdorf et al. introduced the spacer concept in 1978.[50,51] Several monographs and review articles on side chain and main chain liquid crystalline polymers are available.[52-63] This brief introduction attempts to bring the attention to the fact that liquid crystals both low molar mass and polymers are widely spread in nature.

Since the goal of this chapter is to discuss the present state of the art of the molecular engineering of liquid crystalline polymers, we will not review the entire field, but instead will consider those issues which can be and should be used in the molecular design of liquid crystalline polymers with well defined phase transitions. This will, however, require a brief and general introduction to low molar mass and polymeric liquid crystals. For additional information on this topic the reader should consult the literature cited in this introduction. This chapter is addressed mostly to those interested in the synthesis of liquid crystalline polymers with specific phase transitions.

14.2 A BRIEF INTRODUCTION TO LIQUID CRYSTALS

14.2.1 Introduction to Low Molar Mass Liquid Crystals and Definitions

A liquid crystalline or mesomorphic phase or mesophase refers to a state of matter in which the degree of order is between the almost perfect long-range positional and orientational order present in solid crystals and the statistical long-range disorder characteristic of isotropic liquids, amorphous solids and gases. Mesogens or mesogenic groups are compounds which under suitable conditions give rise to mesophases. They can be classified in non-amphiphilic (i.e. most frequently compounds exhibiting a rod-like or disc-like shape) and amphiphilic (i.e. compounds that contain within the same molecule lipophilic and hydrophilic groups which have the ability to dissolve in organic solvents and water respectively). Thermotropic mesophases are induced by a change in temperature, while lyotropic mesophases are induced by a solvent. Some mesogens can generate amphotropic mesophases, i.e. the liquid crystalline phase can be induced either by a change in temperature, by a solvent, or by both.[64a] Other highly immiscible groups like perfluorinated and paraffinic, available within the structure of the same molecule also give rise to amphotropic mesophases.[64b]

Depending on their thermodynamic stability with respect to the crystalline phase, thermotropic mesophases can be virtual (unstable with respect to the crystalline phase), monotropic (metastable with respect to the crystalline phase), or enantiotropic (stable with respect to the crystalline phase).[65,66] Virtual mesophases exist only below the melting and crystallization temperature and therefore can not be observed. Monotropic mesophases can be observed only during cooling due to the fact that the crystallization process is kinetically controlled and therefore is supercooled, while the liquid crystalline phase is thermodynamically controlled and is not supercooled. Enantiotropic mesophases can be observed both on heating and cooling. A detailed discussion on the conversion of a mesophase from virtual into monotropic and into enantiotropic will be presented later.

Traditionally, thermotropic mesophases exhibited by rod-like or calamitic mesogens can be classified in uniaxial, biaxial, and chiral nematic (cholesteric), and a number of different smectic phases which form either an untilted layer (smectic A, s_A etc.) or a tilted layer (smectic C, s_C etc.) structure (Figure 1). Characteristic for the nematic phase is a parallel orientation of the molecules with an axis that corresponds to the long axis of the mesogen. While uniaxial nematic phases (biaxial nematic[67] phases are not of interest for this discussion) exhibit a one-dimensional degree of order, smectic phases can exhibit a two-dimensional (s_A, s_C exhibiting unstructured layer structures) or a three-dimensional (s_B, s_G, s_E, s_H exhibiting structured layer structures) order.[16] Therefore, s_B, s_G, s_E and s_H liquid crystalline phases are in fact crystalline. Disc-like molecules exhibit various columnar or discotic mesophases[68,69] (Figure 2). Plastic crystals are a class of mesophases in which sphere-shaped molecules, though orientationally completely disordered, reside (with minor fluctuations) at the points of a spatial lattice, i.e., there is positional order but orientational disorder (e.g., methane, carbon tetrachloride, carbon tetrafluoride, camphor, cyclohexanol, etc.).

Upon increasing their concentration, amphiphilic mesogens generate isotropic, and then micellar solutions. At higher concentrations rod-like micells generate hexagonal mesophases while spherical micells generate cubic mesophases. Alternatively an isotropic solution of an amphiphilic molecule can assemble directly into a lamellar liquid crystalline phase (Table 1).[11,22,33,36,70,71] Cubic mesophases do not exhibit a texture since they are optically isotropic. A brief inspection of Figure 2 and Table 1 shows that the columnar-hexagonal mesophase of discotic mesogens and the hexagonal mesophase of amphiphilic molecules are from symmetry point of view identical.

14.2.2 Liquid Crystalline Polymers

Liquid crystalline polymers can be classified into main chain, side chain and combined (Figure 3). This classification is based on the place of the polymer where the mesogen is inserted, i.e. within the main chain, as side groups, or both within the main chain and as side groups. More complex polymer architectures are also possible.[9,64,72] The mesogen used in the construction of the liquid crystalline polymer can be rod-like, disc-like or amphiphilic.[9,64,72-74] In addition to linear polymer structures, cyclic,[75] branched and crosslinked[76,77] architectures have also been synthesized. Therefore, liquid crystalline polymers display thermotropic and lyotropic mesophases which are similar to those exhibited by thermotropic and lyotropic low molar mass liquid crystals. In addition, rigid-rod like main chain non-amphiphilic polymers like poly(phenyleneterephthalamide) (Kevlar®),[78] poly(*p*-phenylene-2,6-benzobisthiazole) and poly(*p*-phenylene-2,6-benzobisoxazole)[79] exhibit lyotropic nematic mesophases.

A characteristic of side chain liquid crystalline polymers is that their polymer backbone adopts a random-coil conformation only in solution and in isotropic melt. In a nematic phase the conformation of the polymer backbone is slightly distorted. Depending on the flexibility of the polymer backbone, its conformation in the smectic phase is so highly distorted that it can even be confined to the smectic layer (in the case of polymers based on very flexible backbones) or it can cross the smectic layer (in the case of rigid backbones).[80-82]

14.3 ISOMORPHISM OF LIQUID CRYSTALS

The miscibility of various liquid crystalline low molar mass substances and polymers is of great importance both for the identification of various liquid crystalline phases and for the preparation of mixtures with well defined phase transitions. In the field of low molar mass liquid crystals, Arnold, Sackmann, and Demus have developed the miscibility rules[83-86] which can be summarized as follows: if two liquid crystalline phases are miscible, they are isomorphic, and therefore belong to the same type of mesophase. However, the reverse is not true. The situation is more complicated for mixtures of liquid crystalline polymers with low molar mass liquid crystals and for mixtures of liquid crystalline polymers. Many times similar phases of liquid crystalline polymers and low molar mass liquid crystals are not miscible.[86-89] The same is the case for similar phases of two different liquid crystalline polymers.[90] For a general discussion on this topic and a comparison of isomorphism of crystalline and liquid crystalline polymers and copolymers see reference 90. From the preparative point of view it is valuable to know that when two compounds are isomorphic within a certain mesophase, both their thermal transition temperatures and corresponding thermodynamic parameters exhibit continuous dependences versus composition. The same is the case for a copolymer. When its structural units are isomorphic within a certain phase, the corresponding transition temperatures and thermodynamic parameters exhibit continuous dependences on composition. This means that both the components of mixtures and the structural units of copolymers behave like an ideal solution. Therefore, by knowing the temperature transitions and thermodynamic parameters of the parent compounds we can apply the equations of Schroeder and Van Laar (eq. 1) and predict the phase diagram of the mixture or of the copolymer.[91]

$$F_1 = \left\{ 1 - \frac{\Delta H_1^o T_2 (T-T_1)}{\Delta H_2^o T_1 (T-T_2)} \right\}^{-1} \qquad \text{Eq. 1}$$

where F_1 is the molar fraction of component 1, T_1 and ΔH_1 are the transition temperature and the enthalpy change of pure component 1, T_2 and ΔH_2 have the same meaning for component 2, while T is the transition temperature corresponding to composition F_1. T should be lower than T_2 and higher than T_1. Thus, a phase diagram that exhibits any temperature greater or lesser than the maximum or minimum T_2 or T_1 respectively, violates the T criteria above and must therefore be discussed by the introduction of nonideality of solutions of structural units of copolymers. The negative, positive or linear dependence of T versus F_1 is determined by the parameter:

$$A = \frac{\Delta H_1^o T_2}{\Delta H_2^o T_1} \qquad \text{Eq. 2}$$

from Eq. 1.

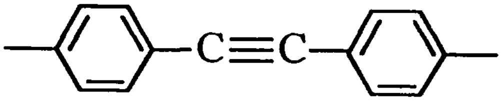
Mixtures of nematic liquid crystals with isotropic solute molecules varying in size and shape have been studied extensively over the past years both experimentally[92-96] and theoretically.[97-100] The addition of an isotropic solute to a liquid crystalline solvent decreases the nematic-isotropic transition temperature of the solvent and leads to a two phase region. This phase behavior is very sensitive to the shape of the solute and its molecular weight. Thus a change of the shape of the solute from elongated to more isotropic and an increase of its molecular weight, are both leading to a sharper decrease of the nematic-isotropic transition temperature. Flexible random-coil polymers are not miscible at all with low molar mass liquid crystals or with liquid crystalline polymers. For example, a smectic low molar mass liquid crystal could theoretically accomodate a random-coil polymer only between the smectic layers.[101]

14.4 SOME CONSIDERATIONS ON THE "RIGIDITY" OF "ROD-LIKE" MESOGENS

The traditional pathway used to synthesize low molar mass liquid crystals[6,9] and both, main chain [42-49] and side-chain[50,51,72] liquid crystalline polymers is based on the use of rigid rod-like mesogenic units. Recently, the concept of flexible rod-like mesogens or rod-like mesogens based on conformational isomerism was advanced and used in the synthesis of both side chain[72,102] and main chain[103,106] liquid crystalline polymers. Low molar mass liquid crystals based on flexible mesogens were discussed elsewhere.[72,102,103] Depending on their conformational or configurational rigidity we have suggested the classification of rod-like mesogenic groups as rigid rod-like, semirigid or semiflexible rod-like and flexible rod-like groups.[107] The flexibility of these mesogens will be important for further discussions.

14.4.1 Rigid Rod-Like Groups

Rigid rod-like mesogenic units as diphenylacetylene (1), oligo-*p*-phenylene (2), and benzoxazole (3) derivatives are based on linearly substituted aromatic or heterocyclic rings. They exhibit free rotation about certain C-C bonds as in the case of (1-3), but this rotation does not perturb the elongated or extended shape, and the molecule retains its rigid rod-like character. Therefore, in rigid rod-like mesogenic units, rigid refers to the rigidity of the linear shape.



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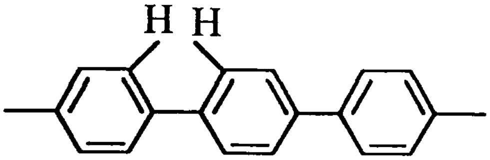

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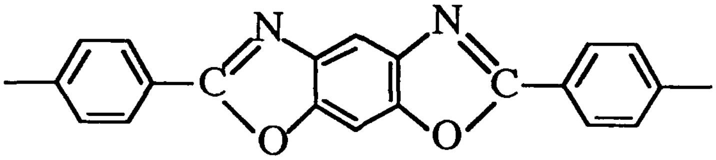
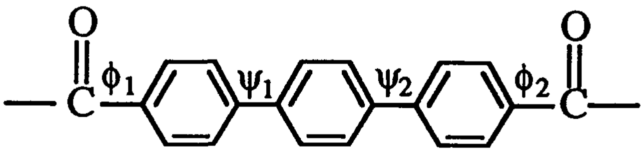


(3)

In oligo-*p*-phenylene (2) the steric interaction of the ortho hydrogens impede this internal rotation and the conjugation effect reinforces the rigidity due to the double bond character of the C-C bond between the phenylene rings. A ^{13}C-NMR study[108] of (4) showed an energy barrier of 5 kcal/mol for the internal rotation of the outer rings. The PCILO (Perturbative Configurational Interaction using Localized Orbitals, a method using semiempirical quantum mechanics), conformational calculations provided for this rotation a value of about 4.8 kcal/mol.[109]



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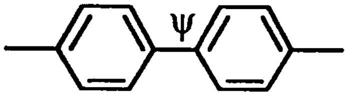
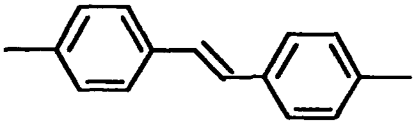


(5)

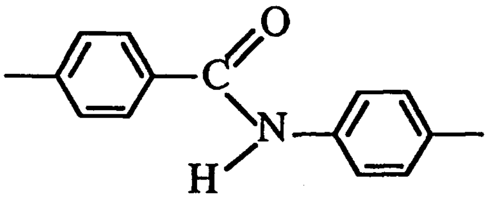
The minimum energy is at $\phi_1=\phi_2=0$ or $\phi_1=0$, $\phi_2=180^\circ$. In the case of 5, the energy barrier is of 1.9 kcal/mole and the minimum energy is at $\phi=40^\circ$. This value is in close agreement with the experimental value obtained in vapor state (i.e. $\phi=42^o$).[109] If the aromatic rings are connected via a double bond as in the case of stilbene (6) the molecule exhibits cis and trans configurational isomers. The structure of the trans isomer is energetically more favorable. The trans isomer can be isomerized into the cis one, but the activation energy for this transformation is very high and, therefore, makes this molecule almost rigid. Kalinowski and Kessler[110] have reported an activation energy of 42.8 kcal/mol for the thermal uncatalyzed isomerization of stilbene.



(6)

14.4.2 Semirigid Rod-Like Groups

The second group of mesogenic units have both conformational and configurational character and refer to semiflexible molecules such as amides (7) and esters (8). However, due to electronic reasons, the rotation about the C-O or C-N bond of (7) and (8) is retarted and can be even prohibited. In esters like (8), there is rotation about three bonds: R, S and T.



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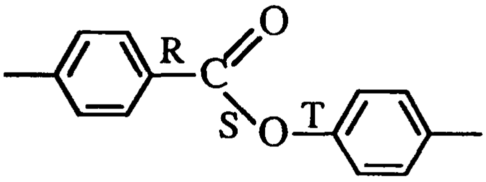
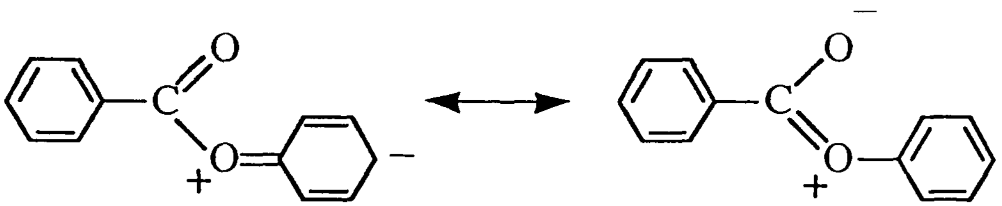


(8)

The most important rotation is about the S-bond, since it determines the kinked (cis) or extended (trans) conformation of the molecule. Theoretical calculations[111] suggest that the trans conformation represents the most stable structure. The arguments for this statement are as follows. In the trans-form of esters and acids there is a better O_n-$C_{\sigma *}$ "hyperconjugation" which decreases the free energy of this conformer.[111] The steric effect in the cis form makes it more unstable than the trans form . The potential energy of the cis form is higher than that of the trans form with 7.9 kcal/mol. In the energy profile there is a hump at 90^o which is due to the O_p-$C_{\pi *}$ overlap which creates a double bond character on the O-C bond. This barrier is smaller for aromatic esters than for aliphatic esters. This is because the delocalization of p-electrons of the oxygen on the aromatic ring attached to the oxygen gives the structure (9) which competes with the contributor (10). This conclusion is supported by the difference between the C-O bond length of aliphatic and aromatic esters. The C-O bond length is 1.33 Å in alkyl benzoate and 1.36 Å in aryl benzoate.[111] This last value is the closest to the typical ether C-O bond length of 1.42-1.43 Å. This double bond character creates a configurational character for the cis and trans conformers of esters and amids and subsequently, these compounds behave close to the class of rigid mesogens. Therefore, they should be classified as semirigid or semiflexible rod-like mesogens.

The structure and conformational behavior of amids (7) is very close to that of esters (8). The different resonance structures (11), (12) and (13) of a typical amide molecule[112] are similar to those of esters. Due to its double bond character, the contribution of (12) hinders the rotation about the C-N bond.



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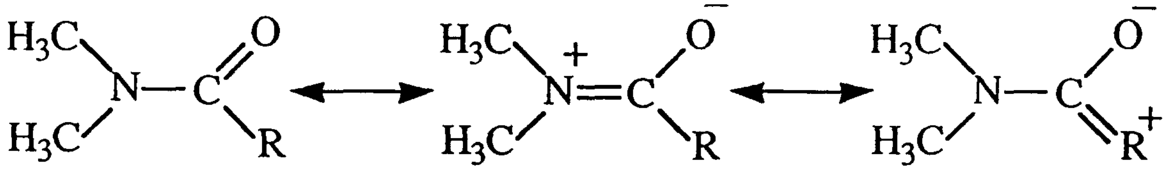
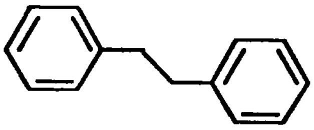


(11) (12) (13)

Pauling[112] predicted a rotational energy barrier of 21 kcal/mol which corresponds to about 40% double bond character for the C-N bond of amides. This double bond character decreases due to the participation of **(13)**, especially when R =aryl. This double bond character contribution was demonstrated by NMR studies performed on $(CH_3)_2$ N-C(O)-R. When R is CH_3- the rotational energy barrier is 18.9 kcal/mol[113] and decreases to 14.4 kcal/mol[114] for R=phenyl. On the basis of an NMR study, Tadokoro et al.[115] reported a rotational energy barrier of about 20 kcal/mol for the rotation about the C-N bond of phenyl benzamide.

14.4.3 Flexible Rod-Like Groups

The third class of rod-like molecules are *flexible*. 1,2-Disubstituted ethane **(14)** and methyleneoxy or benzylethers **(15)** derivatives belong to the class of flexible mesogenic units. Before discussing the fully flexible rod-like mesogens or the mesogens based on conformational isomerism, let us briefly recapitulate the conformational behavior of n-butane molecule **(16)**. n-Butane exhibits a number of different conformers. Out of them, the most stable are the gauche (17) and (18) and the anti (19). The electron diffraction study[116,117] of n-butane in gas phase (at 287 °K)[116] provided an energy difference of 0.6 kcal/mol between the gauche and the anti conformers.



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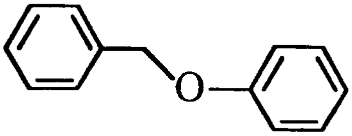

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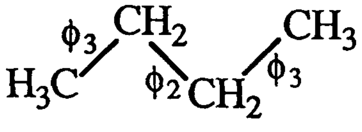

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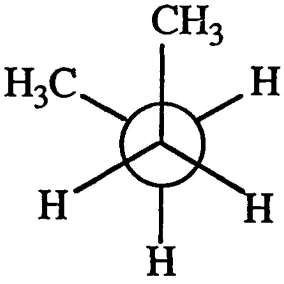

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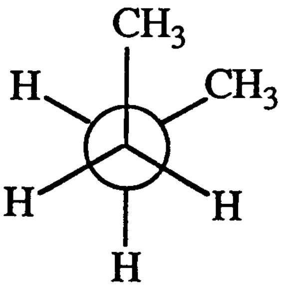

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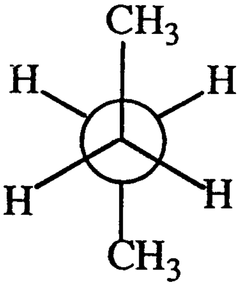


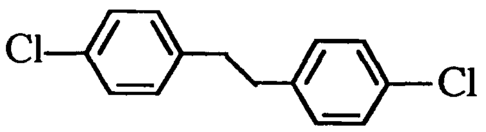
(19)

The same parameter was determined by Raman spectroscopy[118] (0.77 kcal/mol) and ^{1}H-NMR spectroscopy[119] (0.68 kcal/mol). The most recent Raman study[120] performed on n-butane in gas phase shows a potential energy difference of 0.966±0.054 kcal/mol between its gauche and anti conformers. Theoretical SCF-MO (Self Consistent Field-Molecular Orbitals) based calculations[121] led to a rotational energy barrier at ϕ_2=60° (when CH$_3$-

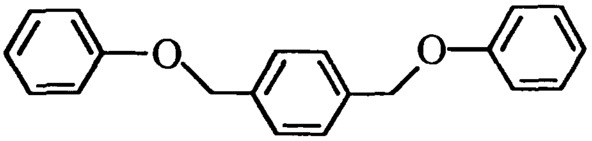
group is eclisped with a hydrogen atom) of 3.7 kcal/mol and to a potential energy difference of 1.19 kcal/mol. Flory et al.[122] have calculated a rotational energy barrier of 2.8 kcal/mol and a potential energy difference of 0.53 kcal/mol. Consequently, the theoretical and experimental results of n-butane agree.

The X-ray study[123] of diphenyl ethane suggests that in solid state the phenyl groups are located exclusively in the anti position. IR and Raman spectroscopy studies[124] performed on 1,2-diphenyl ethane and 1,2-di(*p*-chlorophenyl)ethane (**20**) also demonstrated that both molecules exist in solid state as anti conformers. An optical anisotropy study[125] performed by diffusion Rayleigh depolarization on solutions of 1,2-diphenylethane in CCl_4 and cyclohexane, shows that the anti conformer is preferred also in solution. In solution and Nujol mulls[124] of para substituted 1,2-diphenylethane derivatives some extra bands were observed suggesting the existence of the gauche conformer. At 25°C the ratio of anti to gauche is 84:16, but in case of 1,2-diphenylethane (**14**) the absence of any extra band suggests the possibility that the concentration of gauche conformer is too low to be detected by IR spectroscopy. A ^{13}C-NMR spectroscopy study[126] of 1,2-di(2,6-dimethylphenyl)ethane in CCl_4 solution showed a dynamic equilbrium of 7/3 anti to gauche conformations.

Theoretical calculations performed on 1,2-diphenylethane gave contradictory results. Ivanov et al.[127] concluded that the gauche conformer of (**14**) is more stable than the anti one with 0.57 kcal/mol. Jacobus[128] also indicated that the gauche conformer is more stable and he obtained a difference of 1.15 kcal/mol between the anti and the gauche conformers. On the basis of LCAO-MO (Linear Combination of Atomic Orbitals-Molecular Orbitals) treatment of the benzene rings, Ivanov et al.[127] showed that there is no difference in the stretch, bend, tortion and stretch-bend interactions but there is difference of the nonbonded interactions between the atoms of benzene rings which prefers the gauche conformer. A theoretical study[129] by using the MM2/MMP2 (molecular mechanics based computer program) program provided data which are in agreement with the experimental results, suggesting that the anti-form is more stable than the gauche form. The energy difference between these conformers is of 0.95 kcal/mol and increases to 1.59 kcal/mol when point charge and electrostatic interactions are also considered. Jonsson et al.[105a] calculated the conformational energy barrier of α,α'-diphenyl-*p*-xylene (21), as a model compound for the polymers based on benzyl ether mesogenic units. The potential energy barrier to move one of the outer rings to the position where it becomes linear is 3.87 kcal/mol.



(20)



(21)

From this discussion it is clear that in the crystalline state only the anti conformer exists. However in solution both the anti and the gauche conformers exist in a dynamic equilibrium. To our knowledge, the rotational energy barrier of 1,2-diphenylethane is not available. Ivanov et al.[127] calculated the potential energy at different values of torsional angle (Ph-C-C-Ph) i.e., when they are in the anti, gauche, and eclipse forms. In the eclipse form, the two rings are in the closest geometry (the steric and other nonbonded interactions are maximum). Depending on the method used, the calculated energy of the eclipse form is 3.61, 3.49 and 1.95 kcal/mol. This conformer has the maximum potential energy suggesting that the conformational energy barrier should be lower than the above mentioned values because during the gauche to anti or anti to gauche conformational change the benzene rings eclipse with the ethylenic hydrogen atoms, and this steric interaction is less than for two benzene rings.

In conclusion, based on the difference between the rotational energy barrier of different configurational isomers or conformers of rod-like groups we suggested[107] their classification into three categories: rigid, semirigid or semiflexible, and flexible. Rigid rod-like groups are rigid units whose shape is rigid like for example (**1**), (**2**), and (**3**), and configurational isomeric units which require a high rotational energy barrier or activation energy, like for example stilbene (ΔEa=42.8 kcal/mol). Semirigid or semiflexible rod-like groups are conformationally flexible, but due to some electronic reasons they behave like configurational isomers of medium rotational energy barrier. Classic examples are aromatic amides and esters (ΔEa=14.4 kcal/mol and 7.1 kcal/mol respectively). The rotational energy barrier of these molecules is less than half that of rigid molecules but is much higher than that of flexible molecules. ***Flexible rod-like groups*** are conformationally flexible groups whose rotational energy barrier is within the same range of values with that of butane (ΔEa=2.8-3.7 kcal/mol). Classic examples are phenylbenzylether (ΔEa=3.87 kcal/mol) and 1,2-diphenylethane (ΔEa=3.61 kcal/mol) based molecules.

14.5 MANIPULATION OF PHASE TRANSITION TEMPERATURES THROUGH STRUCTURAL VARIATIONS. SOME THERMODYNAMIC CONSIDERATIONS[65,66]

14.5.1 Equilibrium States

For the considerations to follow it will be sufficient to consider the basic thermodynamic relationship:

$$dG = VdP - SdT \qquad \text{Eq. 3}$$

where G is the free energy, S the entropy, V the volume, P the pressure and T the temperature. For the scheme in question we will consider first the melting of a true crystal at constant pressure (dP=0). As seen from Figure 4, and as follows from Equation 3, the free energies of both crystal (G_k) and isotropic liquid (G_i) decrease with increasing temperature where the decrease in G_i is the steeper, due to $S_i>S_l>S_k$. Where G_i crosses G_k the crystal melts, which of course is at $T_{k\text{-}i}=T_m$, the melting point of the crystal. In this case, as drawn in Figure 4, the free energy of any hypothetical mesophase, G_{lc}, cannot fall below both G_k and G_i, hence corresponds to a stable state at any temperature. While G_{lc} decreases faster with T than G_k it will only cross G_k at a point which is above G_i, i.e. where the isotropic liquid is already the stablest phase. Thus the mesophase is virtual and remains unrealizable as a stable phase.

In order to create a stable mesophase a section of the G_{lc} versus T curve will need to be brought beneath both G_k and G_i (thus to a state of greatest stability). This can be achieved either a) by raising G_i (Figure 5), or b) by raising G_k (Figure 6), or by a combination of both a) and b). As seen in Figures 5 and 6 the mesophase will be "uncovered" in a temperature range bounded by $T_{k\text{-}lc}$ and $T_{lc\text{-}i}=T_i$ corresponding to temperatures of crystal melting and isotropization respectively. (The lowering of G_{lc} would have the same effect; but changes in G_{lc} are expected to be small compared to those in G_i and G_k and will be disregarded in what follows.) In general, raising of G_i (Figure 5) arises from the lowering of the melt entropy (i.e., by increasing the rigidity of the molecule via a permanent structural change or via a temporary change such as shear or any other kind of orientation, constraint or pressure), while raising of G_k (Figure 6) from the reduction in the perfection of the crystal (i.e., by copolymerization or other kind of chemical and/or physical modification) T_m decreases and therefore G_k increases. Note that in case of Figure 5 the crystal melting point, T_m, is raised, while in that of Figure 6 it is lowered.

We can generalize further by considering the influence of change in pressure, i.e. the VdP term in Equation 3. Usually the specific volume is larger for the liquid than for the crystal with the mesophase expected to lie in between; hence $(dG_k/dP)_T<(dG_{lc}/dP)_T<(dG_i/dP)_T$. In principle it could therefore happen that at some P G_{lc} falls below G_k and thus a mesophase may become "uncovered". It has been found that in most experimental systems[130] the effect of increased hydrostatic pressure is to promote the mesophase ("barophyllic" behavior). However, there is no fundamental reason that would make this a general rule. This is clearly illustrated by the example of the sequence of alkanes→polyethylene (as it is described in detail elsewhere[66] where "barophobic" behavior of short n-alkanes changes continuously with increasing chain length toward the "barophyllic" behavior of polyethylene.[131]

14.5.2 Metastable States

Figures 4-6 refer to states of thermodynamic equilibrium. However, systems may not respond immediately when passing from one stable regime to another within the phase diagram, hence the metastable phases can often arise.

The most commonly encountered metastability is that arising on crystallization. As familiar, crystallization only sets in at certain supercooling. In polymers in particular, crystallization temperature $T_{i\rightarrow k}$ can be appreciably below the equilibrium melting point $T_{k\rightarrow i}=T_m$. On the other hand, the formation of a mesophase generally requires less supercooling. Now, if the temperature from the isotropic liquid to a normally unstable mesophase lies somewhere between $T_{k\rightarrow i}$ and $T_{i\rightarrow k}$, such a "virtual" mesophase may materialize on cooling. As the temperature is lowered still further, crystallization will occur. At this state two extreme situations may be envisaged, as depicted in Figures 7 and 8. On crystallization the free energy either drops from G'_k to G_k, i.e. the value for the perfect (Figure 7, where the dotted line indicates a possible pathway), or else there is no continuous change in G, i.e. a highly imperfect crystal is formed with its free energy remaining at G'_k (Figure 8). The realistic path would be somewhere in between these two extremes, i.e. some decrease in G is expected, which may not quite reach the level of G_k.

We shall first consider the extreme situations of Figures 7 and 8. When the perfect crystal of Figure 7 is reheated, it melts directly into the isotropic liquid at $T_{k \to i}$: thus such a system displays the mesophase only on cooling, and is called "monotropic". On the other hand, the imperfect crystal of Figure 8 first changes back into the mesophase at Tk'-lc and then into the isotropic liquid at Tlc-i on reheating; thus the mesophase occurs both on cooling and heating and is called "enantiotropic". The latter case clearly illustrates that an enantiotropic mesophase does not necessarily mean stability of the mesophase, as sometimes implied, although a stable mesophase, naturally, must be enantiotropic. As mentioned before, real systems are in between those described by Figures 7 and 8. Some decrease below G_k' will occur upon crystallization, the magnitude of the drop depending, among others, on crystallization kinetics. Accordingly, neglecting possible perefectioning on subsequent heating, mono- and enantiotropic behavior are distinguished by the magnitude of the drop in G on crystallization; if G stays above a critical value (G_k^c) the system is enantiotropic, if it falls below it is monotropic, the definition of G_k^c being apparent from Figure 7. It is easily seen how crystal perfectioning on annealing can lead to a "conversion" of an enantiotropic into a monotropic mesophase, an effect frequently observed in both polymeric and low molar mass liquid crystals.

It is worth noting further that, under certain conditions, polymers will also display superheating effects, in which case the mesophase may only appear on heating; this can be regarded as "monotropic" behavior in the reversed sense. An example of this in connection with polyethylene was discussed previously[66] and an example with a side chain liquid crystalline polymer was reported recently.[132]

As seen from the above, kinetics will always play part in any phase diagram of a liquid crystalline polymer as determinable in practice. Its influence on our present considerations will depend on its magnitude. If it is small enough, so as not to alter the sequence of appearance (or disappearance) of the different phases with changing temperature, the equilibrium situations in Figures 4-6 will be taken to apply with the kinetics as an overlay, affecting only the exact numerical values of the actual divides. If, however, the phase sequence itself is affected, and in fact new phases are created due to metastability, then the whole phase behavior will become kinetically determined and consideration in Figures 7, 8 will pertain.

Finally a further kinetic factor, the glass transition (T_g), needs invoking, particularly pertinent to liquid crystalline polymers. On cooling the system becomes immobilized at T_g (more precisely also dependent on the rate of cooling), hence phase transformations will be arrested or all together prevented. The inverse will apply when a previously immobilized system is heated above T_g when the system will again be able to follow its course towards the equilibrium state. In practice, this will lead to inaccessibility of certain portions of the phase diagram, or conversely, lead to the freezing in of the liquid or of the liquid crystalline state enabling their attainments at temperatures where by thermodynamic criteria they would be unobtainable otherwise (isotropic or liquid crystalline glass respectively). Even if T_g is not a thermodynamic quantity the indication of its location in the phase diagram can therefore serve as a useful purpose.

General examples from literature following the patterns of the thermodynamic schemes described above are provided elsewhere.[66]

14.5.3 Influence of Molecular Weight on Phase Transition Temperatures

We will now discuss the relationship between phase transition temperatures and polymer molecular weight for three different situations.[65,66] Upon increasing the molecular weight from monomer to polymer, the entropy of the liquid phase (S_i) decreases. The decrease of the entropies of mesomorphic and crystalline phases is lower than that of the isotropic phase. For simplicity, the decrease of the entropy of the crystalline phase will be neglected. The decrease in S_i and S_{lc} tends asymptotically to zero with increasing molecular weight (M). M_0 from Figures 9 to 11 refers to molecular weight of the polymer structural unit. M_1 to M_∞ from the same figures are arbitrary molecular weights of the corresponding polymer. It follows that G_i and G_{lc} increase with the increase of the polymer molecular weight again asymptotically; above a certain molecular weight, we may consider both parameters as remaining constant.

14.5.3.1 Case 1. Both Monomeric Structural Unit and Polymer Display an Enantiotropic Mesophase

The first situation we will consider refers to the case in which the monomeric structural unit displays an enantiotropic mesophase. Upon increasing its molecular weight to dimer, trimer, etc., S_i decreases and, therefore, G_i increases. Beyond a certain molecular weight, G_i remains for all practical considerations constant. Figure 9 transforms the free energy (G) versus transition temperature (T) dependence, into a transition temperature (T) versus molecular weight (M) dependence. The T versus M plot in Figure 9 demonstrates that both melting ($T_{k\text{-}lc}$) and isotropization ($T_{lc\text{-}i}$) temperatures increase with molecular weight up to a certain range of M values beyond which $T_{k\text{-}lc}$ and $T_{lc\text{-}i}$ remain approximately constant with the T_i line lying above the line for Tm for all molecular weights. However, the slope of the increase of $T_{lc\text{-}i}$ is steeper than that of $T_{k\text{-}lc}$. The difference between these two slopes determines the relative thermodynamic stabilities of the mesomorphic versus that of the crystalline phases at different polymer molecular weights.

For this particular case, the higher slope of the $T_{lc\text{-}i}$-M versus that of the $T_{k\text{-}lc}$-M dependence leads to a widening of the temperature range between the two curves with increasing molecular weights of the polymer. This widening of the liquid crystal temperature regime with molecular weight agrees with experimental data reported for the case of both main chain[133-135] and side chain[72,136-145] liquid crystalline polymers. This effect has been repeatedly labelled the "polymer effect", especially in the case of side chain liquid crystal polymers.[72]

14.5.3.2 Case 2. The Structural Unit Displays a Virtual or a Monotropic Mesophase; The Polymer Displays a Monotropic or an Enantiotropic Mesophase

The steeper slope of the $T_{lc\text{-}k(i)}$-M dependence versus that of the $T_{k\text{-}i(lc)}$-M dependence has even more important implications on the molecular weigh-phase transition temperature dependence for the situation when the monomer structural unit displays only a monotropic or a virtual mesophase (Figure 10).

As seen the two lines T_i versus M and T_m versus M intersect. This arises from the fact that $T_i<T_m$ for low molecular weights with a steeper slope for T_i. Specifically (for the illustration in Figure 10) the T_i (i.e. $T_{lc\text{-}k}$) values are below the corresponding T_m (i.e. $T_{k\text{-}i}$) values for M_0 to M_4, hence in the range M_0 to M_4, i.e. the monomer together with its low oligomers up to 4, display only a virtual mesophase. Beyond M_4 the mesophase becomes stable, hence the system enantiotropic. In addition to the thermodynamic criterion, kinetics also influence the phase transitions. A certain amount of supercooling of the isotropic-mesomorphic and especially much more so of the mesomorphic-crystalline

transitions is possible which can lead to monotropic behavior for molecular weights slightly below and at the intersection point (i.e. at M_4). In view of the fact that T_i and T_m are expected to be continuous functions of molecular weight, the intersection point can be arbitrarily closely approached (from below), hence realization of a metastable liquid crystal phase and subsequent monotropic behavior is to be expected for appropriate molecular weights in cases to which Figure 10 pertains. This effect has been observed experimentally both in the case of main chain[146-148] and side chain[149] liquid crystalline polymers and was labelled "transformation of a monotropic mesophase into an enantiotropic mesophase by increasing the molecular weight of the polymer". A series of quantitative experiments on this line will be described later.

14.5.3.3 Case 3. The Structural Unit Displays a Virtual Mesophase; The Polymer Displays a Virtual Mesophase

The third situation is illustrated in Figure 11 and also refers to a different case in which the monomeric unit displays only a virtual mesophase. Here as before, the slope of the T_i (i.e. $T_{lc\text{-}k}$)-M dependence is higher than that of the T_m (i.e. $T_{k\text{-}i}$)-M dependence, the latter lies above the former throughout hence the two curves do not intercept each other. Therefore, the resulting polymer displays also a virtual mesophase. This thermodynamic situation was recently applied to the synthesis of virtual liquid crystal polyethers containing both flexible mesogens and flexible spacers[103] and will be detailed in a subsequent chapter.

14.5.3.4 Case 4. Rigid Rod-Like Polymers

The discussion from Cases 1 to 3 refers to semiflexible or semirigid and flexible polymer systems which exhibit first order transition temperatures (i.e. melting, isotropization) which are molecular weight dependent only up to a certain degree of polymerization. In these systems the melting temperature is determined by the length of the chain fold. Rigid rod-like polymers such as poly(p-phenylene)s, poly(p-phenylenebenzobisthiazole) (PBT), poly(p-phenylenebenzobisoxazole) (PBO) etc. exhibit a linear dependence of their melting transition over their entire range of molecular weights. Consequently, the dependences of their first order transitions on molecular weight follow the pattern from Figure 12. Table 2 summarizes the dependence of the first order transition temperatures of poly(p-phenylene)s H-(C_6H_4)-H as a function of their degree of polymerization and their axial ratio (x=L/d),[150-152] (Figure 13a). As predicted by theory,[39,150] when the axial ratio (x=L/d) of rod-like molecules reaches a value of about 6.2 the compound should exhibit an enantiotropic mesophase. This is indeed the case. For n of 6 or 7 poly(p-phenylene)s exhibit an enantiotropic nematic mesophase (as predicted by Figure 12). At lower n values the nematic mesophase is virtual. However, for oligomers with n larger than 7 the nematic mesophase cannot be observed since the decomposition temperature first overlaps the melting transition and then becomes lower than the melting temperature. Other rigid rod-like polymers like PBT and PBO and even semirigid systems like fully aromatic and unsubstituted polyamids and polyesters decompose before melting.

While in rigid rod-like polymers the axial ratio x=L/d (Figure 13a) defines the chain dimension which is responsible for the generation of an enantiotropic mesophase, in the case of semi-rigid and flexible polymers the ratio l/d (Figure 13b) where l is now a renormalized length (the Kuhn's segment) defines it. In this second case the higher l, the higher the stiffness of the chain.[152]

In conclusion, the steeper slope of the isotropization temperature-molecular weight dependence versus that of the melting temperature-molecular weight dependence should have the following effects on going from monomer to polymer. When the monomer structural unit displays an enantiotropic mesophase, the resulting polymer will display a broader enantiotropic mesophase, i.e. anisotropic temperature interval. When the monomeric unit displays a monotropic mesophase, the resulting polymer will, most probably, display an enantiotropic mesophase. When the monomeric unit displays a virtual mesophase, the resulting polymer may display either an enantiotropic, monotropic or virtual mesophase. For the case of side chain[149,153] and main chain[133,147,148] liquid crystalline polymers containing flexible spacers and displaying a single mesophase, the nature of the mesophase displayed by the polymer is most frequently identical to that of its monomeric unit. Primarily the molecular weight-phase transition dependences are determined by the relationship between the free energies of the crystalline, liquid crystalline and isotropic phases of the monomeric structural unit yet influenced by the molecular weight of the main chain backbone through its effect on the melt entropy as in Case 1 above. Combinations of more than one mesomorphic phases of different thermodynamic stabilities in a monomeric structural unit will follow the same molecular weight dependence trend as those described for the monomers displaying a single mesophase.[139-145] However, there are few examples where the nature of the mesophase displayed by the main chain and side chain liquid crystalline polymers is molecular weight dependent. Both in the case of the main chain[156,157] and side chain[139,140,142,158] liquid crystalline polymers it has been demonstrated that this change in the mesophase represents a continuous dependence of molecular weight. In the case of rigid rod-like polymers both melting and isotropization temperatures reach higher values than the decomposition temperature within the range of low molecular weights.

14.6 MAIN CHAIN LIQUID CRYSTALLINE POLYMERS

14.6.1 Soluble and Fusible Main Chain Liquid Crystalline Polymers

Amorphous polymers are soluble in conventional solvents at room temperature while crystalline polymers are soluble only at temperatures which sometimes are close to their melting point. The solubility of any polymer increases with the decrease of its ability to crystallize. A suppression of the melting temperature below the glass transition temperature (i.e., a kinetically prohibited crystalline phase) makes the corresponding polymer noncrystallizable. Therefore, since most rigid polymers have much higher glass transition temperatures than flexible polymers its is easier to decrease the crystallization tendency of the former polymer and therefore, make it soluble. This is also the case for main chain liquid crystalline polymers. A decrease of the melting transition temperature can be accomplished by raising G_k as shown in Figure 6 and discussed in subchapter 14.5.1. An increase in G_k can be accomplished by any synthetic technique which increases S, i.e. introduces structural defects in the polymer structure. Most conveniently, this is realized by copolymerization, addition of lateral substituents which provide a high configurational entropy (alkyl groups, t-butyl groups), insertion of flexible spacers, increasing the overall flexibility of the molecule and insertion of structural defects such as kinks, etc. The alternative solution is to increase both the glass transition temperature of the polymer and its entropy simultaneously. In order to maintain a high ability towards mesophase formation the increase in solubility should not disturb the ability of the backbone to generate a linear conformation. Therefore, the insertion of kinks or any other nonlinearities is not favorable since increases the solubility and decreases the ability to generate the mesophase. The ability to decrease the crystallization tendency is not so much related to the size of the lateral substituent as it is to the number of different structural units which can result from the monomer which contains the side group. In fact according to thermodynamic considerations a high entropy situation can be realized either by a chain containing a large number of different structural units with different small substituents or by a chain containing a large substituent in each structural unit. The second situation, however, reduces drastically the interchain interactions and therefore, suppresses not only the ability towards crystallization but also the ability to generate a liquid crystalline phase. Therefore, the most profitable synthetic technique is to use the copolymerization of few monomers containing small substituent with different electronegativities and ability to generate more than one constitutional isomeric structural unit from each monomer. Various research groups have used these principles, although in a non-systematic way, and accomplished fusible and soluble polymers. In the following subchapters we will enumerate only selected examples of polymers solubilized by using these principles.

14.6.1.1 Poly(p-phenylene) Derivatives

To our knowledge the first soluble oligo(p-phenylene)s were synthesized by Kern et al. in 1960 by adding methyl substituents on the phenyl ring.[159] The mesomorphic behavior of these oligomers was first reported by Heitz.[160-162] These oligomers and their phase transitions are outlined in Scheme 1. By substitution their solubility increases[159] and their melting points decrease. Methyl substituted oligo(p-phenylene)s have an axial ratio (x) equal to 0.8 times the number of benzene rings. According to theoretical predictions hexamethylsexiphenyl which has $x = 4.8$ and lower oligomers should not exhibit an enantiotropic mesophase. This is indeed the experimental case. However, octamethyloctaphenyl with $x = 6.4$ and longer oligomers (i.e. larger than the critical value $x = 6.2$) should and indeed show an enantiotropic nematic phase. Insertion of meta linkages suppresses their ability to form a mesophase (Scheme 1).

Phenylated poly(p-phenylene)s with and without flexible spacers were synthesized by the 1,4-cycloaddition of biscyclopentadienones (bistetracyclones) with bisethynyl compounds[163-165] (Scheme 2). Although these polymers are soluble in conventional solvents their mesomorphic behavior was not investigated.

Soluble semi-ladder phenylated polyarylenes were synthesized by the Diels-Alder reaction of biscyclodienones and bis-pyrone dienes with bisbenzynes like 3,4,3',4'-didehydrobiphenyl which was generated in situ by the aprotic diazotization of 3,3'-dicarboxybenzidene (Scheme 3).[166] No mesomorphic properties were investigated.

Soluble poly(p-2,5-di-n-alkylphenylene)s were prepared by the Yamamoto route i.e., Ni-catalyzed coupling of 1,4-dibromo-2,5-di-n-alkylbenzene[167] and via Pd(0)-catalyzed coupling of 4-dibromo-2,5-di-n-alkylbenzeneboronic acid (Suzuki reaction)[168,169] (Scheme 4).

Poly(dimethylbiphenylene)s of low molecular weight were prepared by Ullmann reaction and by Semmelhack reaction[170] (Scheme 5). Both poly(p-di-n-alkylphenylene)s and poly(dimethylbiphenylene)s do not exhibit liquid crystallinity. This is most probably due to their low molecular weight.

Soluble phenylated poly(p-phenylene)s were also synthesized by Ni(II) catalyzed polymerization of 2,5-dibromobiphenyl via Kumata reaction, and via anionic polymerization of 2-phenyl-1,3-cyclohexadiene followed by aromatization (Scheme 6).[171] Most probably, both synthetic methods lead to regioregular phenylated poly(p-phenylene)s. The high molecular weight polymer fractions exhibit an enantiotropic nematic mesophase.

Regioirregular substituted poly(p-phenylene)s were synthesized from substituted hydroquinones via Ni(0) catalyzed homocoupling of their bistriflates (Scheme 7).[172] All these polymers are soluble in conventional solvents, however they have low molecular weights and do not exhibit liquid crystallinity.

Water soluble poly(p-phenylene) derivatives were synthesized in water by Suzuki reaction, using a water soluble Pd(0) catalyst[173] (Scheme 8). The mesomorphic properties of these water soluble poly(p-phenylene) derivatives were not investigated.

This brief survey on the synthesis and properties of soluble poly(p-phenylene)s demonstrates that although the rigid rod-like character of these polymers is maintained, most of these polymers do not exhibit liquid crystalline properties. This is probably because bulky side groups attached to these polymers require a much larger x value for the generation of liquid crystalline properties and also because these bulky side groups diminish the interchain interactions which are required for the generation of a thermodynamically stable mesophase.

14.6.1.2 Metal Containing Poly(yne)s

Metal containing poly(yne)s are a relatively new class of rigid rod-like polymers. They can be prepared by a copper chloride-triethylamine coupling of the appropriate metal halide with a dialkyne (Scheme 9).[174,175] A review on their synthesis is available.[176] These polymers exhibit lyotropic liquid crystalline phases.[177] Recently, two novel methods for the synthesis of this class of polymers were reported. The first one consists of the reaction of bis-trimethylstannyl(acetylide)s with trans-$[M(PBu_3)_2Cl_2]$,[178] while the second one of the reaction of $[Rh(PMe_3)_4Me]$ with diacetylenes[179,180] (Scheme 10). These metal containing poly(yne)s can be prepared with weight average molecular weights of up to 100,000[178] and are therefore of interest both for their rigid rod-like character and for their non-linear optical properties.[180] Additional classes of metal containing liquid crystalline polymers were discussed in a recent review.[181]

14.6.1.3 Spinal Columnar Liquid Crystalline Polymers

Dihydroxysilicon (IV) phthalocyanine can be condensed in solid state to yield insoluble phthalocyaninatopolysiloxanes.[182,183] However, octaalkyl substituted derivatives of dihydroxytin (IV) phthalocyanine,[184] dihydroxysilicon (IV) octakis(dodecyloxymethyl)phthalocyanine[185,186] and octaalkoxy substituted silicondihydroxy phthalocyanines[187,188] undergo polycondensation in liquid crystalline phase and yield soluble spinal columnar liquid crystalline polymers (Scheme 11). These polymers exhibit columnar hexagonal liquid crystalline phases which can range from -7 °C up to 300 °C.[184-187] The diameter of the column is determined by the length of the alkyl side groups.[187]

14.6.1.4 Aromatic Polyamides and Polyesters

Synthetic procedures for the preparation of soluble aromatic polyamides and polyesters were developed mostly by Gaudiana et al.[189-193] Their research was recently reviewed.[194] Depending on their structure, these polymers can be either amorphous or liquid crystalline.[194] A discussion of the influence of various molecular factors such as the position, polarizability and size of the substituents on the solubility of aromatic polyamides is available.[192,194] Table 3[192] summarizes some representative polymer structures. Their solubility is described in Table 4. An inspection of the structures from Table 3 and of the solubilities of these polymers presented in Table 4 suggests that the non-coplanar conformation of the biphenyl moiety (introduced by the presence of substituents in their 2,2'-positions), the random distribution of the biphenyl enantiomers, and the presence of structurally dissimilar diacids and diamines, all contribute to an enhanced solubility. The combination of these molecular factors diminish or even eliminate interchain correlations necessary for close packing in crystals and may diminish Van der Waals forces of attraction. These orientation-dependent intermolecular attractive forces are important in the formation of all classes of liquid crystals.[195] Therefore, when these forces of attraction are significantly weakened by various combinations of steric and dipolar repulsive forces the parallel allignment of polymeric chains is prevented.

Soluble aromatic polyamides with a much lower solubility were also realized by attaching phenyl substituents either on the p-phenylene diamine or on the terephthalic acid monomer.[196-198] Some representative structures together with their solubilities are presented in Table 5.[196] All these polymers exhibit lyotropic liquid crystalline phases and melt before decomposition.

A reversible solubilization of poly(p-phenylene terephthalamide) was accomplished by the polycondensation of the chromium tricarbonyl complex of p-phenylenediamine with terephthaloyl chloride in N,N-dimethylacetamide[199] (Scheme 12) by applying low vacuum to remove HCl. The polymer containing tricarbonyl chromium complexed structural units is soluble in dipolar aprotic solvents. Decomplexation can be achieved either by oxidation with I_2 or by heating above 150 °C.

Soluble poly(p-phenylene terephthalamide)s with phenyl and biphenyl units in the terephthalic acid were also synthesized by Heitz et al.[200] The melting temperatures of these polymers were in the range of 440-490 °C and are overlapping their decomposition temperatures.

Aromatic polyamides containing alkyl side chains were reported by Ringsdorf et al.[201,202] and by Ballauff et al.[203] When each structural unit contains four alkoxy groups, depending on their length, these polymers exhibit a board-like, "sanidic" mesophase[201,202] (Figure 14). However, when there are only two alkoxy groups per one of the two monomeric units these polyamides display a new layered liquid crystalline mesophase as that depicted in Figure 15.[203,204] The corresponding polyesters containing four alkoxy groups in each monomeric unit or two alkoxy groups in only one monomeric unit display similar mesophases with the polyamides.[201-204]

Soluble aromatic polyesters were synthesized by using similar synthetic procedures with those used in the synthesis of soluble aromatic polyamides. The research groups from Mainz reported on the solubilization of aromatic polyesters by the addition of alkyl side groups.[201-205] Solubility of aromatic polyesters containing alkyl side groups is easily accomplished when the length of the alkyl groups derived from terephthalic acid monomer and respectively hydroquinone monomer are dissimilar in length[205] (Scheme 13). For example the polyester from the top of Scheme 13, PTA16HQ-16, is highly crystalline and melts directly into an isotropic phase. However, PTA16HQ-6 exhibits much less crystallinity, is highly soluble and melts into a liquid crystalline phase. It is also instructive to compare the phase behavior of polyesters derived from bicyclo[2.2.2]octane-1,4-dicarboxylic acid with 2,5-dialkoxyhydroquinone diacetate (PBCOHQ-n) with those obtained from terephthalic acid and 2,5-dialkoxyhydroquinones (PTAHQ-n). Representative data on these polymers are available in Tables 6 and 7. As we can observe from the data reported in Tables 6 and 7, all PTAHQ-n melt into a liquid crystalline phase while PBCOHQ-n melt directly into an isotropic phase. These results suggest that interchain interactions provided by the wholly aromatic backbone are necessary for the stabilization of a mesophase in this class of polymers.[205] Soluble homologues of poly(p-hydroxybenzoate) were also synthesized by attaching pendant alkyl groups.[206] Thus, while poly(p-hydroxybenzoate) and poly(3-n-alkyl-4-hydroxybenzoate)s with alkyl groups shorter than six are only crystalline, the corresponding polymers with alkyl groups from six to sixteen are soluble and exhibit a thermotropic mesophase.[206] It is interesting to mention that the polyesters with alkyl side groups display a layered mesophase which is different from the classic nematic or smectic mesophases exhibited by conventional rod-like polymers.

A large variety of soluble polyesters were reported by Gaudiana et al.[193,194] by using the same synthetic principles as those used in the preparation of soluble polyamides. Table 8 summarizes few results on the dependence between the structure and solubility of polyesters.[194]

A large group of soluble aromatic polyesters was reported from the group of Heitz by attaching various large substituents such as phenylalkyl,[207,208] perfluoroalkyl,[209] phenoxy and tert-butyl,[210] phenyl and biphenyl,[162,211] or twisted biphenylene units such as 2,2'-dimethylbiphenylene,[212,213] and 1,1'-binaphthyl-4,4'-ylene.[214] The dependence between the stucture of various structural units and the solubility of the resulted polyesters was reviewed.[211,215,216a]

Tables 9 and 10 summarize the dependence between structure, thermal properties and solubilities of polyesters based on substituted hydroquinone and substituted terephthalic acid.[216] The presence of dissimilar substituents on both monomers generates highly soluble polymers. Tables 11 and 12 show the dependence between the properties of polyesters obtained with twisted monomers and their structure.[216]

Additional examples of aromatic polyesters with lower crystallization ability and with enhanced solubility were reported by Kricheldorf et al. Nematic polyesters were obtained by the condensation of 2-phenylthioterephthalic acid, 2-(p-tolylthio)terephthalic acid, 2-(p-chlorophenylthio)terephthalic acid with the diacetates of hydroquinone, methylhydroquinone or 2,5-biphenyldiol.[217] 2-(2-Naphthylthio)terephthalic acid was also used in conjunction with the same bisnucleophiles to obtain noncrystallizable nematic copolyesters.[218] The influence of various groups present in the structure of bisphenols (i.e., O, CO, SO_2, S, $C(CH_3)_2$) on the phase behavior of polyesters with phenylthioterephthalic acid was also investigated.[219] Similar polyesters were synthesized from phenoxyterephthalic acid,[220] 4-fluoro-, 4-chloro, 4-bromo-, 4-phenyl, 4-cyclohexyl-, 4-phenoxy- and 4-cumyl- phenol[221] with hydroquinone or 4,4'-biphenyldiol. The influence of the various polyesterification reaction conditions on the final structure and properties of polymers was also investigated. The synthetic methods used most frequently are outlined in Scheme 14.[220-222]

For example the acetate method results in partial debromination of 4-bromophenoxyterephthalic acid units during their condensation with hydroquinone diacetate but not during the polymerization via the other two methods[221] (Scheme 14). Model reactions have shown that both phenoxyterephthalic acid and its acid chloride yield anthrone-3-carboxylic acid above 180 °C and this product terminates the polymer chain end[222] (Scheme 15). This reaction is less probable when the acid chloride is reacted with the silylated hydroquinone. The interest in aryloxy- and arylthiosubstituted terephthalic acid was mainly determined by their convenient synthesis from dimethyl nitroterephthalate via aromatic nucleophilic displacement by the corresponding phenolate or thiophenolate.

Soluble liquid crystalline aromatic polyesters were also synthesized from terephthalic acid derivatives, tert-butylhydroquinone and aromatic hydroxyfunctional polystyrene macromonomers.[223a] The number average molecular weight of polystyrene side chains varied from 1000 to 2000 (Scheme 16). The resulting polyesters contain polystyrene grafts and are of interest as emulsifiers for nematic aromatic polyesters with polystyrene.[223a]

An additional example of graft copolymer containing a polyester main chain and polymethylmethacrylate graft units was synthesized from a hydroquinone substituted with polymethacrylate, t-butyl hydroquinone and bromoterephthaloyl chloride.[223b] The hydroquinone containing polymethylmethacrylate substituent was prepared by group transfer polymerization. Scheme 17 outlines the synthetic procedure.

14.6.1.5 Rod-Like Soluble Polyimides

Rigid rod-like polyimides were synthesized by the sequence of reactions presented in Schemes 18 and 19.[224,225] The series of polymers from Scheme 18 contain alkyl side groups[224] while the one from Scheme 19 contain oligooxyethylene side groups.[225] The merit of these two synthetic schemes consists in the fact that the resulting polymers contain only imide rings. Soluble polyimides were also reported by the sequence of reactions from Scheme 20 i.e., by conventional imidization.[226] All these rigid rod-like polyimides form layered mesophases.[224-226] It is interesting to mention that polymers containing identical length of their alkyl side groups are isomorphic within their crystalline phase and therefore, form solid solutions regardless of the nature of their polymer backbone.[226] For example the polyimide from the top part of Scheme 20 is isomorphic with the polyester which has an identical number of carbons in its side groups (bottom part of Scheme 20).[226]

Soluble polyimides were also synthesized from 3,6-diphenylpyromellitic dianhydride and various diamines.[227] A lyotropic polyimide was obtained from the twisted 2,2'-bis(trifluoromethyl)-4,4'-diaminobiphenyl and 3,6-diphenylpyromellitic dianhydride (Scheme 21).[227]

14.6.1.6 Thermotropic Poly(1,4-arylenevinylene)s

Poly(phenylenevinylene)s can be synthesized by a variety of reactions including Wittig reaction,[228] Hofmann elimination,[229] McMurry reaction,[230] Heck reaction[231] and Siegrist reaction.[232]

Liquid crystalline oligo(p-phenylenevinylene)s were first reported by Campbell and McDonald.[233] High molecular weight poly(p-phenylenevinylene)s are insoluble and infusible. The first thermotropic poly(phenylenevinylene)s were reported by Memeger.[234] They were synthesized by the Wittig reaction. The insertion of suitable substituents such as Cl on the phenyl ring, the replacement of phenyl rings with anthracene or naphthalene and of vinylene with ethane allowed a synthesis of thermotropic poly(arylenevinylene)s.[234]

Thermotropic poly(arylenevinylene)s were also reported by Heitz et al. who developed various synthetic methods based on the Heck reaction.[211,231,235,236] Some of these procedures are outlined in Scheme 22. The highest solubility is obtained with the polymer with R_1=H and R_2=C_6H_5. The polymers with R_1=H and R_2=C_6H_5 or CF_3 exhibit thermotropic mesophases.[235] Additional examples of poly(p-arylene vinylene)s are presented in Scheme 23.[237] Both homopolymers and copolymers were synthesized by the procedure outlined in Scheme 23. As expected, copolymers with highly dissimilar structural units which can also yield constitutional isomeric structural units yield soluble, thermotropic liquid crystalline polymers which are conjugated.[237] Only qualitative information is available on their liquid crystalline behavior. Thermotropic poly(phenylenevinylene)s containing flexible spacers synthesized by the Heck reaction were reported by Saegusa et al.[238]

14.6.1.7 Polyurethanes

The first series of thermotropic polyurethanes was synthesized beginning with 1981.[239-243] However, they were prepared mostly from isocyanates or primary amines and were not stable above their melting temperature. The first examples of thermally stable polyurethanes were reported by Kricheldorf et al.[244-246] Smectic polyurethanes were synthesized from the bischloroformates of 4,4'-alkylenedioxydiphenols prepared from α,ω-dibromoalkanes and hydroquinone with piperazine, trans-2,5-dimethylpiperazine and 4,4'-bipiperidine by interfacial polycondensation (Scheme 24).[246] Polyurethanes without flexible spacers were synthesized from 4,4'-bipiperidine, 1,2-bis(4-piperidinyl)ethane and 1,3-bis(4-piperidinyl)propane with the bischloroformates of p-phenylene, 2-methyl-1,4-phenylene or 2,5-bisphenylylene. Copolyurethanes were also synthesized.[247] The polymers derived from hydroquinone or methylhydroquinone are semicrystalline with short-term stability up to 310 °C. The polymers obtained from phenylhydroquinone are amorphous with a thermal stability up to 360 °C. Polyurethanes and copolyurethanes prepared from 4,4'-biphenylylene units form a smectic layered structure in the solid state and a nematic mesophase above the melting temperature (Scheme 25). While the research group of Kricheldorf decreases the crystallization ability by suppressing the hydrogen bonding ability of the urethane groups, Mormann et al. have generated thermally stable polyurethanes from diisocyanate substituted benzoates.[248-254] The resulted polyester-urethanes are more flexible and generate broader ranges of mesophases by decreasing the melting temperature.[253,254] Additional examples of polyurethanes were reported by MacKnight et al.[255]

14.6.1.8 Polycarbonates

The first examples of polycarbonates containing flexible spacers were reported by Roviello and Sirigu[256,257] and by Sato et al.[258,259] Poly(ester carbonate)s from tert-butylhydroquinone and terephthalic acid were first reported by Prevorsek et al.[260] Soluble aromatic copolycarbonates were synthesized by Kricheldorf and Lubbers.[261,262] They are conveniently prepared by copolymerization of three or four bisphenols with bis(trichloroacetyl)carbonate. For example, copolycarbonates based on 4,4'-dihydroxybiphenyl, methylhydroquinone and 4,4'-dihydroxybiphenyl ether or 4,4'-

dihydroxybenzophenone are soluble in aprotic organic solvents such as methylene chloride.[262] Poly(ester carbonate)s were also synthesized by melt polycondensation of substituted hydroquinones and diphenylterephthalate with diphenylcarbonate[263] and from p-hydroxybenzoic acid, 4,4'-dihydroxybiphenyl and diphenylcarbonate.[264]

14.6.1.9 Poly(ester anhydride)s

Thermotropic poly(ester anhydride)s were synthesized from terephthaloyl chloride with silylated hydroxy acids.[265] The polymers presented in Scheme 26 are noncrystallizable and exhibit a nematic phase over a broad range of temperatures.[265]

14.6.1.10 Poly(ester imide)s

Thermotropic poly(ester imide)s were developed by Kricheldorf's group. The first series of thermotropic poly(ester imide)s were synthesized starting from trimellitic anhydride and α,ω-diaminoalkanes containing from four to twelve methylene units. The resulting α,ω-diaminoalkane bis(trimellitimide)s were reacted with various 4,4'-diacetoxybisphenols (Scheme 27) including those based on 4,4'-dihydroxybiphenyl,[266] hydroquinone, methyl-, chloro-, phenyl- and tetrachlorohydroquinone, 1,5-, 1,4-, 2,7- and 2,6-dihydroxynaphthalenes.[267] All these polymers crystallize in a layered morphology. The polymers with Ar = 4,4'-biphenylyl melt into a smectic mesophase.[266] The melting varies from 297 °C for the polymer with n = 12 to 393 °C for the polymer with n = 4. The liquid crystalline phase undergoes isotropization at 386 °C for the polymer with n = 12 and at 467 °C for the polymer with n = 4. The rate of crystallization of all these polymers is unusually fast. With the exception of the polymers based on Ar = 1,4-phenylene, 1,4-tetrachlorophenylene and 2,6-naphthalene, which exhibit a smectic mesophase, the other polymers melt directly into an isotropic phase.[267]

The second procedure used in the preparation of poly(ester imide)s is based on the reaction of pyromellitic dianhydride or benzophenone-3,3',4,4'-tetracarboxylic dianhydride with aminoacids or lactams followed by the condensation of the resulting diacids with diacetates of hydroquinone, 2,6-dihydroxynaphthalene or 4,4'-dihydroxybiphenyl[268] (Scheme 28). All polymers presented in Scheme 28 crystallize in a layered structure. With the exception of the polymer with n = 11, all the other polymers based on Ar = 4,4'-biphenylyl exhibit a smectic mesophase. The polymer with n = 10 and Ar = 1,4-phenylene exhibits a smectic mesophase. The other polymers based on Ar = 1,4-phenylene or 2,6-naphthylene melt directly into an isotropic phase.[268]

An additional method for the synthesis of thermotropic poly(ester imide)s is based on the reaction of trimellitic dianhydride with aminoacids or lactams followed by condensation with acetates of bisphenols (Scheme 29). This reaction can be performed as "one pot procedure".[269] Again all homopolymers exhibit a lamellar crystalline phase which in all cases melts into an enantiotropic smectic phase. However, the corresponding copolymers exhibit a nematic mesophase. It is interesting to mention that the homopoly(ester imide)s from Scheme 29 are in fact copolymers since their structural units have two constitutional isomers. Finally, fully aromatic poly(ester imide)s were reported by the same research group by using several different synthetic procedures which are outlined in Scheme 30.[270-273] The imide monomers from Scheme 30 were homopolymerized and copolymerized either between themselves or with other aromatic dicarboxylic acids, bisphenols or hydroxyacids to give fully aromatic poly(ester imide)s with complex thermal behavior.[271,272] However, the fully aromatic poly(imide ester)s from Scheme 31 exhibit glass transition temperatures between 140 and 180 °C and nematic mesophases which undergo isotropization between 375 and 500 °C.[273]

14.6.1.11 Polyhydrocarbons

In addition to the class of poly(arylenevinylene)s described in chapter 14.6.1.6 and poly(phenylene)s and poly(arylene)s described in chapter 14.6.1.1 liquid crystalline polymers containing flexible spacers and only carbon-carbon bonds were also synthesized by homocoupling of bis(4-bromophenyl)alkanes.[274]

14.6.1.12 Polyethers

Thermotropic polyethers based on rigid rod-like mesogens and flexible spacers are of interest since they do not undergo transesterification or other rearrangement reactions during their characterization which requires extensive annealing at high temperatures. The effect of thermally induced rearrangement reactions will be discussed in a subsequent chapter. Polyethers can be conveniently prepared by the phase transfer catalyzed polyetherification of mesogenic bisphenols with α,ω-dibromoalkanes. The main criterion required for their synthesis is good solubility of the resulting polymer in the reaction media.[275-278]

14.6.2 Persistence Lengths of Soluble Polyesters and Polyamides

The persistence length and the Mark-Houwink coeficient, a, were determined both for soluble polyesters and polyamides. For soluble polyesters the persistence length data obtained by various authors are 95 Å (a=0.95),[216a] 120±10 Å (a=0.85 but estimated to be 1.0),[216b] and 110 Å (a=1.0-1.1).[216c] For substituted aromatic polyamides the values of the persistence length reported are 85±26 Å[198] and 200 Å (a=1.1-1.2).[194] Both values are lower than those reported for poly(p-phenylenediamine terephthalic acid) (150-290 Å) and for poly(p-benzamide) (240-750) Å.[198] All these results demonstate that both polyesters and polyamides do not resemble rigid rods but are comparable to typical semiflexible chains containing approximately 2-20 persistence lengths. In addition, the values obtained for the Mark-Houwink coefficient, a, also support the semiflexible character of these chains (a is 0.8 for flexible and 2.0 for rigid chains). While aromatic polyamides, depending on substituent, can generate lyotropic solutions, soluble polyesters do not. Films cast from solutions of aromatic polyesters are transparent (amorphous) and become turbid (anisotropic) only after annealing above their glass transition temperature. In conclusion, although due to interchain interactions the rigidity of polyesters and polyamides increases versus that predicted by gas phase and dilute solutions of low molar mass compounds (chapter 14.4), both types of polymers belong to the class of semiflexible polymers.

14.7 CHEMICAL HETEROGENEITY IN MAIN CHAIN LIQUID CRYSTALLINE COPOLYMERS

As discussed in chapter 14.6, main chain liquid crystalline polymers and copolymers are synthesized by step polymerizations that are based on reversible or irreversible reactions. A polymerization reaction is reversible depending on its mechanism and on the reaction conditions used. In contrast to chain copolymerizations, step copolymerizations performed in a homogeneous phase at high conversion and with a stoichiometric ratio between comonomers always lead to copolymer compositions that are identical with the comonomer feed. Also, the difference between the reactivities of various monomers used in step reactions is lower than that of the monomers used in chain reactions. This implies that the compositional heterogeneity of the copolymers obtained by step reactions is lower than that of copolymers synthesized by chain copolymerizations where copolymer composition is conversion dependent. However, again in contrast to chain copolymerizations, in step copolymerizations the copolymer's sequence distribution can be either kinetically (in irreversible copolymerizations) or thermodynamically (in reversible copolymerizations) determined. In reversible step copolymerizations, the sequence distribution is thermodynamically controlled and the copolymer microstructure is determined by redistribution reactions. The copolymer sequence distribution[279,280] and the configuration of the structural units[104,281,282] are both determined by the type of phase (isotropic, liquid crystalline, or crystalline) in which copolymerization or the copolymer reorganization reaction is performed. Microheterogeneous copolymerization reactions complicate the control of the copolymer's microstructure since the concentration of the comonomers in the proximity of the growing chain is determined by the miscibility and/or the association between the growing chain and the monomers. The concept that the growing chain can control its own environment during copolymerization was explained on the basis of the "bootstrap" model and its implications were recently reviewed.[283] Some of the most recent examples of "bootstrap effects" were observed in the radical copolymerization of macromonomers,[284-286] in the synthesis of block copolymers from immiscible amorphous segments,[287,288] and in the synthesis of ternary copolymers from monomers that can give rise to amorphous and liquid crystalline structural units by reversible copolymerization reactions.[289]

Copolymerization reactions performed in bulk are frequently used in the preparation of liquid crystalline polyesters, poly(ester imide)s, etc. The starting monomers lead to isomorphic melts, nevertheless above a certain conversion this reversible reaction is performed in the liquid crystalline phase. A heterogeneous composition is generated both by the different reactivities of the monomers and by the polydispersities of the polymers. This heterogeneous composition generates a microphase separated reaction mixture which at a given temperature contains isotropic, liquid crystalline and crystalline phases. Each of these phases generates a polymer homologous series of copolymers which have both different compositions and for the same composition a different sequence distribution. The sequence distribution is determined by the phase in which the copolymer is generated i.e., isotropic, liquid crystalline or crystalline. This microheterogeneous copolymerization reaction enhances the chemical heterogeneity of the resulted copolymers. Both the polydispersity and the chemical heterogeneity of liquid crystalline copolymers are responsible for the biphasic or even multiphasic nature of liquid crystalline copolyesters.[45,290-296] The chemical heterogeneity of liquid crystalline copolymers is reduced or even eliminated in the case of azeotropic irreversible copolymerizations.[103d,297,298] Excellent discussions on the change in sequence distribution and molecular weight during the annealing of thermotropic polyesters is available.[45,296,299] The same processes should take place in polyamides, polycarbonates, poly(ether imide)s, polyurethanes, polyanhydrides and any other polymers containing chemical bonds which can undergo rearrangement reactions during thermal treatment.

14.8 FLEXIBLE AND SEMIFLEXIBLE LIQUID CRYSTALLINE POLYETHERS

Flexible liquid crystalline polyethers are based on flexible mesogenic or structural units which are rod-like mesogenic units based on conformational isomerism. In gas phase and dilute solution these units are as flexible as for example butane[107] (see chapter 14.4.2). However, in melt phase interchain interactions are increasing their rigidity. The simplest structural units which can be used for the synthesis of flexible liquid crystalline polymers based on conformational isomerism are diphenylethane, phenylbenzyl ether, and methyleneoxy units (Scheme 32). Flexible rod-like mesogens or rod-like mesogens based on conformational isomerism exhibit a number of different conformers which are in dynamic equilibrium. The two most stable conformers are the anti and gauche. The anti conformer has an extended rod-like shape and therefore is expected to display liquid crystallinity. The gauche conformer is similar to a "kinked" unit which is occasionally introduced within the structure of main chain liquid crystalline copolymers based on rigid rod-like mesogens to decrease their crystallization ability. Therefore, the insertion of flexible units capable of giving rise to extended and kinked conformers within the main chain of a polymer is expected to provide a liquid crystalline polymer having a dynamic composition. To date there are no data on the dynamic equilibrium between different conformers of "flexible" rod-like mesogens. However, it is well established that when rod-like or linear conformations are in dynamic equilibrium with random-coil conformations, the rod-like conformation is preferred in the nematic phase.[300-302] Therefore, it is not excluded that in the nematic phase the preferred conformer may be the anti.

Low molar mass liquid crystals based on benzyl ether and diphenylethane units are well known. Table 13 summarizes the dependence between the structure of some benzyl ether compounds and the thermodynamic stability of their mesophase. A brief inspection of Table 13 shows that all flexible compounds listed exhibit liquid crystalline mesophases. However, the thermodynamic stability of their mesophase with respect to the crystalline phase is drastically dependent on subtle changes in their structure. For example compound 1 exhibits a virtual nematic mesophase at -20 °C. Hydrogenation of one of its phenyl rings enhances its isotropization by 68.6 °C. Nevertheless, the nematic phase of compound 2 is only monotropic. The replacement of the 1,4-cyclohexane ring of 2 with a bicyclooctane unit generates an enantiotropic mesophase. The difference between the isotropization temperature of compounds 1 and 3 from Table 13 is 93 °C. If we replace the cyano group of 2 with a pentyl group the new compound 4 exhibits again a virtual mesophase. The replacement of a methylenic unit of the pentyl group of 4 with an oxygen generates compound 6 which displays a monotropic nematic phase. The substitution of the methyleneoxy group of 6 with an ethane unit generates an enantiotropic nematic mesophase (compound 7).

Table 14 provides some examples of low molar mass liquid crystals based on diphenylethane, cyclohexylphenylethane, dicyclohexylethane and dicyclooctylphenylethane.[303,306-310] The flexible mesogenic units from Table 14 follow the same kind of trend as those from Table 13. For example the phase behavior of 1 and 2 from Table 13 are almost identical to that of 8 and 9 from Table 14. Hydrogenating a phenyl ring from 8 increases the thermal stability of the nematic phase of 9 by about 75 °C versus that of 8. Replacing a phenyl ring from 8 with a bicyclooctane ring enhances the thermodynamic stability of the nematic phase by 137 °C.

Let us now consider that we increase the molecular weight of 1 or 8 by polymerization. According to the thermodynamic trends discussed in chapter 14.5.3, the virtual mesophase of the monomeric structural unit should become at higher molecular weights enantiotropic, monotropic or remain virtual. In the last case the transition of the virtual mesophase of the polymer should however be shifted to higher temperatures.

The synthesis of the first flexible main chain liquid crystalline polyether without spacers is outlined in Scheme 33.[103a] As expected based on the above discussion, the resulted polyethers based on trans 1,4-bis[(methylsulfonyl)methyl]cyclohexane and methylhydroquinone or phenylhydroquinone display an enantiotropic nematic mesophase. The copolymers containing also some amount of cis 1,4-bis[(methylsulfonyl)methyl]cyclohexane also display a nematic mesophase. DSC traces of the polyethers based on methylhydroquinone and trans 1,4-bis[(methylsulfonyl)methyl]cyclohexane are identical to those of the corresponding polyesters based on methylhydroquinone and 1,4-cyclohexanedicarboxylic acid[281,282,311] except that the phase transitions of the polyethers are shifted to lower temperatures.[103a] Based on the thermodynamic principles discussed previously this is an expected result since the corresponding polyesters are identical to the polyether from Scheme 33 except that the methyleneoxy units from the structure of the polyethers are replaced with ester units. This increases only the overall rigidity of the polyesters versus that of the polyethers.

Polyethers based on substituted hydroquinones and p-dibromo- or dichloroxylene also lead to liquid crystalline polyethers.[312,313]

Memeger[313] has synthesized in 1975 high molecular weight polyethers based on α,α'-dichloro-p-xylene and methylhydroquinone in dimethylacetamide using K_2CO_3 as base. Fibers with high modulus (233 gpd) were spun from these polymers. Unfortunately the polyetherification of substituted hydroquinones with α,α'-dichloro-p-xylene leads both to C- and O-alkylation reactions. Nematic polyethers with and without flexible spacers were also synthesized by cationic ring opening polymerization of exo-2-methyl-7-oxabicyclo[2.2.1]heptane and 7-oxabicyclo[2.2.1]heptane as well as by the copolymerization of the later monomer with tetrahydrofuran and/or ethylene oxide[314,315] (Scheme 34).

A comprehensive series of experiments was performed with polyethers based on 1-(4-hydroxyphenyl)-2-(2-R-hydroxyphenyl)ethane (RBPE) and α,ω-dibromoalkanes containing from four to twenty methylenic units,[90,103b-f,316-321] particularly those based on 1-(4-hydroxyphenyl)-2-(2-methyl-hydroxyphenyl)ethane (MBPE). All these polyethers are in fact copolyethers since their structural unit has two constitutional isomers (Scheme 35). With the exception of MBPE-5 and MBPE-9 which exhibit two monotropic nematic mesophases, and MBPE-8 and MBPE-11 which exhibit one monotropic nematic mesophase, all the other MBPE-X polyethers are only crystalline.[103e] Nevertheless, again based on the thermodynamic discussion from chapter 14.5 we can assume that all of them may exhibit virtual mesophases. The virtual transition temperatures and thermodynamic parameters of all MBPE-X polymers were determined by copolymerization experiments of MBPE with two different flexible spacers.[90,103,316-321]

The technique developed and used for the determination of their virtual transition temperatures and thermodynamic parameters is as follows. The structural units of the copolymers resulted from two flexible spacers and one mesogen are isomorphic in their mesophase but not in their crystalline phases. As a consequence, the crystallization temperature of the copolymer is decreased and exhibits an eutectic point while both the temperature and the enthalpy associated with the mesophase are displaying continuous dependences on composition. Therefore, in the mesophase the two structural units behave as an ideal solution and obey the Schroeder-Van Laar equations (chapter 14.3).[91] Since the difference between ΔH_1 and ΔH_2 of the two homopolymers is not large and the values of ΔH_1 and ΔH_2 are proportional to their T_1 and T_2 transition temperatures most of these dependences are linear. Therefore, upon extrapolation to the composition of the two homopolymers the "uncovered" temperature transitions of the copolymers can be used to determine both virtual transition temperatures and their associated thermodynamic parameters of the parent homopolymers. An example of DSC traces for the copolymer MBPE-5/8 (i.e. based on five and eight methylenic units in the spacer) is presented in Figure 16. The dependences of transition temperatures and enthalpy changes of MBPE-5/8 versus composition for the results collected from Figure 16 together with their extrapolations are presented in Figure 17.[317] The virtual phase transition temperatures and thermodynamic parameters of MBPE-X determined from various pairs of flexible spacers agree very well.[103e] Figure 18 presents the plot of the dependence of the virtual isotropic-nematic transition temperatures as a function of the number of carbons (x) in the flexible spacer and its inverse (1/x).[103e] We can observe from Figure 18 that the virtual mesophase of these polymers does not vanish even at very long spacer length. This suggests that polyethylene should also exhibit a virtual mesophase as was indeed theoretically predicted.[322] The highest temperature nematic mesophase of MBPE-X homopolymers and copolymers was confirmed by X-ray experiments.[103f,323] The entire series of ClBPE-X homopolymers behaves almost identical to the series of MBPE-X polymers and confirms all these data.[324]

The thermodynamic parameters associated with the isotropic-nematic phase transition temperatures of MBPE-X[103e] and ClBPE-X were plotted as a function of the number of carbons in the spacer and the orientational contribution of the mesogen and conformational contribution per -CH_2- group at the isotropic-nematic transitions were determined.[103e,324] These values are summarized in Table 15 together with the corresponding data obtained for the polyethers based on 4,4'-dihydroxy-α-methylstilbene (HMS-X)[278] and of the polyesters based on 4,4'-dihydroxy-2,2'-dimethylazoxybenzene and α,ω-alkanedioic acids (DMAB-X).[48] The polymers HMS-X and DMAB-X contain rigid rod-like mesogens, while MBPE-X and ClBPE-X contain flexible rod-like mesogens. As we can see from Table 15 both the enthalpic and entropic contributions per -CH_2- are independent of the nature of the mesogen. They are higher for the polymers based on even spacers and all data are in good agreement. However, the orientational entropic contributions per mesogen are higher in the case of flexible mesogens than in the case of rigid mesogens. This result suggests that at the isotropic-nematic transition, the flexible mesogen undergoes in addition to the orientational arrangement also a transition from its gauche into its anti conformer.

The determination of the virtual phase transition temperatures of polymers can be also done by preparing mixtures with low molar mass liquid crystals or blends with other virtual liquid crystalline polymers. However, these two techniques are less reliable than the copolymerization based technique.[90]

It has been also shown that copolymerizations based on two and more than two flexible spacers or mesogenic units can be used to engineer phase transition temperatures and corresponding thermodynamic parameters of copolymers.[103d,321] The only requirement for these experiments is that the structural units of these copolymers should be isomorphic within the mesophase we want to tailor make and the molecular weight of the homopolymers and copolymers should be higher than the molecular weight below which phase transitions are molecular weight dependent. When the thermal transition temperatures and the corresponding enthalpy changes of the homopolymers are not highly dissimilar both the transition temperatures of the copolymers and their associated enthalpies can be calculated from Equations 4 and 5, in which X_n is the mole fraction of the structural unit n from copolymer and T and ΔH are the transition temperature and the enthalpy change associated with the same phase transition of the parent homopolymer based on an identical structural unit.[321]

MBPE-X and ClBPE-X with x = 5, 7, 9, 11 and 13 exhibit a second uniaxial nematic mesophase which in certain polymers is monotropic while in other is virtual.[103e,324] This second nematic mesophase was transformed into an enantiotropic one by copolymerization experiments and was subsequently characterized by X-ray experiments.[325] This second uniaxial nematic phase was theoretically predicted.[326]

The influence of the size of various substituents on the phase transitions of RBPE-X was also investigated.[327] It has been demonstrated that phase transition temperatures of polymers depend on the nature of lateral substituent by following the same trend as that followed by low molar mass liquid crystals. Some data are summarized in Table 16. A detailed discussion is available.[327] When the substituent of RBPE-X polymers is H, i.e.

BPE, they do not exhibit anymore a nematic mesophase. For example, BPE-8/10 (i.e. the copolymer containing a 50/50 molar ratio of spacer lengths containing eight and ten carbon atoms) displays an enantiotropic s_B mesophase.[328] At the same time, BPE-8/12 (i.e. the copolymer containing a 50/50 molar ratio of spacer lengths containing eight and twelve carbon atoms) exhibits an enantiotropic columnar hexagonal (Φ_h) mesophase.[329] By increasing the length of the mesogenic unit from BPE to 4,4'-bis[2-(4-hydroxyphenyl)ethyl]benzene (PEB) (Scheme 36), the resulting homopolyethers PEB-X and the copolyethers based on PEB, BPE and various flexible spacers all exhibit columnar mesophases.[330,331] Both the phase transition temperatures and the corresponding thermodynamic parameters of the columnar hexagonal mesophases can be tailor made by similar copolymerization experiments[330,331] as those used to tailor make nematic mesophases.[103d,f] The columnar hexagonal mesophase of BPE and PEB copolymers is not unexpected if we consider them as being "copolymers" of polyethylene and poly(p-xylylene). Since both polyethylene and poly(p-xylylene) display a columnar hexagonal mesophase it is expected that RBPE-X with R = H or even F to display the same mesophases.[329] Figure 19 outlines the columnar hexagonal phases of polyethylene, poly(p-xylylene) and of some of the copolymers based on BPE and PEB.[329] As we can observe from Figure 19 the columnar hexagonal mesophase is induced by the conformational disorder of the spacer.

So far, with few exceptions, all the experiments with polyethers based on RBPE generate mesophases which are either thermodynamically unstable (virtual) with respect to the crystalline phase or metastable (monotropic). Based on the thermodynamic discussion from chapter 14.5 an increase of the rigidity of the mesogen and a simultaneous increase in its disorder or entropy should decrease the ability towards crystallization and increase the ability towards the generation of a mesophase. Scheme 37 outlines the development of a series of polyethers based on this concept.[332] A 4-hydroxyphenyl group from BPE was replaced with 4-hydroxybiphenyl to increase its rigidity. The ethyl group from BPE was replaced with 1,2-butane group. Thus a new mesogenic group 1-(4-hydroxy-4'-biphenyl)-2-(4-hydroxyphenyl)butane (TPB) results.[332] TPB has a chiral center and therefore the racemic monomer leads to TPB-X "copolymers" based on four constitutional isomeric structural units (Scheme 37). These polymers are soluble in conventional solvents. The phase transitions of TPB-X (with x = 4 to 20) are summarized in Figure 20.[332] The dependences of glass transition, isotropization and melting transition temperatures versus x are different and as a consequence, they generate polymers exhibiting glassy (TPB-5), noncrystallizable nematic (TPB-4, TPB-6 to TPB-10), crystallizable nematic (TPB-11 to TPB-15), monotropic nematic (TPB-16 and TPB-17) and virtual nematic (TPB-18 to TPB-20) mesophases. This behavior is self-explanatory if we follow the plots from Figure 20. For example, some polymers are noncrystallizable since their glass transition temperature prohibits for kinetic reasons their crystallization. TPB-5 is only glassy since its glass transition temperature does not allow the formation of the mesophase, again for kinetic reasons. When the melting temperature is higher than the glass transition, these polymers can crystallize, while when melting is higher than isotropization they exhibit a virtual nematic mesophase only.

TPB-10 was synthesized with a perdeuterated spacer and the conformational and orientational order in the nematic phase was determined by D-NMR measurements and conformational calculations.[333] Since this polymer does not undergo redistribution reactions as the polyesters do, its behavior is as predicted by theory.[334] Beginning at the isotropic-nematic transition at 104 °C, the polymer chains in the nematic phase adopt nearly fully extended (alternate trans) conformations and a rather high degree of orientational order parameter of ca. 0.85 is attained. As the temperature is lowered to 96 °C, the isotropic peak disappears completely, indicating the absence of any isotropic phase and hairpin conformations. With increasing supercooling, the conformational order shows little change, but the orientational order parameter increases continuously to ca. 0.95 at 80 °C. These results are therefore, in good agreement with the predictions of a recent theory on the nematic phase of a polymer comprising rigid and flexible sequences in alternating succession.[334] When the 1,2-butane group from TPB is replaced by 1,2-propane, the new mesogen 1-(4-hydroxy-4'-biphenyl)-2-(4-hydroxyphenyl)propane (TPP) has a more cylindrical shape. This new mesogen, therefore resembles RBPE with R = H. The polyethers TPP-X with x containing an even number of methylenic units display columnar hexagonal mesophases while those with an odd number of methylenic units exhibit nematic mesophases.[335]

14.9. HYPERBRANCHED DENDRITIC LIQUID CRYSTALLINE POLYMERS

Hyperbranched dendritic macromolecules are a novel class of branched polymers which contain a branching point in each structural unit. For a review see reference 336. Although dendritic polyphenylenes,[337,338] polybenzyl ethers[339,340] and aromatic polyesters[341,342] were synthesized, none of them displayed liquid crystallinity. A lamellar lyotropic liquid crystalline phase was reported for a mixture of octanoic acid and a dendrimeric polyethyleneimine of the third generation $N\{CH_2CH_2N[CH_2CH_2N\{CH_2CH_2N\}_2]_2\}_3$.[343]

The first thermotropic dendrimer is a polyether based on a mesogenic unit which exhibits conformational isomerism (TPD-b).[344] The conformational isomerism of the mesogen allows both the synthesis of the dendrimer and the generation of a thermotropic nematic mesophase (Scheme 38).[344] The thermotropic behavior of this dendrimer is strongly dependent on the nature of its chain ends R groups (Table 17).

An aromatic polyamide lyotropic dendrimer was obtained by the polycondensation of 5-amino-isophthaloyl chloride. However, the dendrimer obtained from the polymerization of 3,5-diaminobenzoyl chloride does not display a lyotropic phase.[345]

14.10 CYCLIC MAIN CHAIN LIQUID CRYSTALLINE POLYETHERS

The cyclic monomer, dimer, trimer, tetramer, pentamer and high molecular weight polyethers based on 1-(4-hydroxy-4'-biphenyl)-2-(4-hydroxyphenyl)butane (TPB) and 1,10-dibromodecane were synthesized and characterized and their phase behavior was compared to that of the linear TPB-10 polymer with high molecular weight.[346] Figure 21 outlines their structure. The cyclic monomer is liquid. All other cyclics, dimer and larger exhibit a thermotropic nematic phase. The cyclic tetramer and pentamer display higher isotropization temperatures than of the linear polymer with high molecular weight.[346]

14.11 SIDE CHAIN LIQUID CRYSTALLINE POLYMERS

14.11.1 General Considerations

The field of side chain liquid crystalline polymers was recently reviewed.[58] Therefore, we will discuss only recent progress made on their molecular engineering. For basic introduction to the various aspects of the field of side chain liquid crystalline polymers we suggest reference 58 to be consulted. Most of the present discussion will be made on side chain liquid crystalline polymers with mesogenic groups normally attached to the polymeric backbone.[72] Figure 22 outlines the concept of side chain liquid crystalline polymers. It has been theoretically predicted[347] that the conformation of the polymer backbone should get distorted in the liquid crystalline phase. Both small-angle neutron scattering (SANS) experiments[80,81,348-350] and X-ray scattering experiments,[82b,351,352] have shown that the statistical random-coil conformation of the polymer backbone is slightly distorted in the nematic phase and highly distorted in the smectic phase.

Let us now consider very briefly the influence of various parameters (i.e., nature of flexible spacer and its length, nature and flexibility of the polymer backbone and its degree of polymerization) on the phase behavior of a side chain liquid crystalline polymer. According to the thermodynamic schemes from chapter 14.5, the increase of the degree of polymerization decreases the entropy of the system and therefore if the monomeric structural unit exhibits a virtual or monotropic mesophase, the resulting polymer should most probably exhibit a monotropic or enantiotropic mesophase. Alternatively, if the monomeric structural unit displays an enantiotropic mesophase, the polymer should display an enantiotropic mesophase which is broader. It is also possible that the structural unit of the polymer exhibits more than one virtual mesophase and therefore at high molecular weights the polymer will increase the number of its mesophases. All these effects were observed with various systems.[72]

The length of the flexible spacer determines the nature of the mesophase. Long spacers favor smectic phases while short spacers favor nematic phases. This effect is similar to that observed in low molar mass liquid crystals.

At constant molecular weight the rigidity of the polymer backbone determines the thermodynamic stability of the mesophase. According to the thermodynamic schemes described in chapter 14.5 the isotropization temperature of the polymer with more rigid backbone should be higher. However, experimentally this situation is reversed. The highest isotropization transition temperature is observed for polymers with more flexible backbones. This conclusion is based on systematic investigations performed with two mesogenic groups which are constitutional isomers i.e., 4-methoxy-4'-hydroxy-α-methylstilbene (4-MHMS)[353] and 4-hydroxy-4'-methoxy-α-methylstilbene (4'MHMS)[354] and polymethacrylate, polyacrylate, polysiloxane and polyphosphazene backbones[353-355] (Scheme 39). This dependence can be explained by assuming that a more flexible backbone uses less energy to get distorted and therefore generates a more decoupled polymer system. In fact the more flexible backbones do not generate only higher isotropization temperatures but also higher ability towards crystallization. However, contrary to all expectations the entropy change of isotropization is higher for those polymers which are based on more rigid backbones and therefore, exhibit lower isotropization temperatures (Figure 23a,b).[82a] This contradiction between the values of the entropy change and the isotropization temperatures can be accounted for by a different mechanism of distortion of different polymer backbones as outlined in Figure 24, that is, while a rigid backbone gets more extended and therefore, in the smectic phase it can cross the smectic layer, in the case of a flexible backbone it gets squeezed between the smectic layers. The higher configurational entropy of the flexible backbone versus that of the rigid backbone in the smectic phase can account for the difference between the entropy change of isotropization from Figure 23. At shorter spacer lengths, there is not much difference between the contribution of various backbone flexibilities since most probably, in order to generate a mesophase they should get extended. Therefore the entropy change of isotropization is less dependent of backbone flexibility (Figure 23).

Based on this discussion it is quite obvious that copolymers containing structural units with and without mesogenic groups and flexible backbone display a microphase separated morphology of their smectic phase (Figure 25).[72,82b,352] Therefore, the highest degree of decoupling is expected for copolymers containing mesogenic and nonmesogenic structural units and highly flexible backbones, i.e., microphase separated systems. In this last case, when the monomeric structural unit of the polymer exhibits a virtual mesophase, the high molecular weight polymer might also display only a virtual or a monotropic mesophase. The transformation of a virtual and/or monotropic mesophase of the homopolymers into an enantiotropic mesophase can be most conveniently accomplished by making copolymers based on two monomers which are constitutional isomers such as monomers based on 4-MHMS and 4'-MHMS.[356,357] Since the structural units of the homopolymers based on 4-MHMS and 4'-MHMS are isomorphic within their liquid crystalline phase, but not within their crystalline phase, the crystalline melting transition decreases while the mesophase exhibits a continuous almost linear dependence on composition. As a consequence, the virtual or monotropic mesophase of the homopolymer becomes enantiotropic.[356,357] Finally, the molecular weight at which the isotropization temperature becomes independent of molecular weight should be, and indeed is, dependent on the flexibility of the polymer backbone. For example, the isotropization temperature of polysiloxanes[75,358] containing mesogenic side groups is molecular weight dependent up to much higher molecular weights than polymethacrylates containing mesogenic side groups.[72]

Based on this discussion and on the thermodynamic discussion from chapter 14.5, we can easily consider that the "polymer effect" can provide via its molecular weight and backbone flexibility the same effect. In an oversimplified way it can be considered that it provides an overall change in the entropy of the system. Through this change, it can transform, in a reversible way, a virtual mesophase into a monotropic and into an enantiotropic one. In addition, the kinetic factors provided by the glass transition and crystallization should always be considered. For example, the formation of a mesophase located in the close proximity of a glass transition temperature becomes kinetically controlled or even can be kinetically prohibited.

14.11.2 Molecular Engineering of Liquid Crystalline Polymers by Living Polymerization

14.11.2.1 General Considerations

Several polymerization methods were investigated in order to develop living polymerization procedures for the preparation of side chain liquid crystalline polymers with well defined molecular weight and narrow molecular weight distribution. They include cationic polymerization of mesogenic vinyl ethers,[359,360] cationic ring opening polymerization of mesogenic cyclic imino ethers,[361] group transfer polymerization of mesogenic methacrylates,[153,362-364] and polymerization of methacrylates with methylaluminium porphyrin catalysts.[365] Cationic polymerization has been proved to be the most successful since it can be used to polymerize under living conditions mesogenic vinyl ethers containing a large variety of functional groups.[139-145,154,158,366-378]

Scheme 40 provides some representative examples of mesogenic vinyl ethers which could be polymerized by a living mechanism by our preferred initiating system (i.e., CF_3SO_3H, $(CH_3)_2S$, CH_2Cl_2, 0 °C).[379] As we can observe from Scheme 40, vinyl ethers containing nucleophilic groups such as methoxybiphenyl,[371] electron-withdrawing groups such as cyanobiphenyl,[139-144,371,372] nitrobiphenyl and cyanophenylbenzoate,[371] double bonds like in 4-alkoxy-α-methylstilbene,[373] double bonds and cyano groups like in 4-cyano-4'-α-cyanostilbene,[143] aliphatic aromatic esters,[145] acidic protons and perfluorinated groups,[371,374] oligooxyethylene and aromatic ester groups,[376] crown ethers and triple bonds,[377] all can be polymerized by a living cationic mechanism. In addition, cationic polymerization of any of these monomers can be performed in melt phase either in liquid crystalline phase or in isotropic phase by using thermal[380], or photo cationic initiators.[381,382] When the polymerization is performed in liquid crystalline phase with alligned films of liquid crystalline monomers, perfectly alligned single crystal liquid crystalline polymer films are obtained.[381,382]

In the following two subchapters we will discuss two topics. The first one refers to the influence of molecular weight on the phase transitions of poly{ω-[(4-cyano-4'-biphenylyl)oxy]alkyl vinyl ether}s with alkyl groups containing from four to eleven methylene units. In the second one we will demonstrate the molecular engineering of phase transitions of side chain liquid crystalline polymers by azeotropic living copolymerization experiments.

14.11.2.2 Influence of Molecular Weight on Phase Transitions of Poly{ω-[(4-cyano-4'-biphenylyl)oxy]alkyl vinyl ether}s

Scheme 41 outlines the general method used for the synthesis of ω-[(4-cyano-4'-biphenylyl)oxy]alkyl vinyl ethers (6-n) and of the model compound for the polymer with degree of polymerization of one i.e., ω-[(4-cyano-4'-biphenylyl)oxy]alkyl ethyl ethers (8-n). We will use over the entire discussion the same short notations as in the original publications. The synthesis and characterization of poly(6-n) and (8-n) with n = 2, 3, 4,[140] 5, 7,[141] 6, 8,[371] 9, 10,[142] and 11[139] will be briefly discussed. Details are available in the original publications. All polymers have polydispersities of about 1.10. Scheme 42 outlines the polymerization mechanism and the structure of the resulted polymers. This structure was confirmed by 300 MHz 1-D and 2-D ^{1}H-NMR spectroscopy.[383]

All data were classified according to their similarities. Figure 26 presents the dependence of phase transition temperatures of poly(6-n) with n = 3, 4, 7 and 9 as a function of molecular weight. These data were collected from second heating scans. The data for 8-n are not plotted . 8-3 is crystalline, 8-4 and 8-7 exhibit a monotropic nematic mesophase while 8-9 monotropic nematic and smectic mesophases. As we can observe from Figure 26 by increasing the molecular weight all four polymers show a broadening of the thermal stability of their mesophase. The mesophase of 8-7 and 8-9 changes from nematic to s_A by increasing the degree of polymerization from one to about 3.

Figure 27 presents similar data for poly(6-2), poly(6-6) and poly(6-8). In all cases the nature of the mesophase is molecular weight dependent. Poly(6-2) has a nematic mesophase only at degrees of polymerization lower than 5. 8-2 is only crystalline. At degrees of polymerization higher than 5 poly(6-2) is only glassy. This is because its glass transition temperature becomes higher than the isotropization temperature and therefore, the mesophase is kinetically prohibited. 8-6 exhibits an enantiotropic nematic mesophase. At low degrees of polymerization poly(6-6) and poly(6-8) exhibit nematic and s_A mesophases. Due to the difference between the slope of the dependences of the nematic phase transition temperature on molecular weight and of the s_A phase transition temperature on molecular weight, above a certain molecular weight the nematic phase disappears. Both poly(6-6) and poly(6-8) show a second smectic mesophase (s_X, i.e. unassigned). Qualitatively, this behavior is in agreement with the influence of molecular weight on phase transitions predicted by thermodynamics (chapter 14.5). Quantitative predictions of these phase diagrams require more theoretical research.

Finally, Figure 28 presents the behavior of poly(6-5), poly(6-10) and poly(6-11). 8-5 shows an monotropic nematic phase, 8-10 a monotropic s_A phase while 8-11 an enantiotropic s_A mesophase. Poly(6-5) exhibits above a degree of polymerization of 10 the unusual sequence isotropic-nematic-s_{Ad}-n_{re}-glassy.[384] This will be discussed in more detail in a subsequent subchapter. At high molecular weights poly(6-10) and poly(6-11) exhibit s_A and s_X phases.

As a general observation we can mention that polymers with short spacers (n = 2, 3, 4) and medium length spacers containing an odd number of methylene units (n = 7, 9) do not generate polymorphism at different molecular weights. Polymers with medium length and an even number of methylene units (n = 6, 8), as well as polymers with long length with both even and odd numbers of methylenic units (n = 10, 11) generate a rich polymorphism which is molecular weight dependent. The borderline polymer is poly(6-5) which is the only one displaying n and s_A mesophases over a broad range of molecular weights and therefore also generates the reentrant nematic mesophase.[384]

14.11.2.3 Molecular Engineering of Liquid Crystalline Phases by Living Cationic Copolymerization

In order to tailor make mesophases of side chain liquid crystalline copolymers we first need to synthesize copolymers with constant molecular weight and controllable composition. Copolymer composition is conversion dependent in all statistic copolymerizations. The only exception is provided by azeotropic copolymerizations in which the copolymer composition is identical to the monomer feed at any conversion.[385] This situation is provided by monomers with $r_1 = r_2 = 1$. Since the reactivity of the polymerizable vinyl ether groups is not spacer length dependent, all 6-n monomers have the same reactivity. Therefore, all 6-n pairs of monomers lead to azeotropic copolymerizations, and when the copolymerization is performed under living conditions they lead to copolymers with controllable molecular weight. The azeotropic copolymerization of various pairs of 6-n monomers is outlined in Scheme 43. We will discuss selected examples of copolymers prepared from monomer pairs which give rise to homopolymers exhibiting nematic and nematic, s_A and s_A, nematic and s_A, and glassy and s_A phases as their highest temperature mesophases.

Figure 29 presents the dependence of phase transition temperatures obtained from second DSC heating scans (a,d), cooling scans (b, e) and the enthalpy changes associated with the highest temperature mesophase of copolymers poly[(6-3)-co-(6-5)]X/Y and poly[(6-6)-co-(6-11)]X/Y. The degrees of polymerization of all copolymers are equal to 20.[386] Copolymers poly[(6-3)-co-(6-5)]X/Y are based on a monomer pair which gives rise to two homopolymers displaying an enantiotropic nematic mesophase as their highest temperature mesophase. As we can observe from Figure 29a,b,c the nematic-isotropic transition temperature and its associated enthalpy change show linear dependences of composition. This means that the structural units derived from poly(6-3) and poly(6-5) are isomorphic into their nematic mesophase. However, the same two structural units are isomorphic within the s_A mesophase exhibited by poly(6-5) only over a very narrow range of compositions. The linear dependence of the isotropization temperature is predictable by the Schroeder-Van Laar equations.[91] The same discussion is valid for the copolymer system poly[(6-6)-co-(6-11)]X/Y except that the isotropization temperature of these copolymers exhibit an upward curvature. This upward curvature is also predicted by the Schroeder-Van Laar equations[91] and is due to the more dissimilar enthalpy changes associated with the isotropization temperatures of the two homopolymers.

Figure 30 presents the phase diagrams of copolymers poly[(6-3)-co-(6-11)]X/Y[342,344] and poly[(6-5)-co-(6-11)]X/Y.[384] Both sets of copolymers have degrees of polymerization of 20. Both pairs of copolymers are based on monomers which give rise to homopolymers exhibiting nematic and s_A as their highest temperature mesophases. However, poly(6-5) displays a nematic and a s_A mesophase, while poly(6-3) only a nematic mesophase. Both sets of copolymers display continuous dependences of their highest temperature mesophase with a triple point at a certain composition. This triple point generates over a very narrow range of compositions copolymers exhibiting the sequence isotropic-nematic-s_A-n_{re}. Again the shape of the dependences of the phase transition temperature on composition obeys the Schroeder-Van Laar equations.[91]

Figure 31 presents two sets of phase diagrams obtained from monomer pairs giving rise to homopolymers which exhibit isotropic and s_A mesophases as their highest temperature mesophases, i.e., poly[(6-2)-co-(6-8)]X/Y with degree of polymerization of 10,[387] and poly[(6-2)-co-(6-11)]X/Y with degree of polymerization of 15.[388] Both sets of copolymers display a similar phase diagram. Over a certain range of compositions the two structural units are isomorphic within the s_A phase, after which follows a triple point. After this triple point the two structural units are isomorphic within a newly generated nematic mesophase. Both copolymers generate within a certain range of compositions on the left side of the triple point the sequence isotropic-nematic-s_A-n_{re}.[384] Again the shape of the dependence of the highest temperature mesophase on composition is predictable by the Schroeder-Van Laar equations. This means that the stuctural units of all binary copolymers based on an identical mesogenic unit but different spacer lengths behave as an ideal solution. This behavior allows the engineering of mesomorphic phase transition temperatures and of their thermodynamic parameters in a straight forward manner by living azeotropic copolymerizations. The same behavior was demonstrated for monomer pairs which both give rise to homopolymers exhibiting a chiral smectic C mesophase.[389]

14.11.2.4 Side Chain Liquid Crystalline Polymers Exhibiting a Reentrant Nematic Mesophase

The reentrant nematic phase (n_{re}) was discovered in 1975 in low molar mass liquid crystals.[390] Since then it has received substantial theoretical and experimental interest.[391-399]

The first side chain liquid crystalline polymers exhibiting a n_{re} phase were reported in 1986.[400,401] Some other examples of polymers exhibiting the sequence isotropic-nematic-s_{Ad}-n_{re} were reported in the meantime.[155,384,402-405] All these polymers are based on mesogenic units containing a cyano group, five or six atoms in the flexible spacer and a polyacrylate or polyvinyl ether backbone. The replacement of these quite flexible backbones with a more rigid one like polymethacrylate does not allow the formation of the n_{re} phase. As discussed in the previous subchapter a n_{re} mesophase can be generated by copolymerization of two monomers which lead to homopolymers with nematic or isotropic and s_A as their highest temperature mesophases, since these copolymers exhibit a triple point on their phase diagrams.[384] According to our experimental results any polymer which exhibits the sequence isotropic-nematic-s_A should also display a n_{re} phase. The most probable mechanism for the generation of a n_{re} phase is outlined in Figure 32.[399] The most stable s_A phase of mesogens containing cyano groups is based on layers containing dimers of mesogens. On cooling, the nematic phase formed directly from the isotropic phase contains both dimeric mesogens and monomeric mesogens and so does the first s_A phase. In order to go from the less ordered s_A phase to the s_A phase based on dimeric mesogens, a n_{re} phase is required (Figure 32).[399]

14.11.2.5 Influence of Tacticity on Phase Transitions

The tacticity of the main chain determines its flexibility. Therefore, tacticity should affect the phase behavior of side chain liquid crystalline polymers in the same way as different polymer backbones with different flexibilities. Liquid crystalline polymethacrylates with atactic, syndiotactic and isotactic backbones were synthesized and characterized.[406-409] Although there are differences between the phase behavior of polymers with different tacticities, there is no quantitative understanding of this trend. This would require the investigation of the influence of both molecular weight and tacticity on phase transitions and therefore, it still remains an open subject of research.

14.11.2.6 Cyclic Polysiloxanes Containing Mesogenic Side Groups

Low molecular weight[410,411] and high molecular weight[75] cyclic polysiloxanes containing mesogenic side groups were reported. Figure 33 presents the dependence of the isotropization temperature on the degree of polymerization for linear and cyclic polysiloxanes containing cyanophenyl benzoate groups connected to the backbone by a pentyl spacer.[75] Isotropization temperatures of cyclic polymers are higher than those of the linear polymers. However, more research is required to reach the same level of understanding between structure and properties in this class of polymers as that available presently for glassy and crystalline polymers.[412]

14.11.2.7 Side Chain Liquid Crystalline Polyacetylenes

Monoacetylenic monomers containing mesogenic groups were reported from several laboratories.[413-415] However, the first report on the synthesis, polymerization and characterization of a liquid crystalline polyacetylene was reported only recently.[416] 4-Methoxy-4'-(hexyloxy)biphenyl dipropargyl acetate was cyclopolymerized by various transition metal catalysts and the resulting poly(1,6-heptadiyne) derivative containing mesogenic side groups exhibits an enantiotropic smectic mesophase (Scheme 44).[416]

14.12 LIQUID CRYSTALLINE POLYMERS CONTAINING CROWN ETHERS AND POLYPODANTS

Mesomorphic host-guest systems of low molecular weight and polymer liquid crystals containing macroheterocyclic ligands and polypodants provide a novel approach to self-assembled systems which combine selective recognition with external regulation.[417-420] Three basic architectures can be considered for liquid crystalline polymers containing crown ethers (Figure 34): main chain liquid crystalline polymers containing crown ethers in the main chain of the polymer and side chain liquid crystalline polymers containing crown ethers either in the mesogenic group or in the main chain. Alternatively, the same series of polymers with polypodants instead of crown ethers can be considered.

Main chain polyamides and polyethers containing crown ethers were reported.[421,422] A variety of side chain liquid crystalline polymers containing crown ether groups at one end of the mesogenic unit were designed.[377,423-428] Side chain liquid crystalline polymers containing crown ethers in the main chain were synthesized by living cationic cyclopolymerization and cocyclopolymerization of 1,2-bis(2-ethenyloxyethoxy)benzene derivatives containing mesogenic side groups.[375,376] Polymers containing crown ethers in the side groups dissolve ion-pairs and behave as copolymers containing two different mesogenic groups, i.e., complexed and uncomplexed. Their behavior is similar to that of copolymers derived from two different mesogenic groups. Therefore, their phase behavior is directed by molecular recognition.[429] The use of oligooxyethylenic spacers in main chain,[430] and side chain[431-433] liquid crystalline polymers leads to liquid crystalline polypodants. Both main chain[430] and side chain[433] liquid crystalline polypodants dissolve large amounts of alkali metal salts, and the resulting liquid crystalline polyelectrolytes are ionic conductors.[434]

14.13 ELECTRON DONOR-ACCEPTOR (EDA) COMPLEXES OF LIQUID CRYSTALLINE POLYMERS CONTAINING DISCOTIC MESOGENS

Ringsdorf et al. have studied the effect of doping with electron acceptor molecules on the phase behavior of polymers containing disc-like donor mesogens.[435-440] They found that charge transfer interactions both increase the degree of order within the liquid crystalline phase, and also stabilize the liquid crystalline mesophase. For example, when a discotic main-chain polyester was doped with 2,4,7-trinitrofluorenone (TNF), the width of the the discotic columnar hexagonal mesophase was increased by ~50 °C, for molar ratios of polymer/TNF equal to 3/1 and 2/1 (Scheme 45).[436] The intermolecular spacing decreased also considerably, proportional to the amount of TNF present in the complex. The same authors doped a non-liquid crystalline main-chain polyester containing disc-like mesogens and this resulted in the induction of a discotic columnar mesophase (Scheme 45). The intercolumnar spacings found were extremely large and the authors assumed that considerable amounts of TNF molecules were uncomplexed and were located in the intercolumnar spacing. Further, doping of a non-liquid crystalline polymethacrylate containing donor disc-like groups in the side-chain resulted in the formation of a nematic columnar mesophase (Scheme 46). Doping also induced compatibility and liquid crystallinity in an incompatible mixture of non-mesogenic electron donor polymers, i.e. a polymethacrylate and a polyester. The resulting discotic polymer blend exhibited a nematic columnar phase (Scheme 47).[436]

Finally, chirality was induced in a discotic liquid crystalline polymer by doping with a chiral acceptor.[437]

14.14 MOLECULAR RECOGNITION DIRECTED SELF-ASSEMBLY OF SUPRAMOLECULAR LIQUID CRYSTALLINE POLYMERS

The molecular recognition of complementary components leads to systems able to self-assembly or self-organize i.e., systems capable to generate spontaneously a well defined supramolecular architecture from their components under a well-defined set of conditions.[417,418]

Although self-assembly is a well recognized process in biological systems,[440,441] the general concept of self-assembly of synthetic molecules by molecular recognition of complementary components, received a revived interest only after it was integrated by Lehn in the new field of supramolecular chemistry.[417,418,442,443]

Several examples in which molecular recognition induces the association of complementary nonmesomorphic components into a low molar mass or polymeric supramolecular liquid crystal are described below.

The principles of formation of a mesogenic supramolecule from two complementary components is outlined in Scheme 48. The particular example used by Lehn et al.[444] to generate a supramolecular mesogenic group which exhibits a hexagonal columnar mesophase is by formation of an array of three parallel hydrogen bonds between groups of uracil and 2,6-diaminopyridine type as those depicted in Scheme 48.

The transplant of the same concept to the generation of a supramolecular liquid crystalline polymer is outlined in Scheme 49.[445] The complementary moieties used TU_2 and TP_2 are uracil (U) and 2,6-diacylamino-pyridine (P) groups connected through tartaric acid esters (T). The tartaric acid (T) unit provides in addition, the opportunity to investigate the effect of changes in chirality on the species formed. Thus the components LP_2, LU_2, DP_2, MP_2 and MU_2 are derived from L(+), D(-) and meso (M) tartaric acid respectively. Although all monomers (LP_2, LU_2, DP_2, MP_2 and MU_2) are only crystalline, the corresponding supramolecular "polymers" obtained through hydrogen bonding (LP_2 + LU_2, DP_2 + LU_2 and MP_2 and MU_2) exhibit hexagonal columnar mesophases. These hexagonal columnar mesophases are generated from cylindrical helical suprastructures.[445]

An additional example of supramolecular liquid crystalline polymer obtained through the hydrogen bonding of nonmesomorphic monomers was recently reported.[446]

Examples in which a mesophase was generated through dimerization of carboxylic acid derivatives via hydrogen bonding were available in the classic literature on liquid crystals and were extensively reviewed.[6,447] New and interesting examples on the generation of nonsymmetrical liquid crystalline dimers,[448] twin dimer[449] and side chain liquid crystalline polymers[450] by specific hydrogen bonding "reactions" continue to be reported (Scheme 50).

Recently, a new approach to molecular recognition directed self-assembly of a liquid crystalline supramolecular structure by a mechanism which resembles that of self-assembly of tobacco mosaic virus (TMV) was reported.[451] The self-assembly mechanism of TMV is outlined in Figure 35.[441] The synthetic approach can be summarized as follows. A flexible polymer backbone containing tapered side groups self-organizes the side groups into a column which surrounds the polymer backbone (Figure 36). These polymers exhibit thermotropic hexagonal columnar mesophases (Figure 37). Although the number of chains penetrating through the center of the column is not yet known and requires further research (Figure 37), it seems that this self-assembling system is complementary to those elaborated by Lehn et al.[444,445] In the model elaborated by Lehn et al.[444,445] the complementary pairs are self-organized through hydrogen bonding type interactions (endo-recognition), while in the last case[441,451] only the shape of tapered side groups is responsible for the generation of a polymeric column (exo-recognition).

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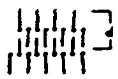
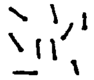
Table 1 Some properties of lyotropic systems composed of an amphiphile and water

Suggested structural arrangement						
% Water[a] (approximate range)	0	5-22-50	23–40	34–80	30–99.9	Greater than 99.9
Physical state	Crystalline	Liquid crystalline, lamellar	Liquid crystalline, face-centered cubic	Liquid crystalline, hexagonal compact	Micellar solution	Solution
Gross character	Opaque solid	Clear, fluid, moderately viscous	Clear, brittle, very viscous	Clear, viscous	Clear, fluid	Clear, fluid
Freedom of movement	None	2 directions	Possibly none	1 direction	No restrictions	No restrictions
Microscopic properties (crossed nicols)	Birefringent	Neat soap texture	Isotropic with angular bubbles	Middle soap texture	Isotropic with round bubbles	Isotropic
X-Ray data	Ring pattern 3–6 Å	Diffuse halo at about 4.5 Å	Diffuse halo at about 4.5 Å	Diffuse halo at about 4.5 Å		
Structural order	3 dimensions	1 dimension	3 dimensions	2 dimensions	None	None

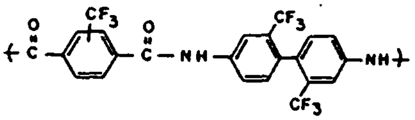
[a] The different percentages of water show that different amphiphiles require different amounts of water. For soaps, the lamellar structure generally occurs between 5 and 22% water; with some lipophiles the water may be as high as 50%. The cubic structure generally occurs between 23 and 40%.

Table 2 Melting and Isotropization Transitions of Poly(p-phenylene)s

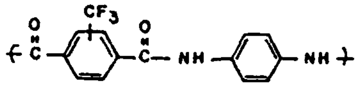
n	$x = L/d$	$T_{n\text{-}i}$ (°C) Theoretical	Polymorphism
2	≈ 2	---	$T_{k\text{-}i} = 70$ °C
3	≈ 3	---	$T_{k\text{-}i} = 210$ °C
4	≈ 4	≈ 120	$T_{k\text{-}i} = 320$ °C
5	≈ 5	≈ 450	$T_{n\text{-}i} = 430$ °C
6	≈ 6	≈ 1900	$T_{n\text{-}i} = 560$ °C
7	≈ 7	isotropic	$T_{k\text{-}n} \approx 550$ °C (also decomposition)

Table 3 Molecular structures of aromatic polyamides

Head-to-head phenyl and biphenyl polyamides



I



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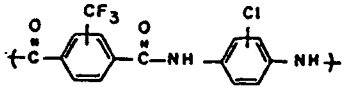

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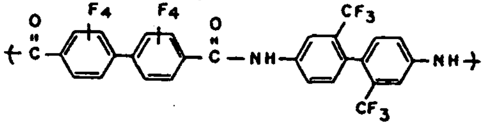

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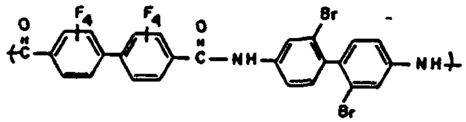

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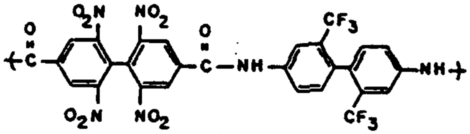

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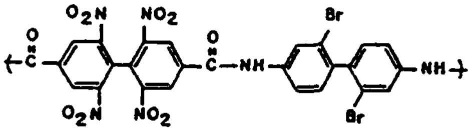
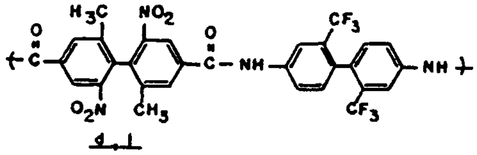


VII



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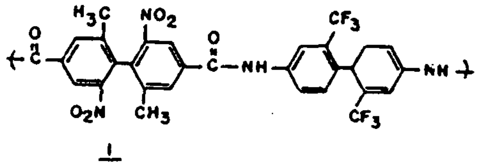
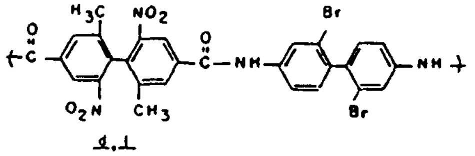
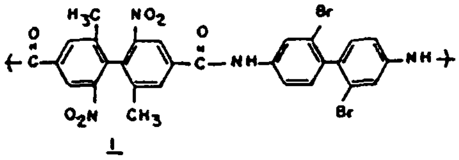


IX



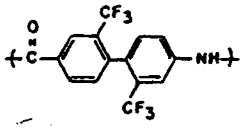
X

Table 3 (continued)

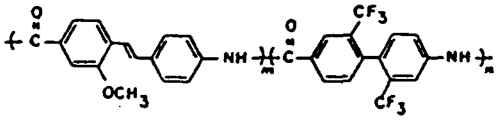


XI

Head-to-tail biphenyl polyamides

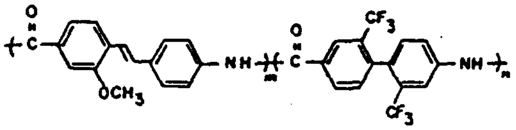


XII



XIII

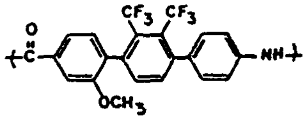
$m = 0.24$, $n = 0.76$



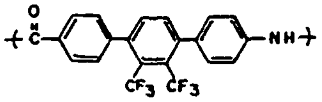
XIV

$m = 0.10$, $n = 0.76$

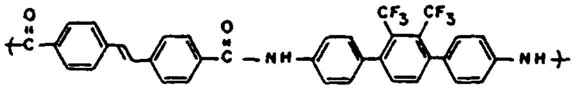
Substituted terphenyl and quaterphenyl polyamides



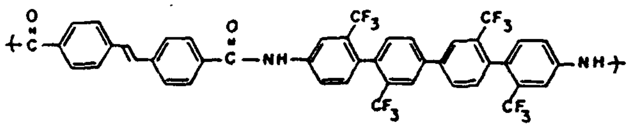
XV



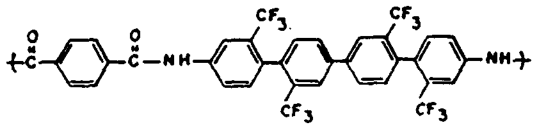
XVI



XVII



XVIII



XIX

Table 4 Viscosity and Solubility Properties of Biphenyl Polyamides

Polymer	η_{inh}(dl/g)[a]	Solubility			
		LiCl/ Amides[b]	Amides	Ethers[c]	Ketones[d]
I	3.23	S[e]	44-48[f]	Sw	Ins
II	1.84 (DMAc)	S	S	Ins	Ins
III	2.34 (DMAc)	S	S	Ins	Ins
IV	1.19	S	Sls	Ins	Ins
V	1.68	S	Ins	Ins	Ins
VI	1.27	S	S	S[g]	Ins
VII	1.10	S	S	Ins	S
VIII	1.75	S	S	36 (THF)	S
IX	0.91	S	S	25 (THF)	S
X	2.46	S	S	17 (THF)	Ins
XI	1.68	S	S	14 (THF)	Ins
XII	5.0	S	S	S	S
XIII	4.74	S	S	Ins	Ins
XIV	4.94	S	S	S	S
XV	1.39	S	S	Ins	Ins
XVI	---	Ins	Ins	Ins	Ins
XVII	2.30	S	Ins	Ins	Ins
XVIII	1.31	S	S	S	S
XIX	6.04	S	S	Sls	S

---

[a] 0.5% polymer (w/v) / 5% (w/v) LiCl/DMAc at 30 °C

[b] Amide solvents: DMAc, TMU, and NMP

[c] Ether solvents: THF, glymes, but not diethyl ether, dioxane

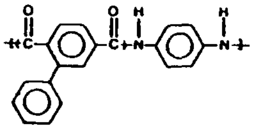
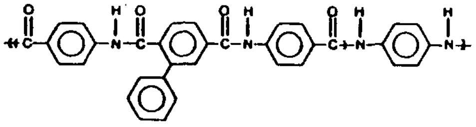
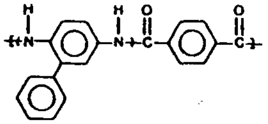
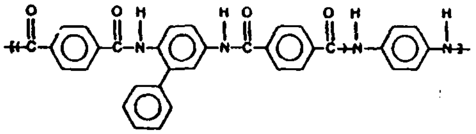
[d] Ketone solvents: acetone and cyclohexanone

[e] S, soluble; Sw, swells; Sls, slightly soluble; Ins, insoluble

[f] w/v%

[g] Methoxy ethanol but not THF

Table 5 Phenyl-substituted aromatic polyamides[a]

	Inherent viscosity η_{inh},[b] dL/g		Solubility in DMAc or NMP, g/100g[d]
	H_2SO_4[c]	DMAc[d]	
	0.61	1.10	50
	3.28	7.55	18
	1.45	2.52	20
	2.28	3.32	14-15

[a] All polymers prepared by the phosphorylation method

[b] 0.5% concentration at 25 °C

[c] 96% H_2SO_4

[d] Containing 4% LiCl

Table 6 Characterization of polymers from bicyclo[2.2.2]octane-1,4-dicarboxylic acid and 2,5-dialkoxyhydroquinone diacetates (PBCOHQ-n)

			Thermal transitions[c]			
			Heating		Cooling	
n[a]	[η][b]	layer spacing d, Å	T_s	T_m	T_s	T_m
6	1.10	10.1	63[d]	315		254
8	0.99	11.5	60[d]	255		210
10	1.21	12.8	55[d]	243		204
12	0.53	15.2	28	223	-2	186
14	0.87	16.5	46	206	30	166
16	0.59	17.8	60	193	49	160

[a] Number of carbon atoms in the side chain

[b] In dL/g, measured in CH_2Cl_2/TFA (95/5 (v/v)) at 20 °C

[c] In °C. Heating and cooling rates: 20 °C/min

[d] Transition observed only in the first heating scan

Table 7 Characterization of polymers from terephthalic acid and 2,5-dialkoxyhydroquinones (PTAHQ-n)

				Thermal transitions[e]					
		layer spacing		Heating			Cooling		
n[a]	[η][b]	d, Å[c]	d, Å[d]	T_s	T_m	T_i	T_s	T_m	T_i
6	1.20	10.3	11.7	79[f]	275	292		234	279
8	1.71	12.8	14.0	75[f]	255	282		217	256
10	1.21	13.3		78[f]	270			245	
12	0.73	15.5	18.2	78	236		32	181	215
14	0.72[g]	17.6	20.5	91	215	230	62	160	207
16	0.70[g]	19.1	21.8	104	190	215	83	162	202

[a] Number of carbon atoms in the side chain

[b] In dL/g, measured in CH_2Cl_2/TFA (95/5 (v/v)) at 20 °C

[c] Measured at room temperature

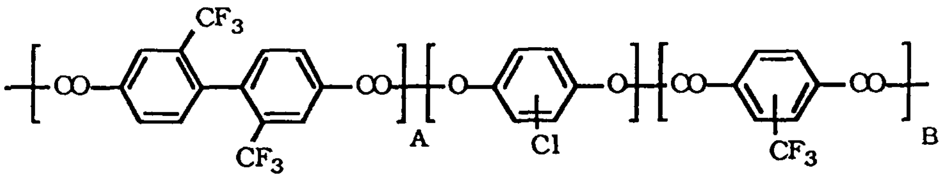
[d] Measured at 10 °C below the isotropization temperature

[e] In °C. Heating and cooling rates: 20 °C/min

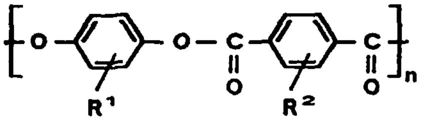
[f] Transition observed only in the first heating scan

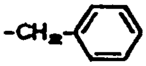
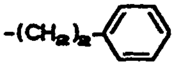
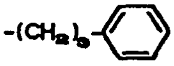
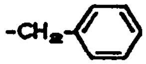
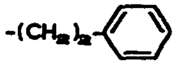
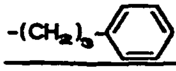
[g] In dL/g, measured in $CHCl_3$/TFA (95/5 (v/v)) at 25 °C

Table 8 The effect of CF_3-substituted biphenyl content on the solubility of aromatic polyesters in THF



Polyester	Maximum solubility in THF (%w/v)
A = 1.0, B = 0	53.0
A = 0.5, B = 0.5	49.8
A = 0.4, B = 0.6	48.5
A = 0.2, B = 0.8	11.1
A = 0.1, B = 0.9	<5.0
A = 0, B = 1.0	insoluble

Table 9 Properties of polyesters 

R¹	R²	η_{inh} (dl/g)	T_g/°C	T_m/°C	Phase $>T_m$	Solubility[b)] pCP	TCE	$CHCl_3$
	-H	1.0	-	380[a)]	-	++	+	-
	-H	0.7	-	340	aniso.	++	+	-
	-H	4.2	-	325	aniso.	++	+	-
	-Br	2.0	91	(207)[c)]	nem.	++	+	-
	-Br	2.5	79	(195)[c)]	nem.	++	+	-
	-Br	1.0	58	(249)[c)]	nem.	++	+	++

[a] melting in the decomposition range

[b] ++: stable solution (>0.5 g/dl) at room temperature

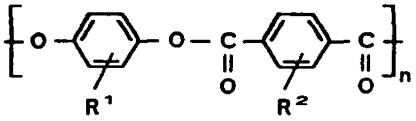
+ : soluble on heating, precipitation on cooling

- : insoluble; pCP: p-chlorophenol,

TCE: 1,1,2,2-tetrachloroethane

[c] weak endotherm on annealed samples

Table 10 Properties of polyesters



R^1	R^2	η_{inh} (dl/g)	T_g/[a)] °C	T_m/[a)] °C	Phase >T_m	Solubility[b)]		
						pCP	TCE	$CHCl_3$
-CH_2CH_2- 	-CH_2CH_2- 	0.3-3.6	60	195	nem.	++	++	++
-$C(CH_3)_3$	-CH_2CH_2- 	0.3-5.0	100	225	nem.	++	++	++
-$C(CH_3)_3$	-Br	0.2-2.6	131	-	-	+	0	-
-$C(CH_3)_3$	-CF_3	0.3-1.9	141	228	nem	++	++	++
-O- 	-Cl	1.8	85	241	nem.	++	++	0
-O- 	-Br	0.5-3.0	90	220	nem.	++	++	++
-O- 	-CF_3	0.35	88	-	iso.	++	++	++
-O- 		0.4-0.7	112	-	iso.	++	++	++

[a] products of the highest molecular weights

[b] ++: stable solution (>0.5 g/dl) at room temperature

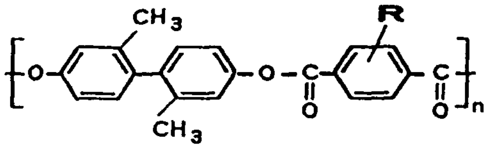
+ : completely soluble on heating

o : partially soluble at elevated temperatures

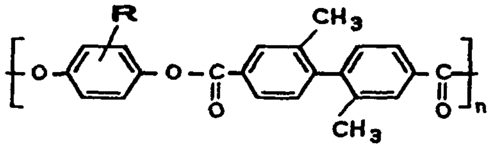
- : insoluble; pCP: p-chlorophenol,

TCE: 1,1,2,2-tetrachloroethane

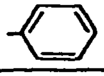
Table 11 Polyesters with twisted biphenyl units



1



2

Polymer	R	η_{inh} [a] (dl/g)	T_g	T_m	Phase	Solubility [b]		
			(°C)			pCP	TCE	$CHCl_3$
1	H	1.43	nontractable			+	-	-
	Br	1.21	100	230	nem.	+	-	-
		1.10	125	-	nem.	+	+	+
2	CH_3	0.81	nontractable			+	+	-
	tert -Butyl	1.43	150	-	nem.	+	+	+

[a] Measured in p-chlorophenol at 45 °C

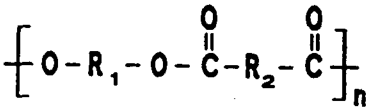
[b] ++: stable solution (>0.5 g/dl) at room temperature

+ : soluble on heating, precipitation on cooling

- : insoluble; pCP: p-chlorophenol,

TCE: 1,1,2,2-tetrachloroethane

Table 12 Amorphous polyesters with binaphthyl units



$$\left[O-R_1-O-\overset{O}{\overset{\|}{C}}-R_2-\overset{O}{\overset{\|}{C}} \right]_n$$

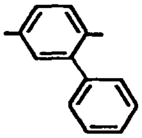
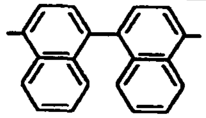
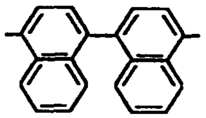
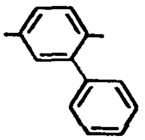
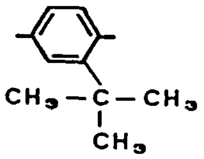
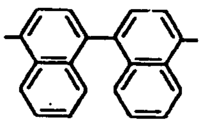
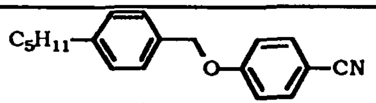
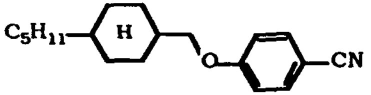
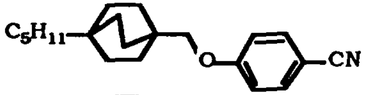
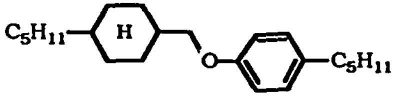
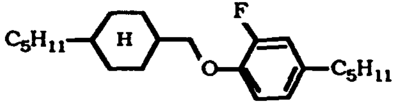
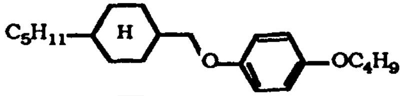
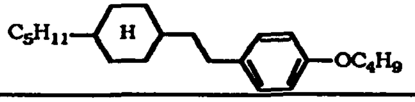
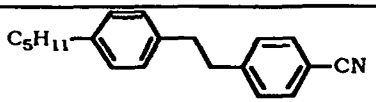
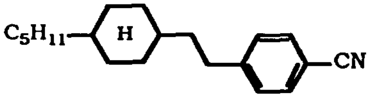
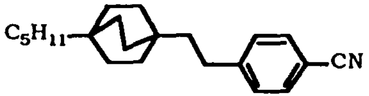
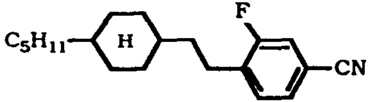
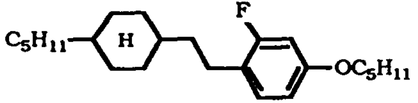
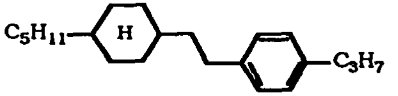
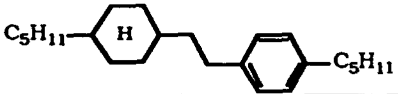
R_1	R_2	η_{inh} (dl/g)	T_g (°C)
		0.72	163
		1.90	183
		1.51	189

Table 13 Low molar mass liquid crystals based on benzyl ether and methyleneoxy flexible units[303-305]

No	Structure	Phase transitions (°C)
1		k 49 n [-20] i
2		k 74.3 n (48.6) i
3		k 72 n 73 i
4		k 35 s_B (31) n [21] i
5		k 43 n [-10] i
6		k 55 s_B (47) n (53) i
7		k 22 s_B 44.5 n 45.5 i

[ ]: virtual; ( ): monotropic

Table 14 The dependence between structure and phase transitions of some low molar mass liquid crystals based on disubstituted ethane derivatives[303,306-310]

No	Structure	Phase transitions (°C)
8		k 62 n [-24] i
9		k 30 n 51 i
10		k 76 n 113 i
11		k 45 n 54 i
12		k 26 n (12) i
13		k 4 s_B 18 i
14		k 46 s_B 109 i

[ ]: virtual; ( ): monotropic

Table 15 Thermodynamic Parameters Corresponding to the Orientational and Conformational Order Contributions of HMS-X,[278] MBPE-X,[103e] ClBPE-X,[324] and of Polyesters Based on 4,4'-Dihydroxy-2,2'-Dimethylazoxybenzene and α,ω-Alkanedioic Acids (DMAB-X)[48].

Nature of Order	(ΔHin)even (kcal/mru)				(ΔHin)odd(kcal/mru)			
	HMS-X	MBPE-X	ClBPE-X	DMAB-X	HMS-X	MBPE-X	ClBPE-X	DMAB-X
Orientational/ mole of mesogen	1.45	2.00	1.63	1.12	0.34	0.30	0.20	0.22
Conformational/ mole of $-CH_2-$	0.03	0.01	0.03	0.38	0.04	0.03	0.04	0.045

Nature of Order	(ΔSin)even(cal/mol°K)				(ΔSin)odd(cal/mol°K)			
	HMS-X	MBPE-X	ClBPE-X	DMAB-X	HMS-X	MBPE-X	ClBPE-X	DMAB-X
Orientational/ mole of mesogen	2.15	4.02	3.60	1.80	0.45	0.85	0.62	0.34
Conformational/ mole of $-CH_2-$	0.15	0.17	0.12	0.21	0.13	0.11	0.07	0.14

Table 16 Thermal Transitions (°C) and Corresponding Thermodynamic Parameters, ΔH_{in} (kcal/mru) and ΔS_{in} (cal/mru °K)[a] of 1-(4-Methoxyphenyl)-2-(2-R-4-methoxyphenyl) (RBMPE) and 1-(4-Hydroxyphenyl)-2-(2-R-hydroxyphenyl)ethane (RBPE) and of the corresponding RBPE-8 and RBPE-5 polymers. Van der Waal's Radius of R (Å) and Electronegativity of R, Ar-R bond length (Å), and breadth of molecule (Å)

R	RMBPE	RBPE	Radius of R	Electronegativity of R	Breadth of RBPE	Ar-R Bond Length	RBPE-8				RBPE-5		
							Tni	Tin	ΔH_{in}	ΔS_{in}	Tin	ΔH_{in}	ΔS_{in}
H	125-127	200[b]	1.2	2.19	6.69	1.4	155	146	--	--	--	--	--
F	73-74	172-173	1.35	4.0	7.03	1.30	165	152	2.82	6.8	92	0.92	2.5
Cl	62-64	126	1.8	3.0	7.82	1.70	130	118	2.27	5.83	52	0.65	2.0
Br	81-82	114-115	1.95	2.8	8.10	1.85	111	102	2.12	5.3	47	0.59	1.86
CH_3	52-54	148	2.0	2.3	7.76	1.33	132	119	2.33	5.9	38	0.49	1.57
CF_3	69-70	64-65	2.3	3.29	8.15	1.33	76	43	0.93	2.94	--	--	--

[a] Data from Ref. 327

Table 17 Characterization of hyperbranched polyethers based on TPD-b with different tail lengths R. Data collected from second heating and first cooling DSC scans [344]

Tail R	Yield (%)	$(Mn)_{GPC}$	$(Mw/Mn)_{GPC}$	thermal transitions (^{o}C) and corresponding enthalpy changes (Kcal/mru) in parentheses	
				heating	cooling
Octyl	80.0	7900	2.6	g 20 n 40 (0.75) i	i 30 (0.70) n 15 g
Hexyl	82.2	4700	3.9	g 24 n 39 (0.15) i	i 30 (0.18) n 18 g
Butyl	70.3	4400	3.5	g 40 i	i 34 g
Benzyl	79.2	4700	3.8	g 48 n 60 (0.10) i	i 53 (0.15) n 43 g

FIGURE CAPTIONS

Figure 1. Schematic representation of the molecular arrangement in the (a) isotropic phase; (b) nematic phase; (c) smectic A phase; (d) smectic C phase; (e) cholesteric or chiral nematic phase; (f) crystalline state (dots represent molecules).

Figure 2. A schematic representation of the molecular arrangement (a) in the nematic phase N_D; (b) in the cholesteric phase N^*_D; (c) in the columnar phase D, of disc-like liquid crystals.

Figure 3. Schematic representation of main chain, side chain, and combined liquid crystal polymers.

Figure 4. Schematic plot of free energies versus temperature for a system that does not show a mesophase. G_k, G_{lc} and G_i are, respectively, the free energies of the crystalline, mesomorphic (virtual) and isotropic liquid states. $T_{k\text{-}i} = T_m$ is the crystalline melting point. Here, as in subsequent Figures 5 and 6, the heaviest lines correspond to the stablest state at a given temperature.

Figure 5. Schematic plot of free energies versus temperature for the system in Figure 4 but with G_i raised (to G_i') so as to "uncover" the mesophase. $T_{k\text{-}lc}$ and $T_{lc\text{-}i}$ are the crystal-mesophase transition and the isotropization transition temperatures.

Figure 6. Schematic plot of free energies versus temperature for the system in Figure 4 but with G_k raised (to G_k') so as to "uncover" the mesophase.

Figure 7. Schematic plot of the free energy diagram illustrating the origin of a monotropic liquid crystal. Here, as in Figure 4, the arrows represent heating and cooling pathways.

Figure 8. Schematic free energy diagram for an enantiotropic liquid crystal, where the mesophase is metastable.

Figure 9. The broadening of the temperature range of an enantiotropic mesophase of the monomeric structural unit (M_0) by increasing the degree of polymerization. The upper part (a) describes the influence of molecular weight on the dependence between the free energies of the crystalline (G_k), liquid crystalline (G_{lc}) and isotropic (G_i) phases and transition temperatures. The translation of this dependence into the dependence phase transition temperature-molecular weight is presented in the lower part (b).

Figure 10. Transformation of a virtual or monotropic mesophase of the monomeric structural unit (M_0) into an enantiotropic mesophase by increasing the degree of polymerization. The upper part (a) describes the influence of molecular weight on the dependence between the free energies of the crystalline (G_k), liquid crystalline (G_{lc}) and isotropic (G_i) phases and transition temperatures. The translation of this dependence into the dependence phase transition temperature-molecular weight is presented in the lower part (b).

Figure 11. The narrowing of the temperature range of a virtual mesophase of the monomeric structural unit (M_0) by increasing the degree of polymerization. The

upper part (a) describes the influence of molecular weight on the dependence between the free energies of the crystalline (G_k), liquid crystalline (G_{lc}) and isotropic (G_i) phases and transition temperatures. The translation of this dependence into the dependence phase transition temperature-molecular weight is presented in the lower part (b).

Figure 12. The dependence of various first order transitions on molecular weight for a rigid rod-like polymer.

Figure 13. a) Definition of the axial ratio in the model of rod-like mesogen; b) model for nonrigid main chain liquid crystalline polymer: l defines the Kuhn's segment.

Figure 14. a) Board formation of highly substituted rigid rod polymers, caused by hindered rotation of their mesogenic units;[201] b) schematic representation of a sanidic (from Greek for boardlike) mesophase.[202]

Figure 15. a) Layer spacing *d* calculated according to Bragg's law from low angle X-ray reflections obtained from mesophases of polyamides 1 and 2 as function of n, the number of carbon atoms in the side chains; b) model of molecular packing in the layered mesophase.[204]

Figure 16. DSC curves of polyethers based on MBPE and 1,5-dibromopentane (MBPE-5), MBPE and 1,8-dibromooctane (MBPE-8) and corresponding copolyethers [MBPE-5/8(A/B)]. a): First (——) and second (- - -) heating scans; b): cooling scans.

Figure 17. a) Thermal transitions of polyethers (MBPE-5 and MBPE-8) and copolyethers [MBPE-5/8(A/B)]. First heating scan [(⦻): T_{ki}, (◑): T_{ni}, (◨): T_{kn}, (⬗): T_{kk}]; second heating scan [(✖): T_{ki}, (●): T_{ni}, (■): T_{kn}]; cooling scan [(⊗): T_{in}, (□): T_{nk}, (Δ): T_{ns}]. Arrows point to virtual transition temperatures for the homopolymers.

b) Enthalpy changes of polyethers (MBPE-5 and MBPE-8) and copolyethers [MBPE-5/8(A/B)]. First heating scan [(⦻): ΔH_{ki}, (◑): ΔH_{ni}, (◨): ΔH_{kn}, (⬗): ΔH_{kk}]; second heating scan [(✖): ΔH_{ki}, (●): ΔH_{ni}, (■): ΔH_{kn}]; cooling scan [(O): ΔH_{in}, (□): ΔH_{nk}]. Arrows point to enthalpies of virtual transitions for the homopolymers.

Figure 18. a) Dependence of the virtual isotropic-nematic (T_{in}) phase transition temperature of MBPE-X homopolymers on the number of methylene units in the flexible spacer (X). Upper right side corner presents the logarithmic plot of this dependence. b) Dependence of the virtual isotropic-nematic (T_{in}) phase transition temperature of MBPE-X homopolymers on the inverse of the number of methylene units in the flexible spacer (1/X). The logarithmic dependence is presented with a continuous line.

Figure 19. Schematic representation of columnar and smectic mesophases exhibited by polyethers and copolyethers based on BPE, PEB and 1,9-dibromononane.

Figure 20. Dependence of phase transition temperatures of TPB-X polyethers on the number of methylenic units in the flexible spacer (X): a) data from the second

heating scan (T_g data of TPB-11 to TPB-20 are from the first heating scan);

b) data from the first cooling scan.

Figure 21. Structure of cyclic main chain liquid crystalline polyethers.

Figure 22. Schematic representation of side chain liquid crystalline polymers showing the necessity of decoupling the mesogenic groups and the polymer backbone through flexible spacers.

Figure 23. a) The dependence between the entropy change of isotropization (ΔS_i) determined from the cooling DSC scans, the nature of the polymer backbone and the number of methylenic units (n) in the flexible spacer for the series of polymers based on 4-MHMS isomer.

b) The dependence between the entropy change of isotropization (ΔS_i) determined from the cooling DSC scans, the nature of the polymer backbone and the number of methylenic units (n) in the flexible spacer for the series of polymers based on 4'-MHMS isomer.

Figure 24. a) Schematic representation of the theoretical distortion of the statistical random-coil conformation of the polymer backbone in the nematic and smectic phases; b) Two possible modes of distortion of the random-coil conformation of a rigid (left) and a flexible (right) polymer backbone. $R_{\parallel}$ refers to the radius of gyration paralled to the magnetic field. The radius of gyration perpendicular to the magnetic field is labelled as $R_{\perp}$

Figure 25. Microphase separated morphology of smectic copolymers.

Figure 26. The influence of molecular weight on the phase behavior of poly(6-3), poly(6-4), poly(6-7) and poly(6-9) (determined from second DSC heating scans)

Figure 27. The influence of molecular weight on the phase behavior of poly(6-2), poly(6-6) and poly(6-8) (determined from second DSC heating scans)

Figure 28. The influence of molecular weight on the phase behavior of poly(6-5), poly(6-10) and poly(6-11) (determined from second DSC heating scans)

Figure 29. The dependence of phase transition temperatures obtained from second heating scan (a,d), cooling scan (b,e), and the enthalpy changes associated with their highest temperature mesophase of copolymers poly[(6-3)-co-(6-5)]X/Y and poly[(6-6)-co-(6-11)]X/Y (all with degrees of polymerization equal to 20)

Figure 30. The dependence of phase transition temperatures obtained from second heating scan (a,d), cooling scan (b,e), and the enthalpy changes associated with their highest temperature mesophase of copolymers poly[(6-3)-co-(6-11)]X/Y and poly[(6-5)-co-(6-11)]X/Y (all with degrees of polymerization equal to 20)

Figure 31. The dependence of phase transition temperatures obtained from second DSC heating scan (a,d), cooling scan (b,e), and the enthalpy changes associated with their highest temperature mesophase of copolymers poly[(6-2)-co-(6-8)]X/Y

and poly[(6-2)-co-(6-11)]X/Y (with degrees of polymerization equal to 10 and 15, respectively)

Figure 32. The mechanism of formation of the re-entrant nematic mesophase.[390]

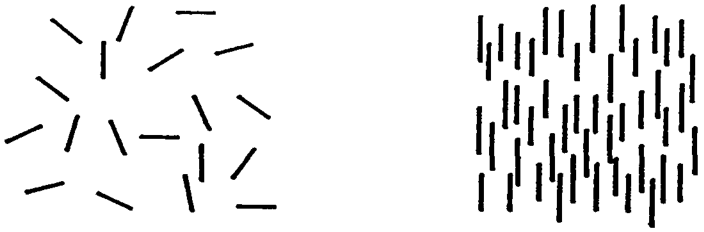
Figure 33. Isotropization transition temperatures of cyclic (●) and linear (□) polysiloxanes containing cyanophenyl benzoate mesogen connected to the backbone via a pentyloxy group.[75]

Figure 34. The molecular architecture of liquid crystalline polymers containing crown ether ligands.

Figure 35. Self-assembly of tobacco mosaic virus (TMV). The protein subunits define the shape of the helix and the RNA defines the helix length. All information for assembly is contained within the component parts. The structure contains 16 1/3 protein subunits per turn and 2130 identical protein subunits (17,500 daltons each). The virus dimensions are 3000 Å in length, 180 Å in diameter, a helical pitch of 23 Å, a central hole of 40 Å, with 3 nucleotides bound per protein subunit.[441]

Figure 36. The self-organization of a randomly coiled flexible polymer containing tapered side groups into a rigid rod-like columnar structure.

Figure 37. A representative structure of a flexible polymer containing tapered side-groups and its self-assembling into a columnar structure which exhibits a hexagonal columnar mesophase.[451]

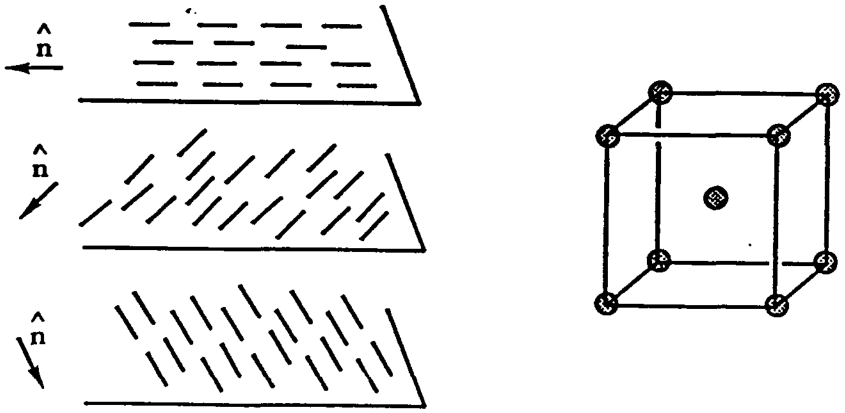


(a) LIQUID

(b) ORDINARY NEMATIC LIQUID CRYSTAL

(c) SMECTIC A LIQUID CRYSTAL

(d) SMECTIC C LIQUID CRYSTAL



(e) CHOLESTERIC-NEMATIC LIQUID CRYSTAL

(f) CRYSTALLINE (BODY-CENTERED CUBIC)

Figure 1

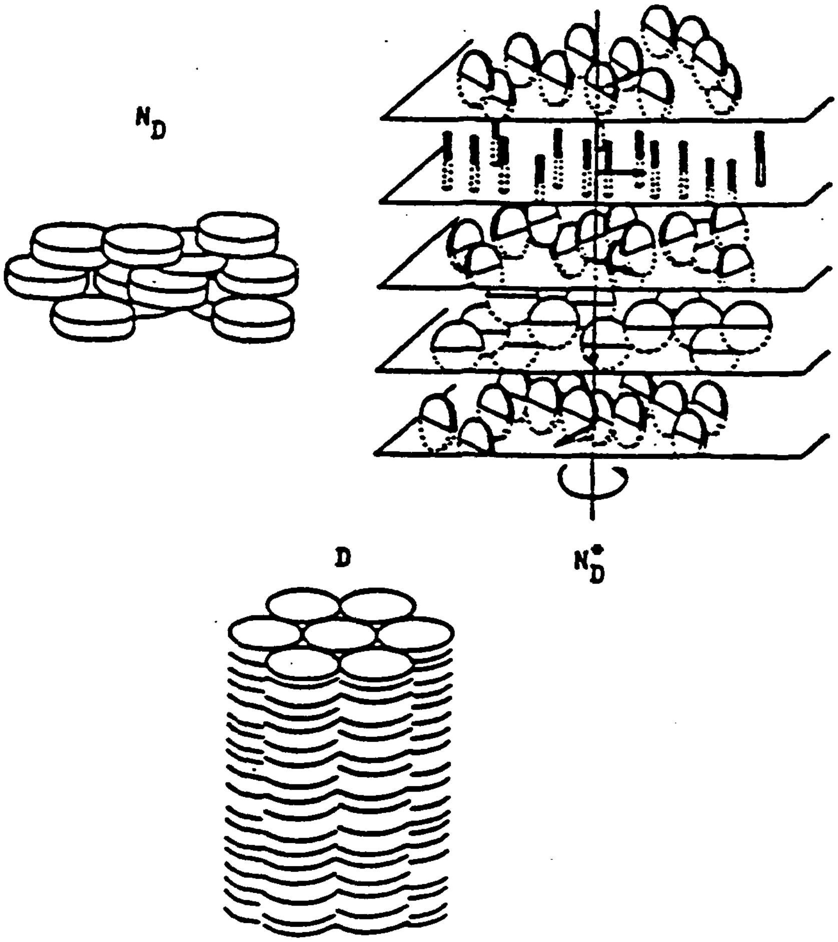
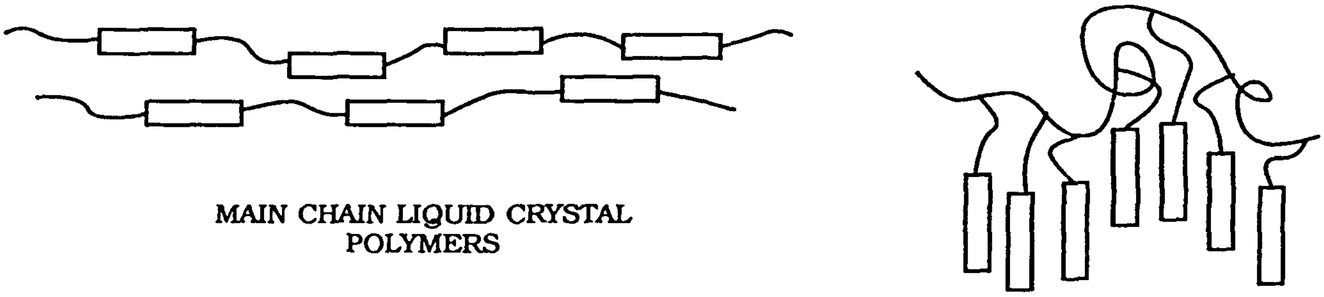
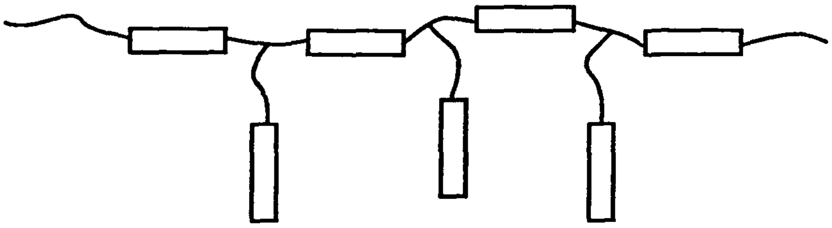


Figure 2



MAIN CHAIN LIQUID CRYSTAL POLYMERS

SIDE CHAIN LIQUID CRYSTAL POLYMERS



COMBINED LIQUID CRYSTAL POLYMERS

Figure 3

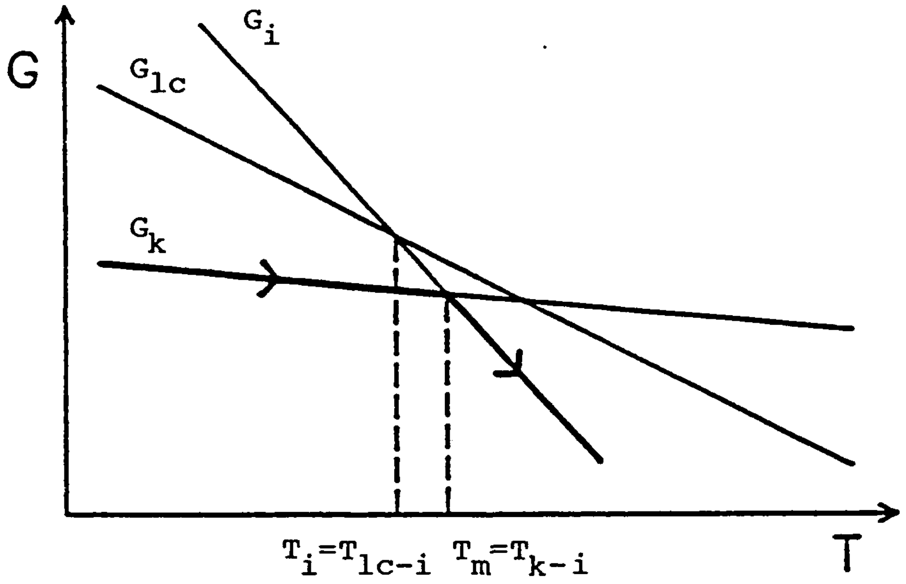


Figure 4

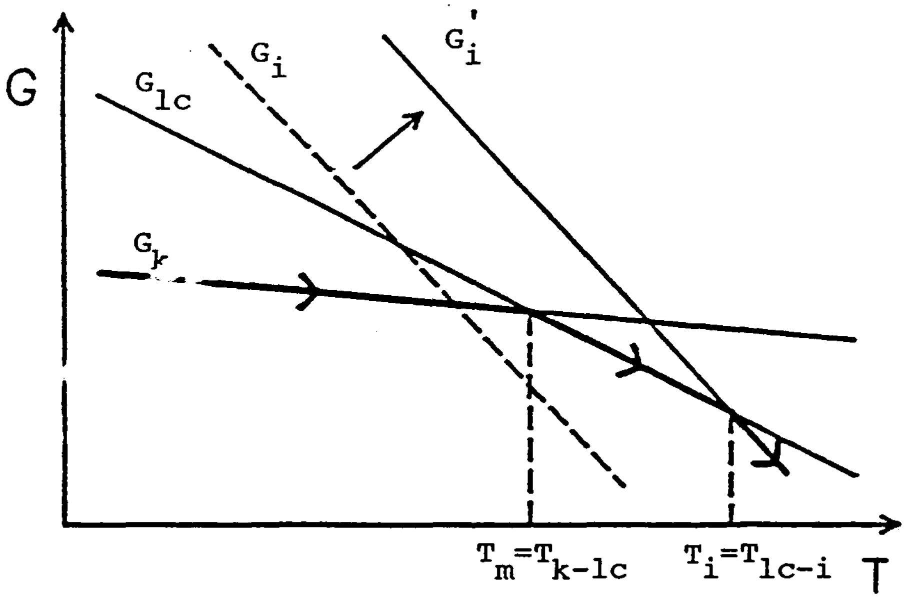


Figure 5

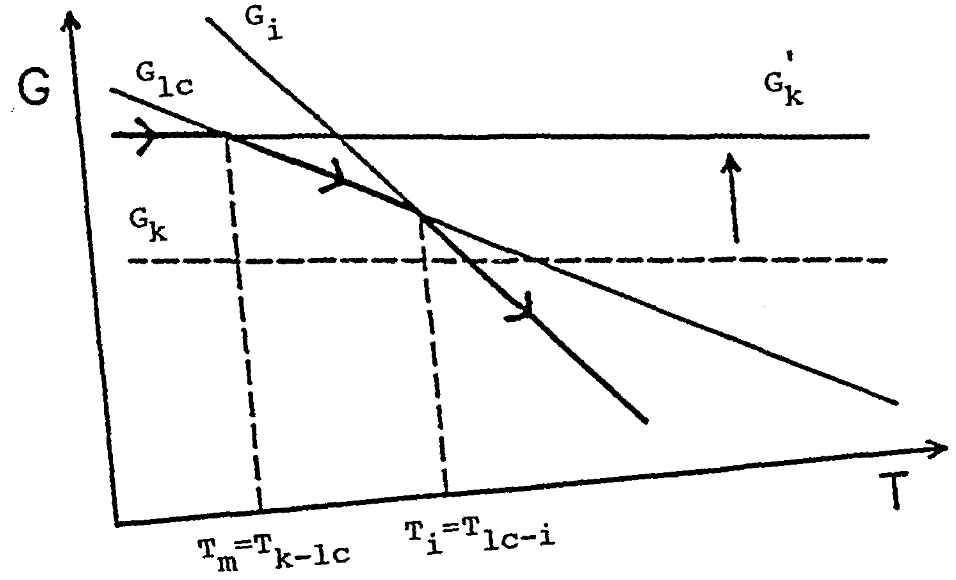


Figure 6

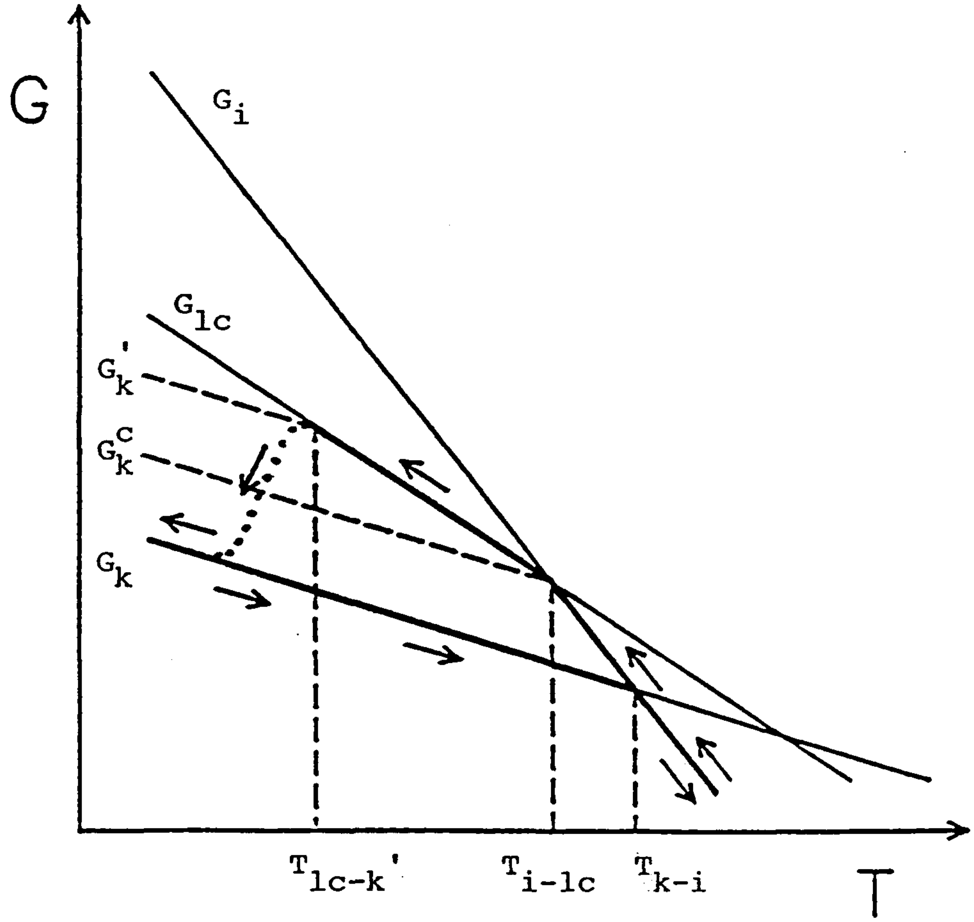


Figure 7

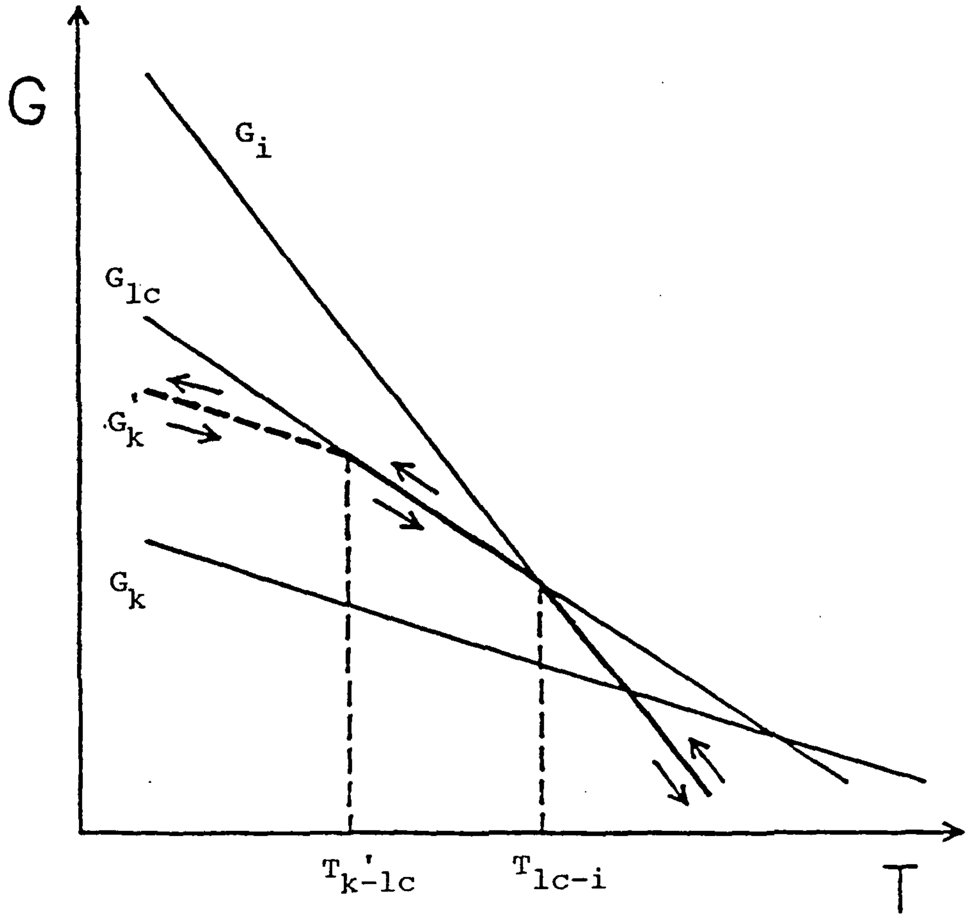
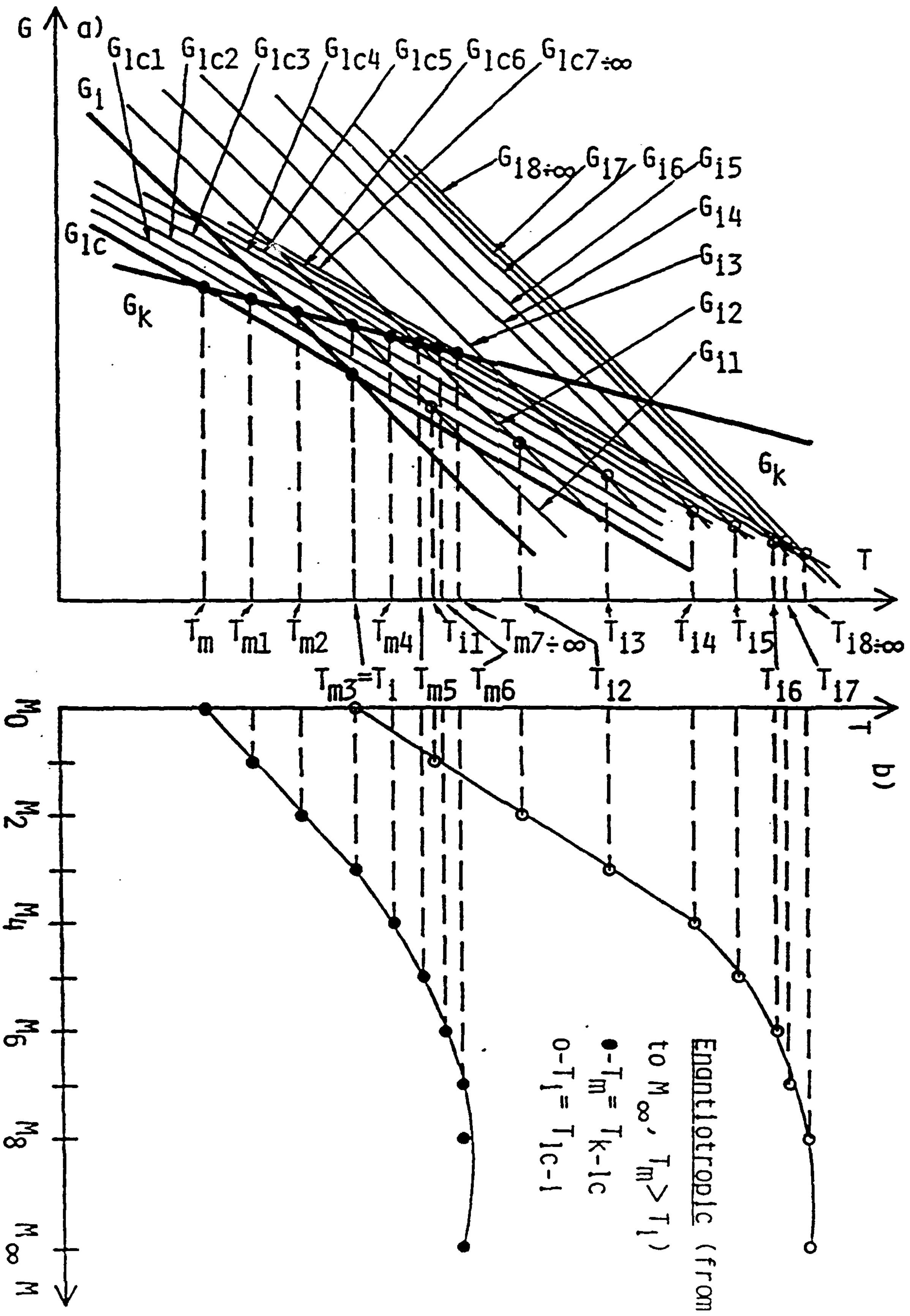


Figure 8


G
a)
G_{lc1}
G_{lc2}
G_{lc3}
G_{lc4}
G_{lc5}
G_{lc6}
$G_{lc7\div\infty}$
G_l
G_{lc}
G_k
$G_{l8\div\infty}$
G_{l7}
G_{l6}
G_{l5}
G_{l4}
G_{l3}
G_{l2}
G_{l1}
G_k
T
T_m
T_{m1}
T_{m2}
$T_{m3}=T_l$
T_{m4}
T_{m5}
T_{l1}
T_{m6}
$T_{m7\div\infty}$
T_{l2}
T_{l3}
T_{l4}
T_{l5}
T_{l6}
T_{l7}
$T_{l8\div\infty}$
T
b)
M_0
M_2
M_4
M_6
M_8
M_∞
M
Enantiotropic (from M_0 to M_∞, $T_m > T_l$)
● - $T_m = T_{k-lc}$
o - $T_l = T_{lc-l}$

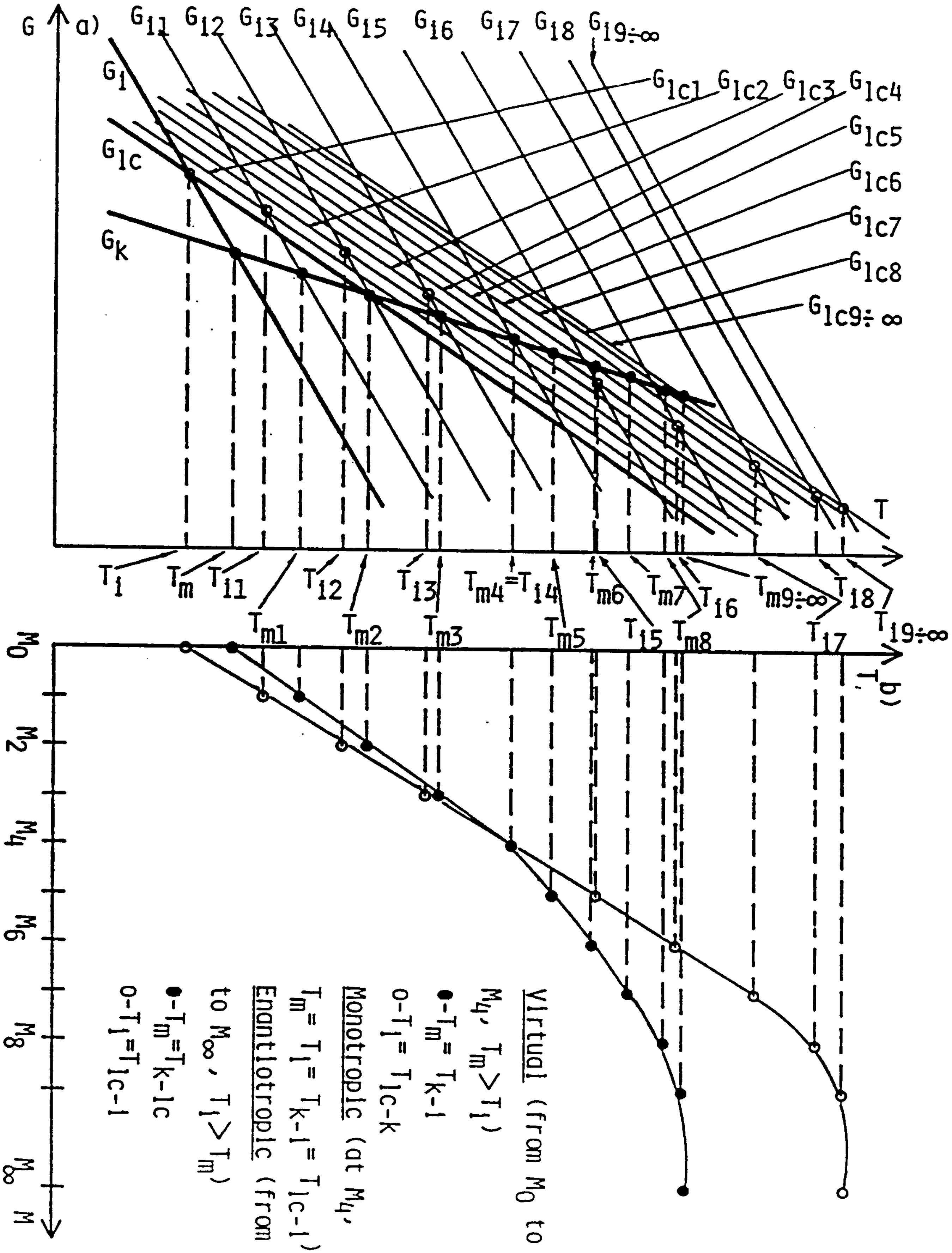
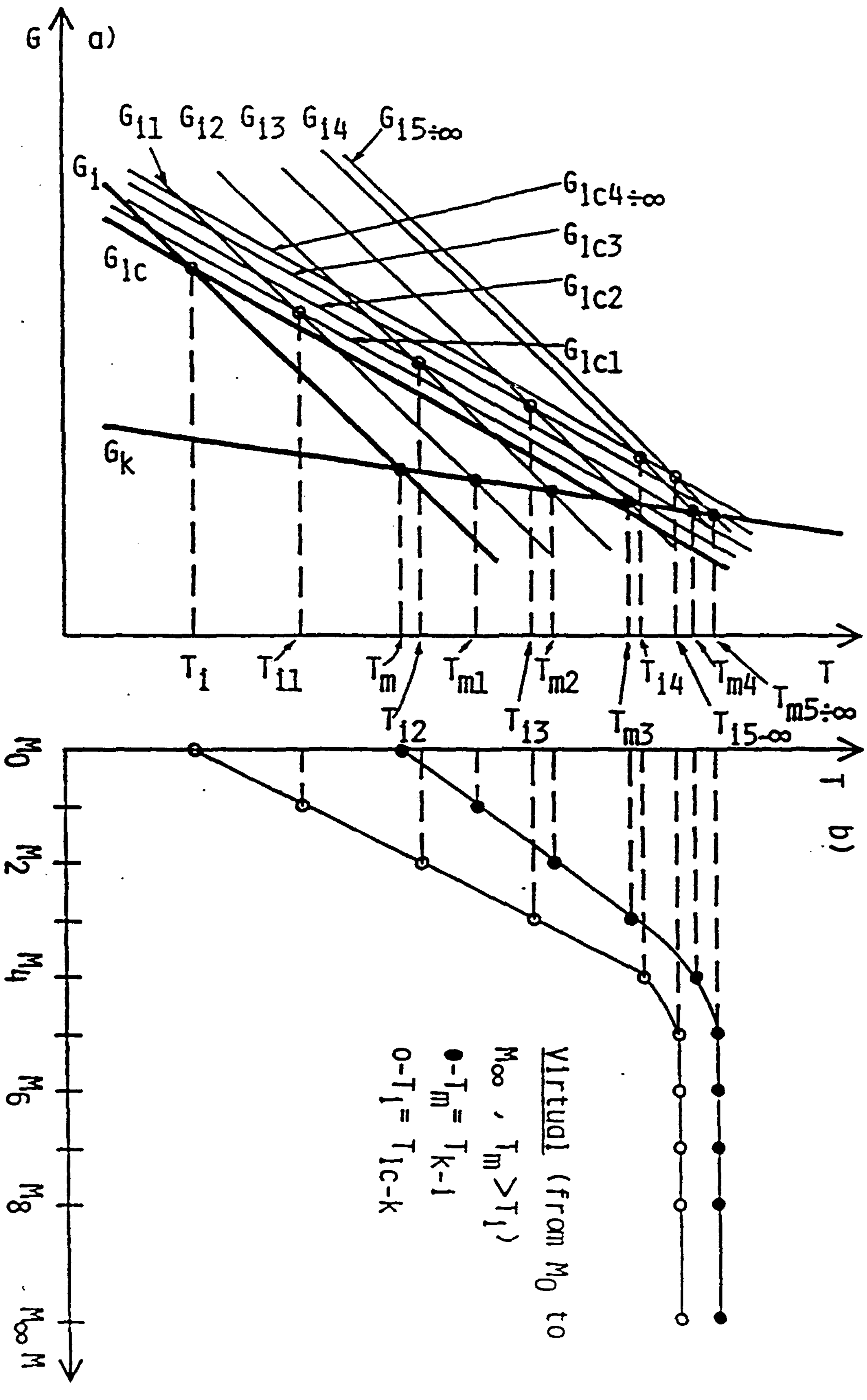

G
a)
G1
G1c
Gk
G11 G12 G13 G14 G15 G16 G17 G18 G19÷∞
G1c1 G1c2 G1c3 G1c4 G1c5 G1c6 G1c7 G1c8 G1c9÷∞
T
T1 Tm T11 Tm1 T12 Tm2 T13 Tm3 Tm4=T14 Tm5 Tm6 T15 Tm7 Tm8 T16 Tm9÷∞ T17 T18 T19÷∞
M0 M2 M4 M6 M8 M∞ M
T
b)
Virtual (from M0 to M4, Tm>T1)
●-Tm= Tk-l
o-T1= T1c-k
Monotropic (at M4, Tm= T1= Tk-l= T1c-l)
Enantiotropic (from M5 to M∞, T1>Tm)
●-Tm=Tk-lc
o-T1=T1c-l

Figure 10


G
a)
G_{i1}
G_{i2}
G_{i3}
G_{i4}
$G_{i5\div\infty}$
G_i
$G_{ic4\div\infty}$
G_{ic3}
G_{ic}
G_{ic2}
G_{ic1}
G_k
T_i
T_{i1}
T_m
T_{m1}
T_{m2}
T_{i4}
T_{m4}
T
T_{i2}
T_{i3}
T_{m3}
$T_{i5-\infty}$
$T_{m5\div\infty}$
M_0
M_2
M_4
M_6
M_8
M_∞
M
T
b)
Virtual (from M_0 to M_∞, $T_m>T_i$)
●-$T_m = T_{k-i}$
o-$T_i = T_{ic-k}$

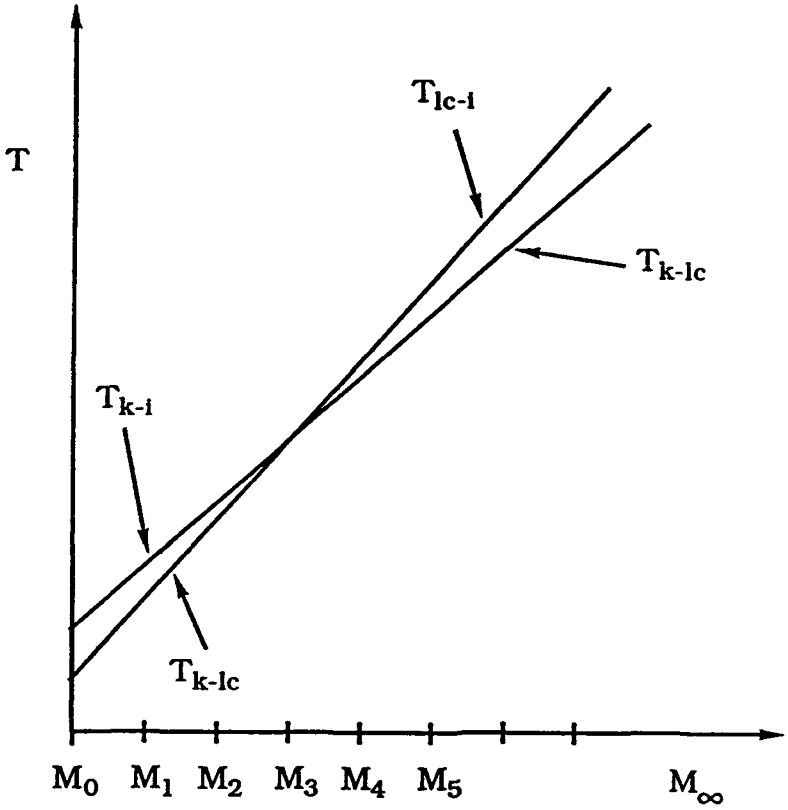


Figure 12

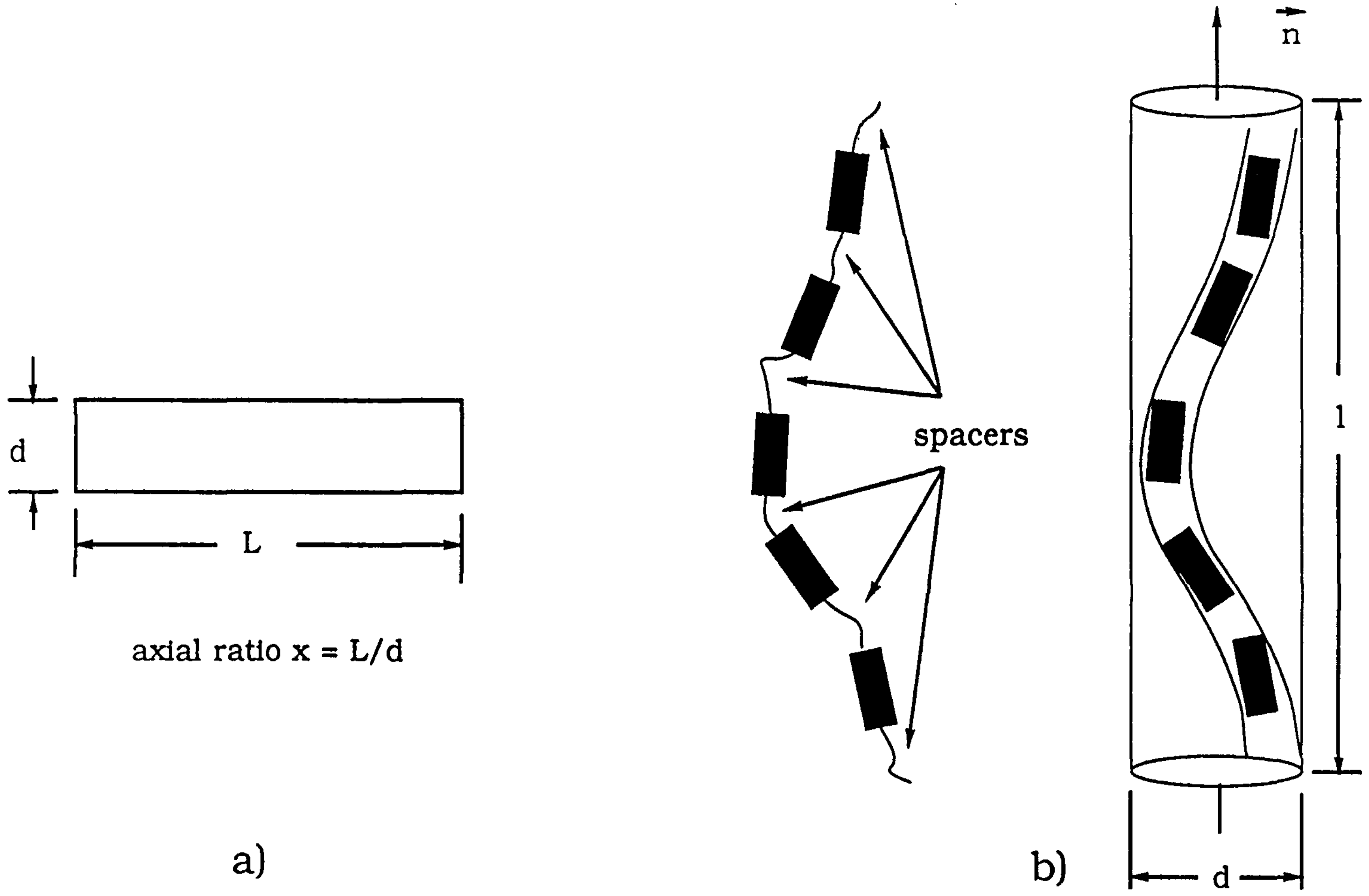


Figure 13

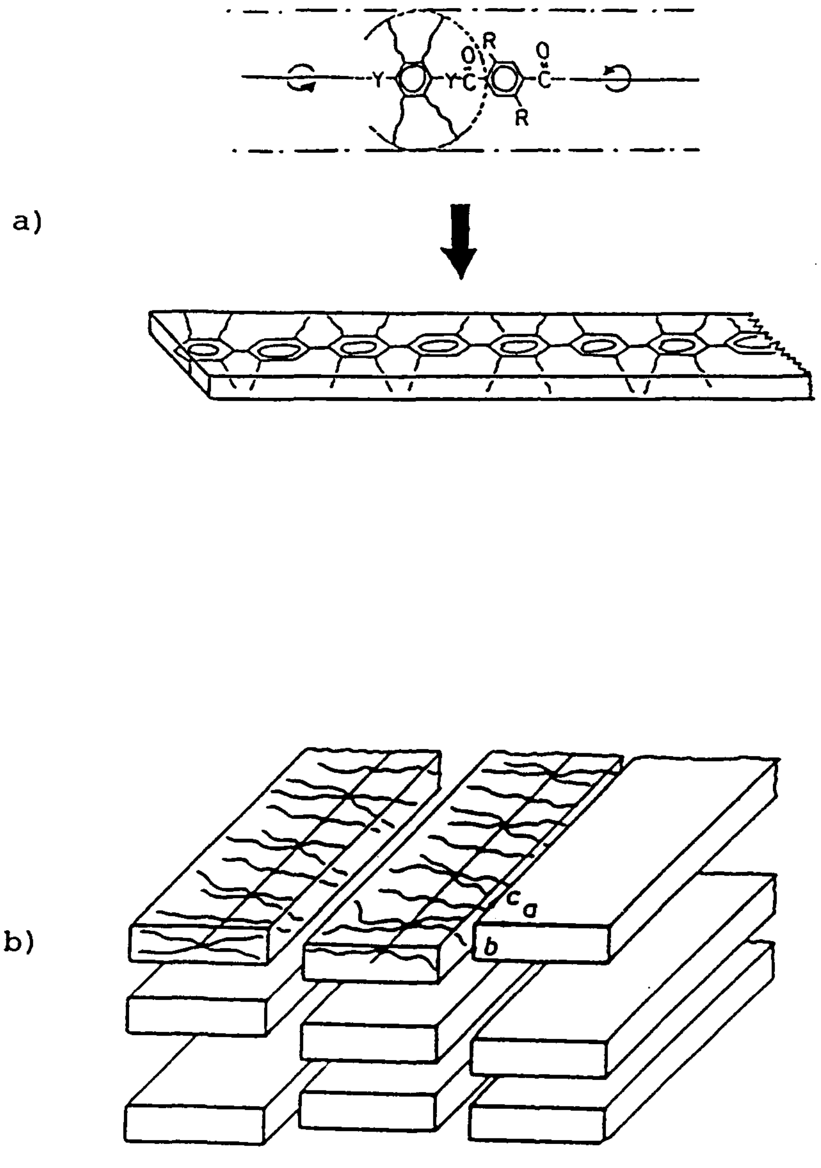
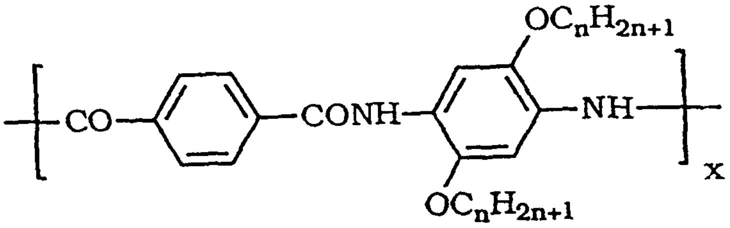
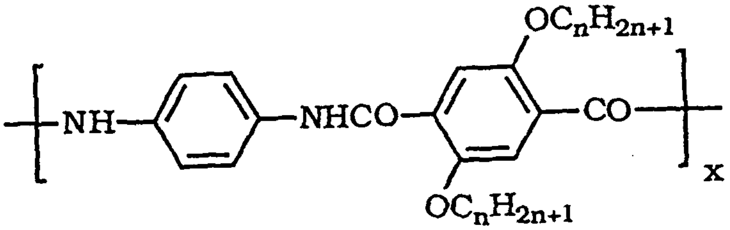


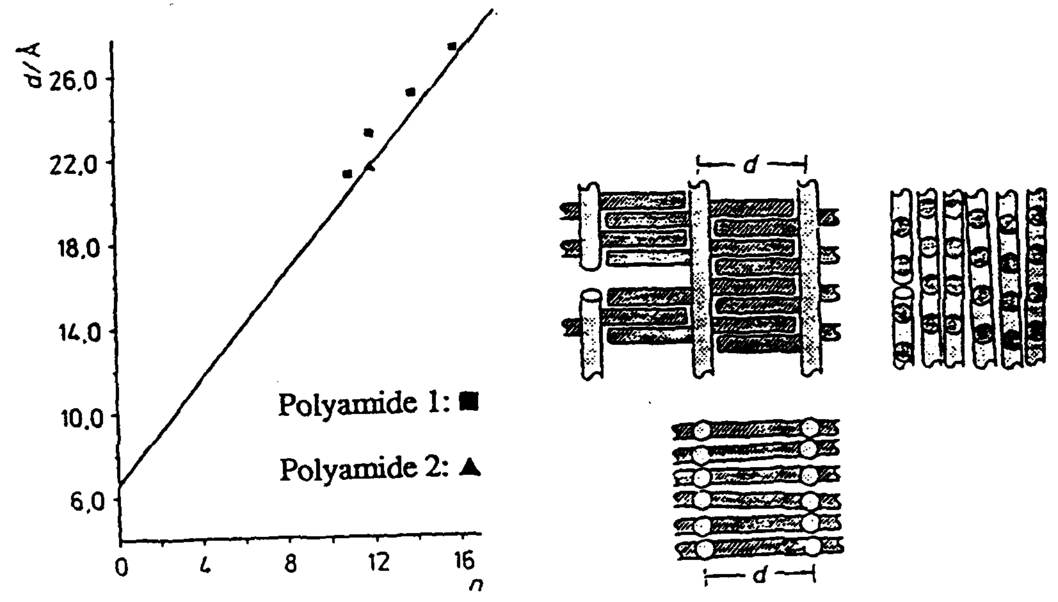
Figure 14

Polyamide 1 :



Polyamide 2 :

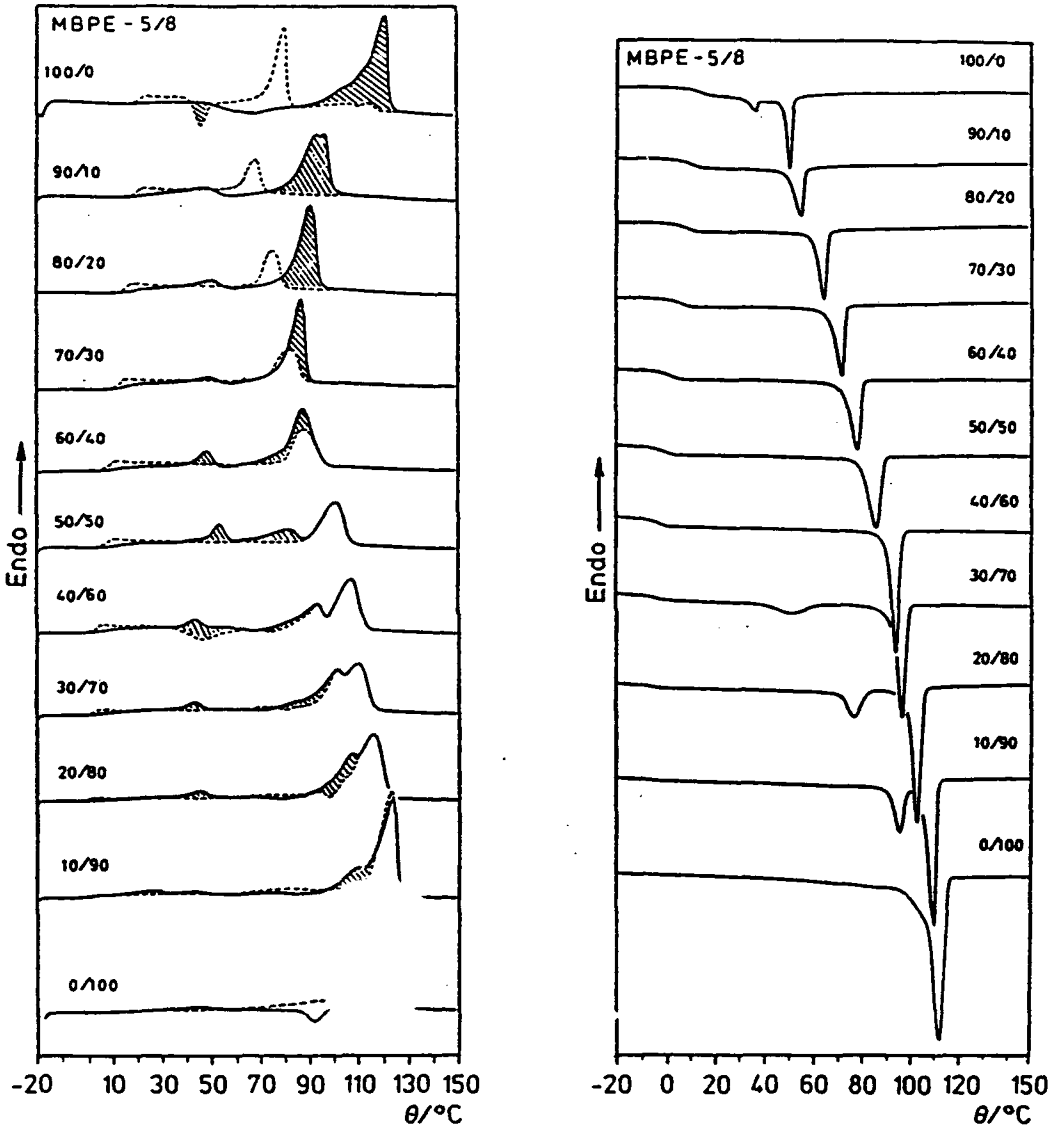




a)

b)

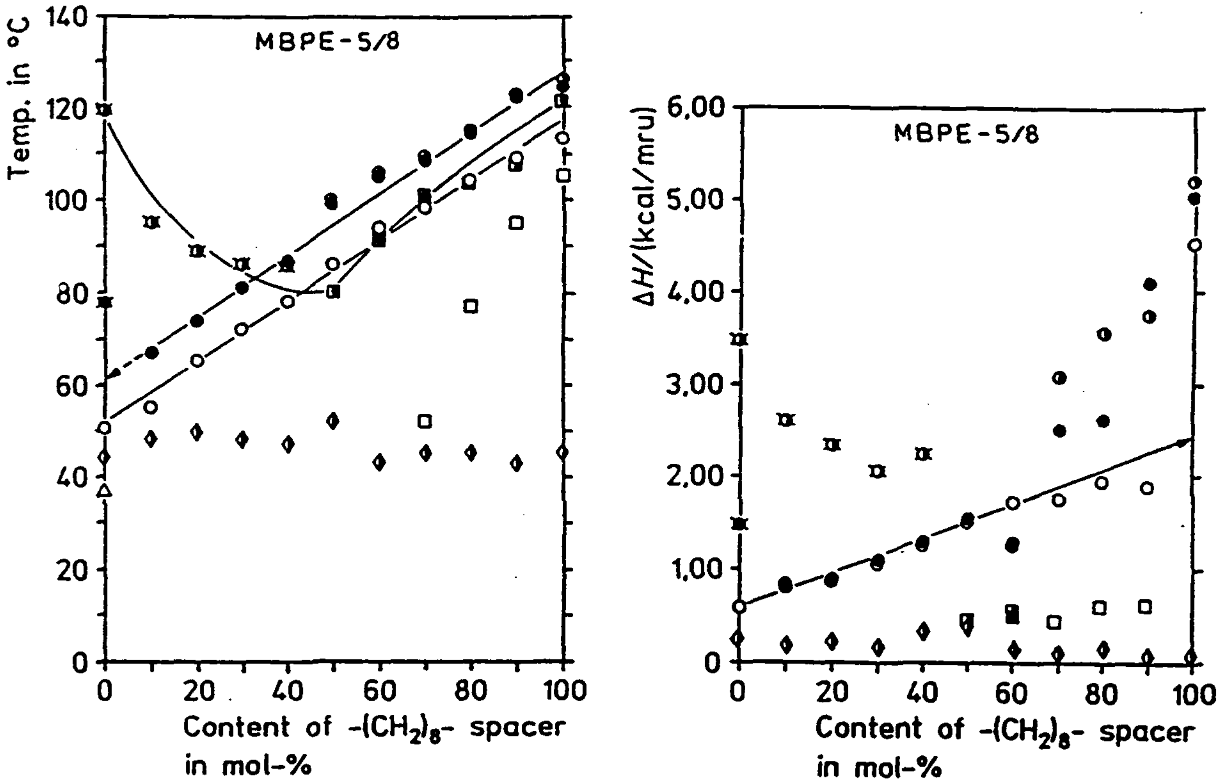
Figure 15


MBPE - 5/8
100/0
90/10
80/20
70/30
60/40
50/50
40/60
30/70
20/80
10/90
0/100
Endo
-20
10
30
50
70
90
110
130
150
θ/°C
MBPE-5/8
100/0
90/10
80/20
70/30
60/40
50/50
40/60
30/70
20/80
10/90
0/100
Endo
-20
0
20
40
60
80
100
120
150
θ/°C

a)

b)

Figure 16


MBPE-5/8
Temp. in °C
140
120
100
80
60
40
20
0
0
20
40
60
80
100
Content of -(CH$_2$)$_8$- spacer in mol-%
MBPE-5/8
ΔH/(kcal/mru)
6,00
5,00
4,00
3,00
2,00
1,00
0
0
20
40
60
80
100
Content of -(CH$_2$)$_8$- spacer in mol-%

a)

b)

Figure 17

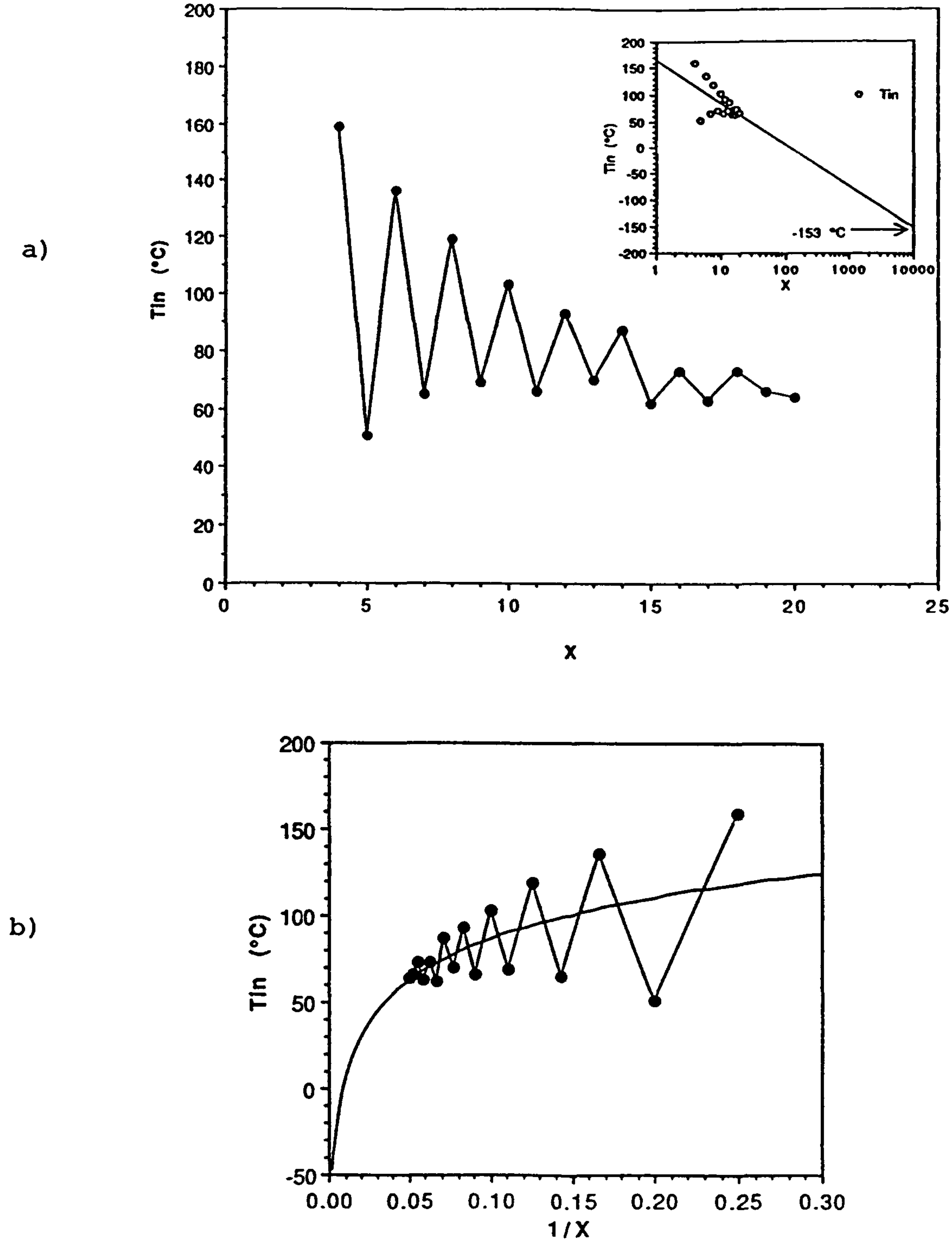
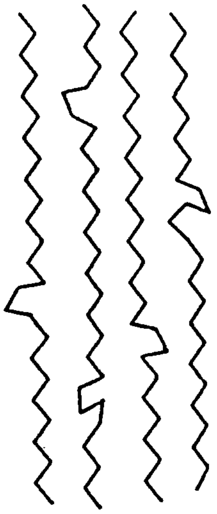
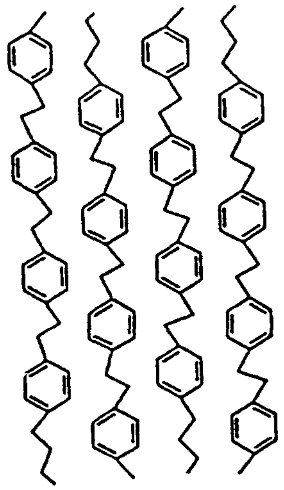

a)
Tin (°C)
200
180
160
140
120
100
80
60
40
20
0
0
5
10
15
20
25
X
200
150
100
50
0
-50
-100
-150
-200
Tin (°C)
1
10
100
1000
10000
X
Tin
-153 °C
b)
Tin (°C)
200
150
100
50
0
-50
0.00
0.05
0.10
0.15
0.20
0.25
0.30
1/X

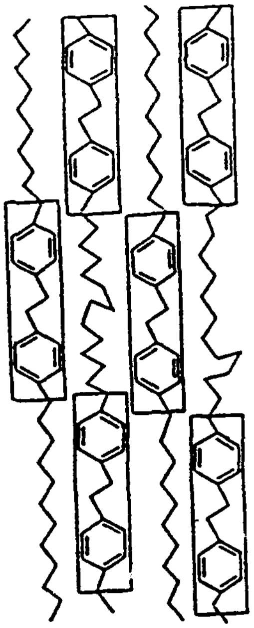
Figure 18



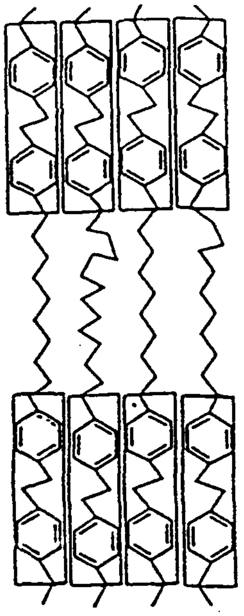
PE
columnar



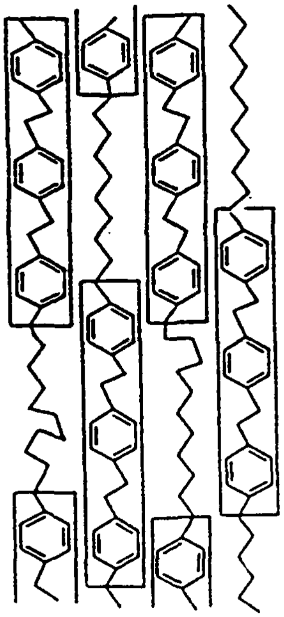
PX
columnar



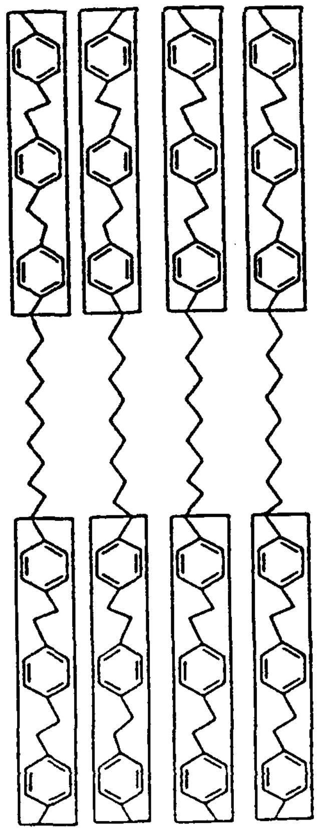
BPE-8/12
columnar



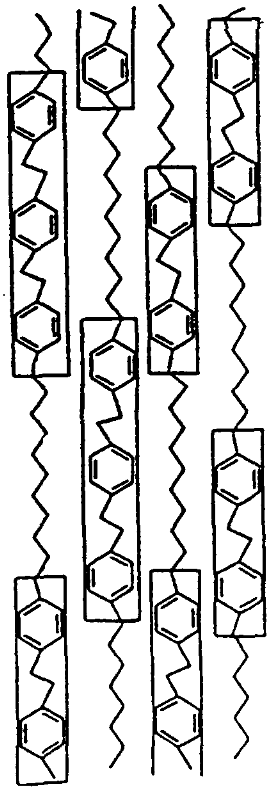
BPE-8/12
s_B



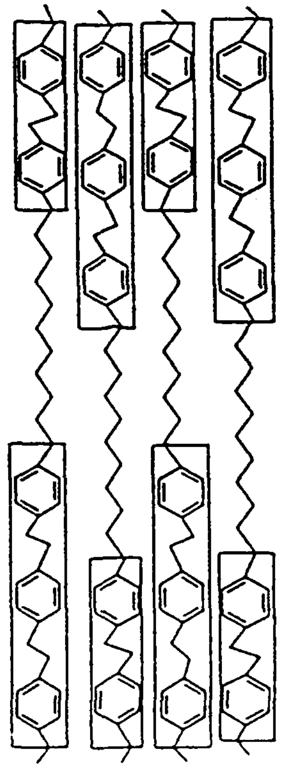
PEB-9
columnar



PEB-9
s_B

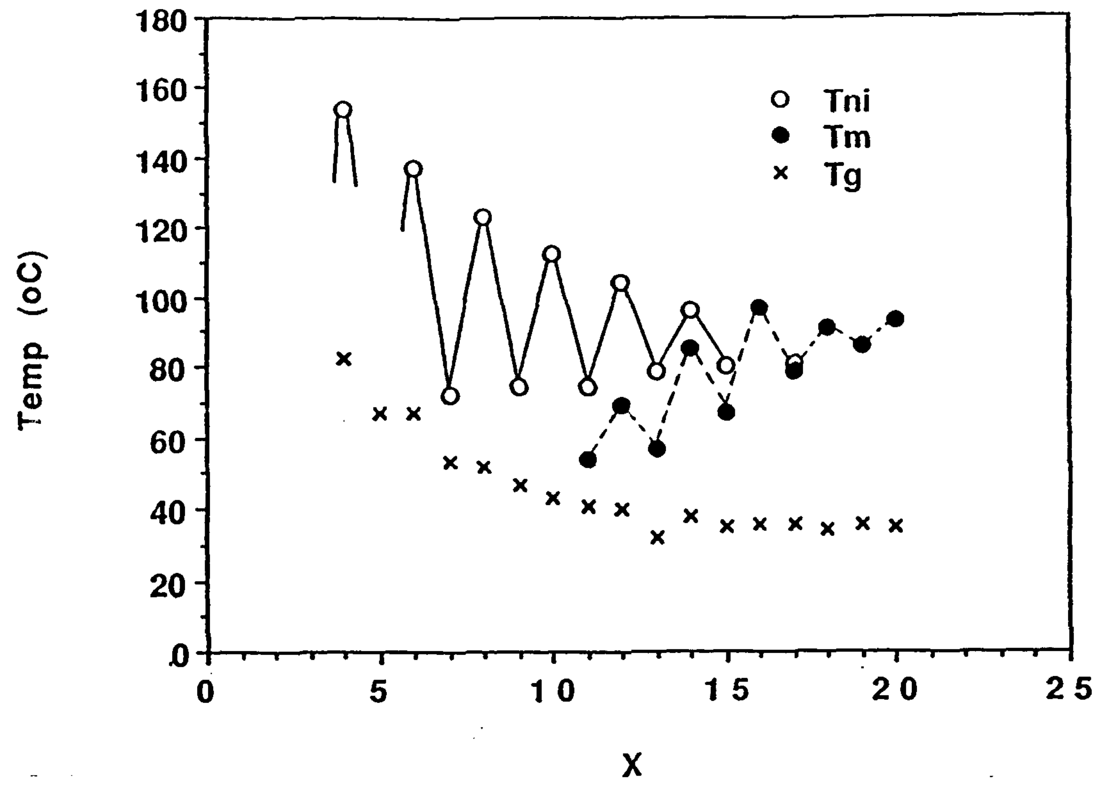


BPE/PEB(A/B)-9
columnar



BPE/PEB(A/B)-9
smectic

a)


Tni
Tm
Tg
Temp (oC)
X
0
20
40
60
80
100
120
140
160
180
0
5
10
15
20
25

b)

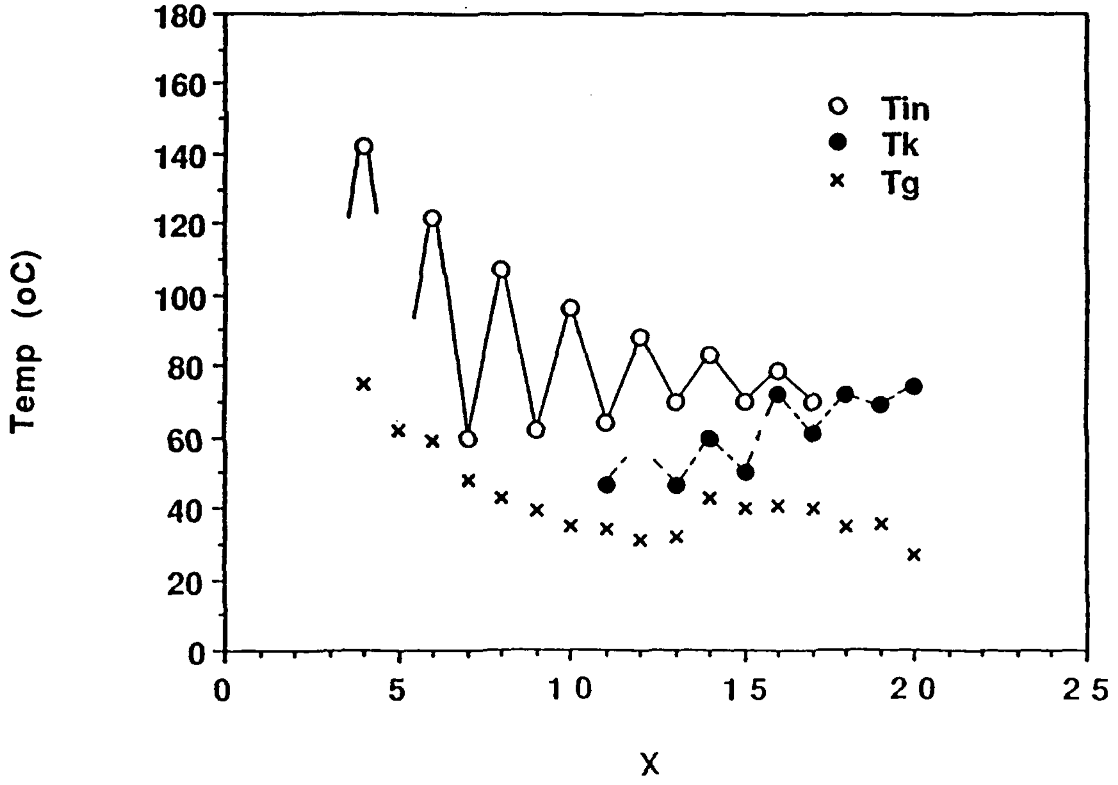

Tin
Tk
Tg
Temp (oC)
X
0
20
40
60
80
100
120
140
160
180
0
5
10
15
20
25

Figure 20

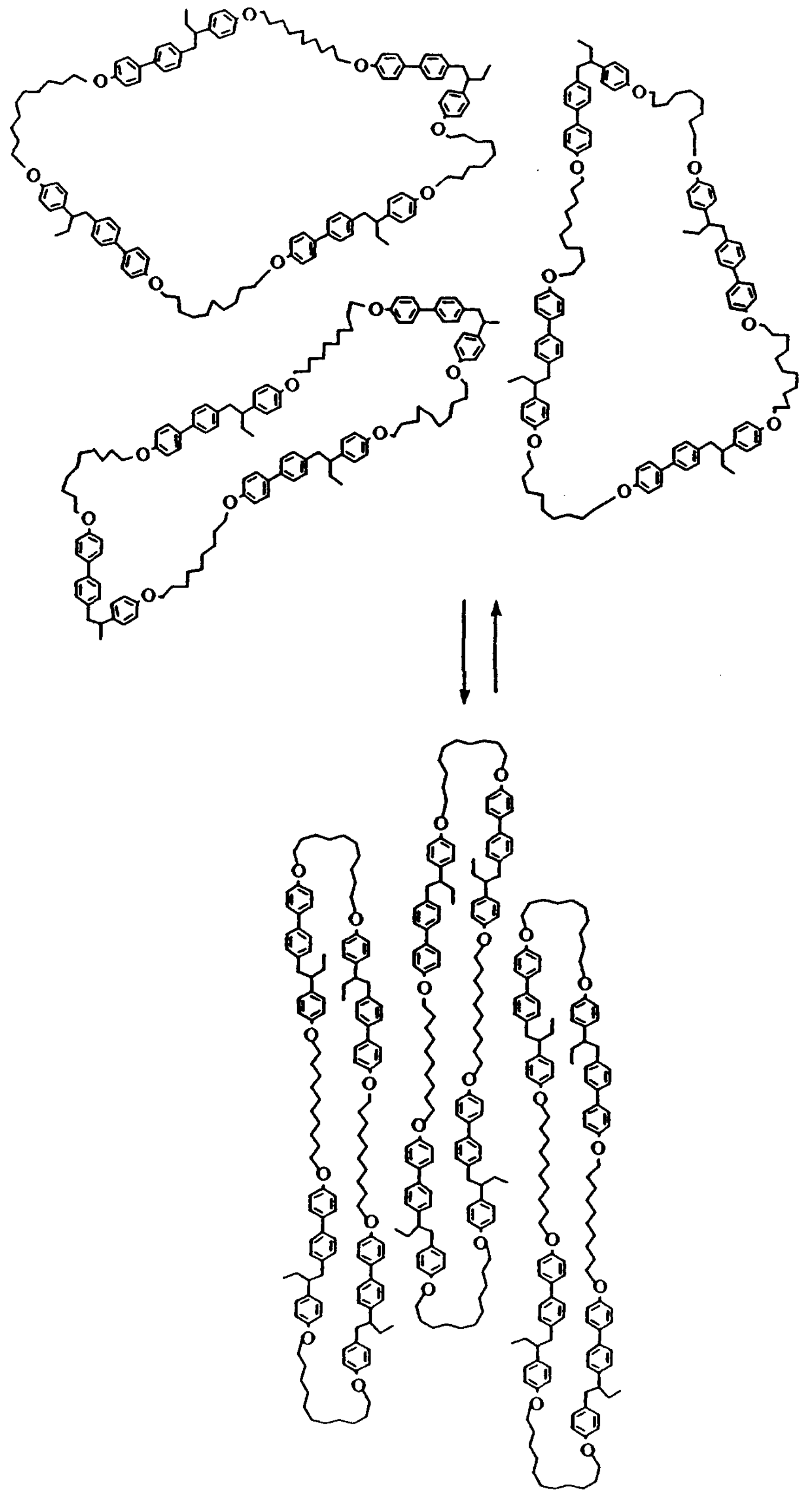


Figure 21

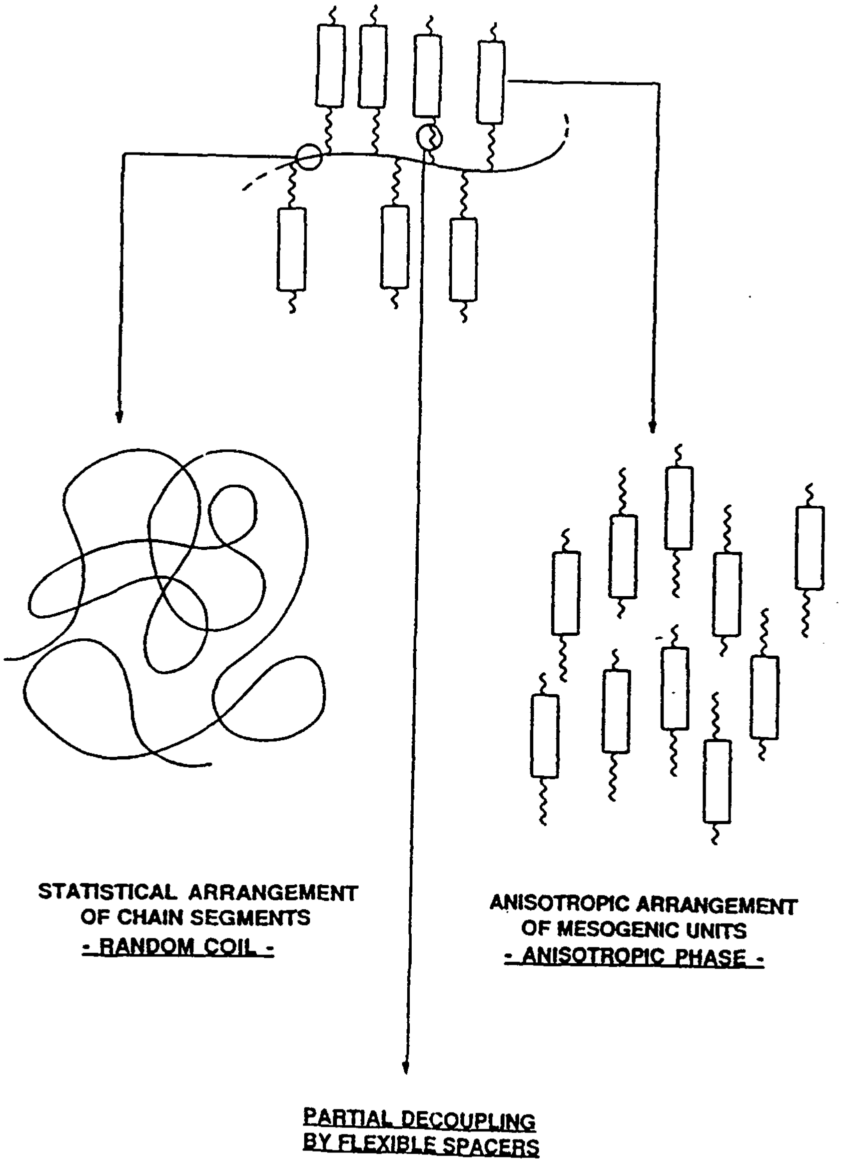

STATISTICAL ARRANGEMENT
OF CHAIN SEGMENTS
- RANDOM COIL -
ANISOTROPIC ARRANGEMENT
OF MESOGENIC UNITS
- ANISOTROPIC PHASE -
PARTIAL DECOUPLING
BY FLEXIBLE SPACERS

Figure 22

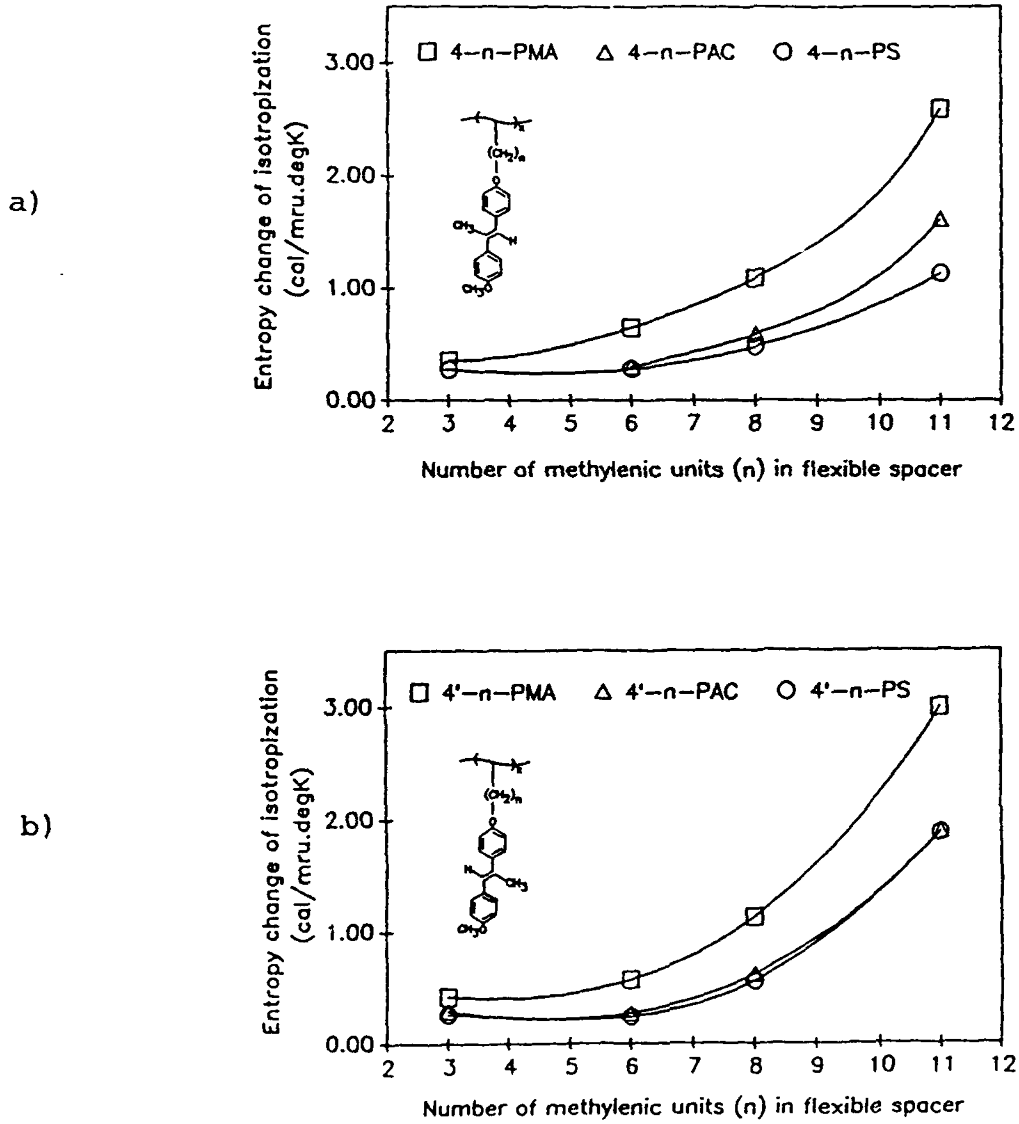

a)
□ 4–n–PMA
△ 4–n–PAC
○ 4–n–PS
$(CH_2)_n$
CH_3
H
CH_3O
Entropy change of isotropization (cal/mru.degK)
0.00
1.00
2.00
3.00
2
3
4
5
6
7
8
9
10
11
12
Number of methylenic units (n) in flexible spacer
b)
□ 4'–n–PMA
△ 4'–n–PAC
○ 4'–n–PS
$(CH_2)_n$
H
CH_3
CH_3O
Entropy change of isotropization (cal/mru.degK)
0.00
1.00
2.00
3.00
2
3
4
5
6
7
8
9
10
11
12
Number of methylenic units (n) in flexible spacer

Figure 23

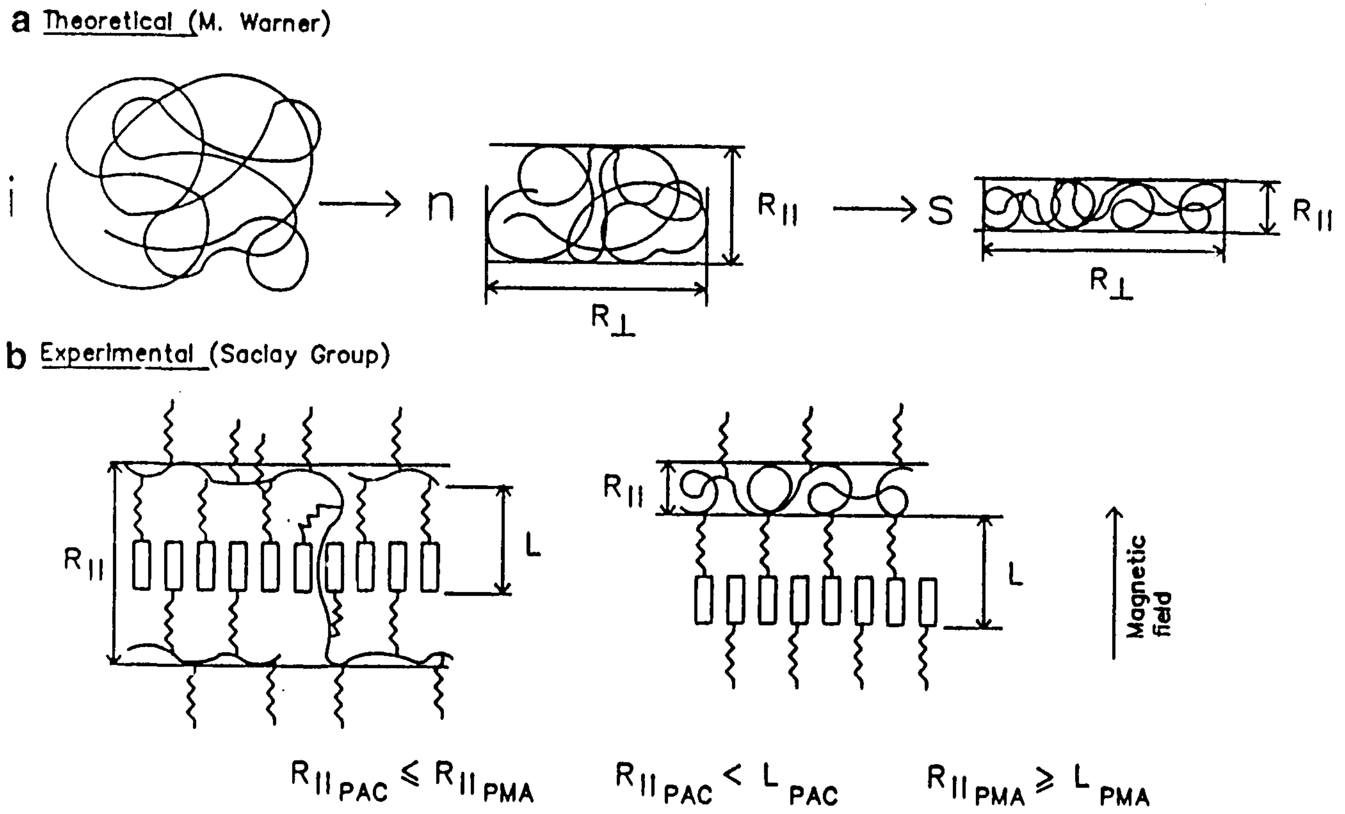
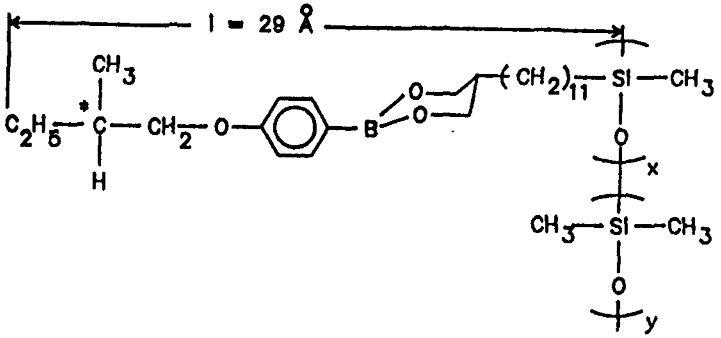
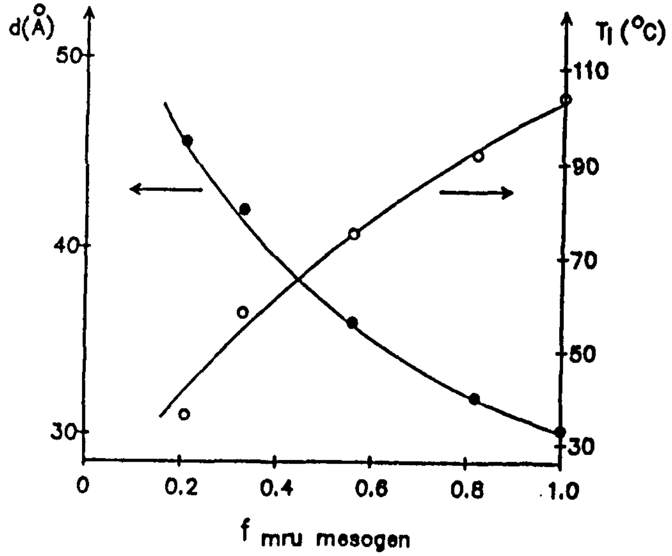
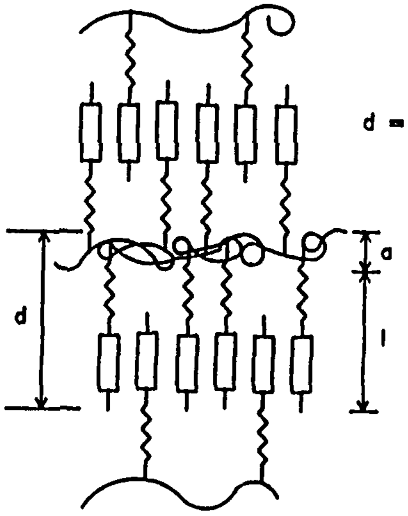

a Theoretical (M. Warner)
i
n
$R_{\parallel}$
s
$R_{\parallel}$
$R_{\perp}$
$R_{\perp}$
b Experimental (Saclay Group)
$R_{\parallel}$
L
$R_{\parallel}$
L
Magnetic field
$R_{\parallel PAC} \leqslant R_{\parallel PMA}$
$R_{\parallel PAC} < L_{PAC}$
$R_{\parallel PMA} \geqslant L_{PMA}$

Figure 24

mesogen(%)	d(Å)	a(Å)	T_I(°C)
100	30.4	1.4	104
82	32.0	3.0	92
56	36.0	7.0	75
33	42.0	13.0	58
21	45.6	16.6	36







d = a + l ; d > l

Figure 25

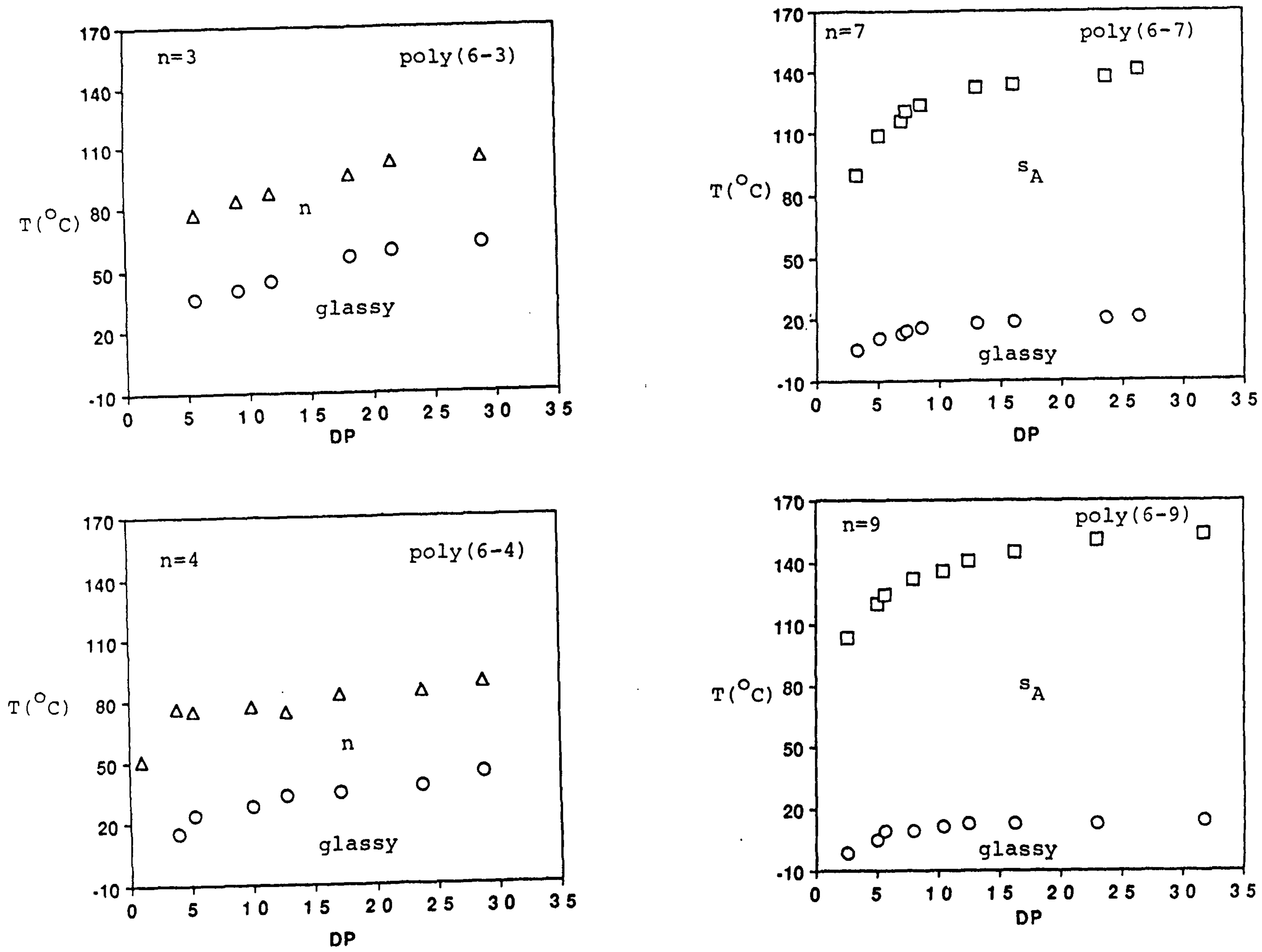

n=3
poly(6-3)
n
glassy
n=7
poly(6-7)
s_A
glassy
n=4
poly(6-4)
n
glassy
n=9
poly(6-9)
s_A
glassy
T(°C)
170
140
110
80
50
20
-10
DP
0
5
10
15
20
25
30
35

Figure 26

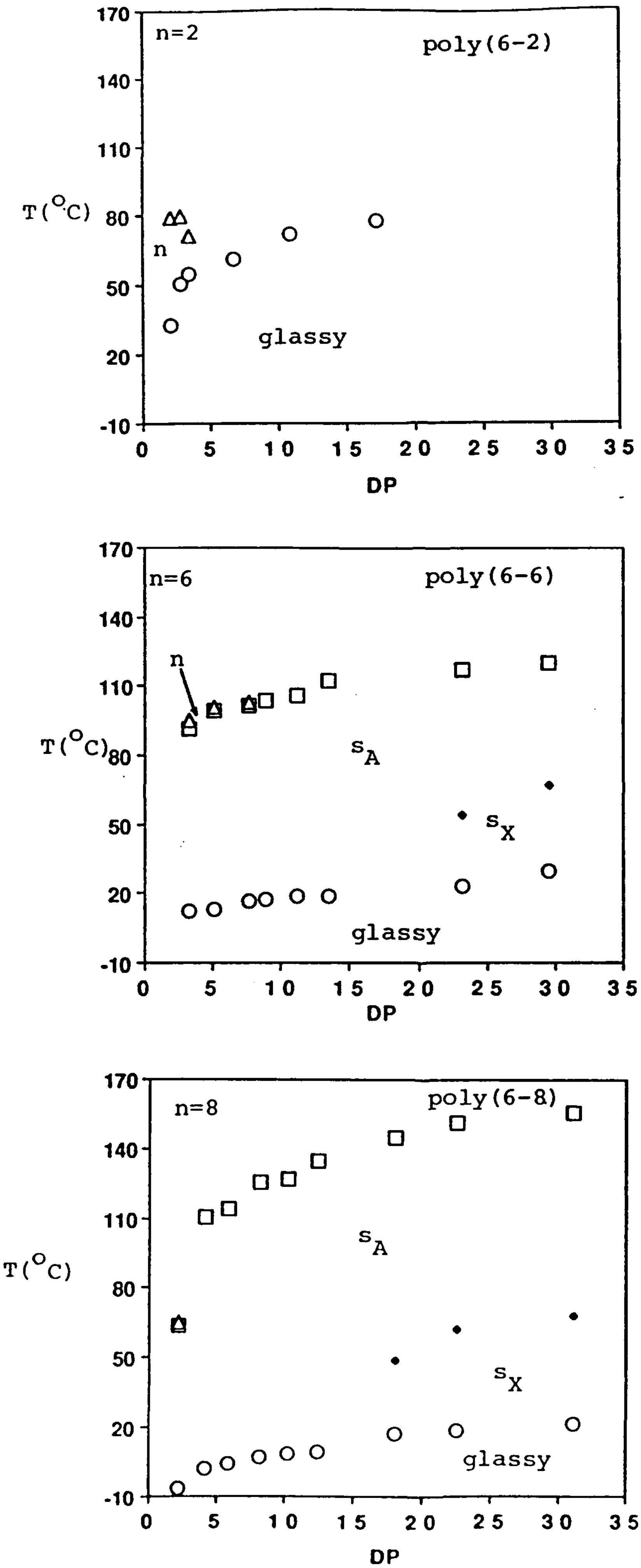

n=2
poly(6-2)
T(°C)
n
glassy
DP
n=6
poly(6-6)
n
s_A
s_X
glassy
n=8
poly(6-8)
s_A
s_X
glassy
170
140
110
80
50
20
-10
0
5
10
15
20
25
30
35

Figure 27

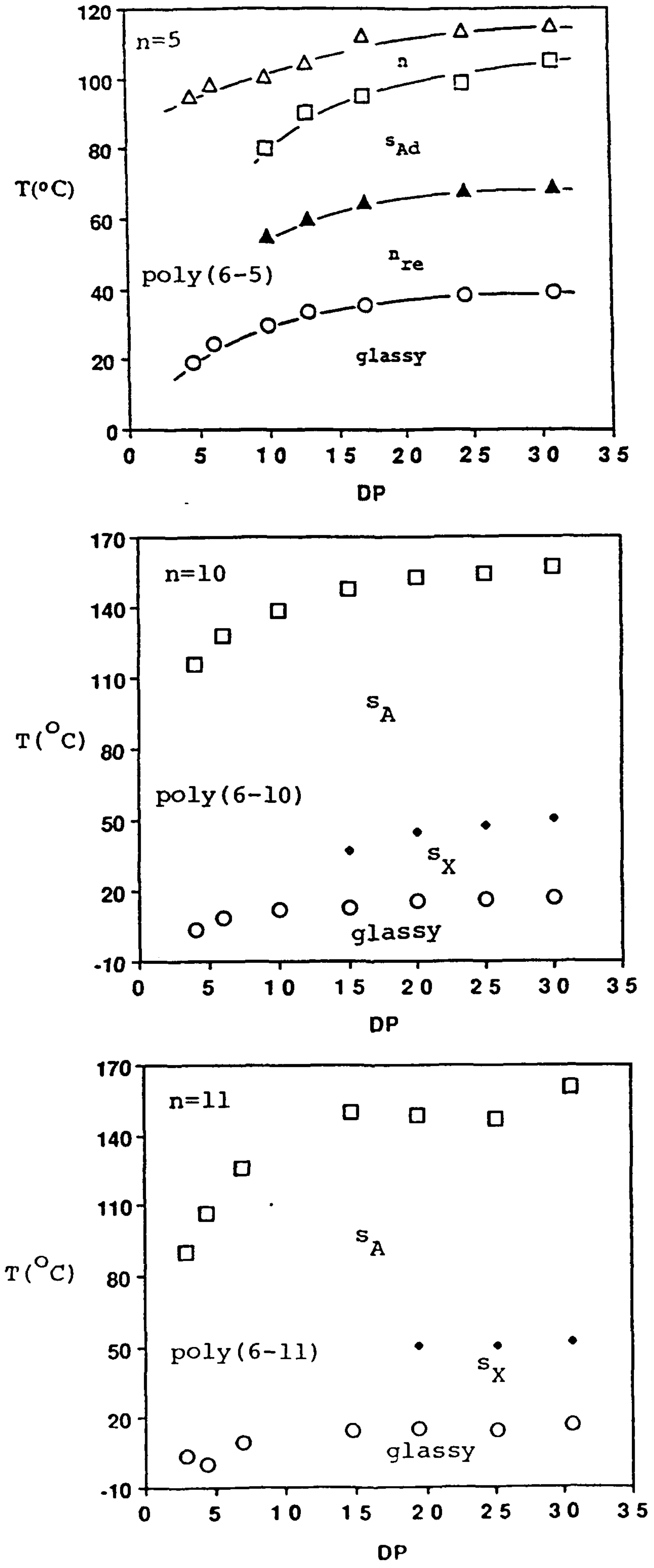

n=5
n
s$_{Ad}$
n$_{re}$
poly(6-5)
glassy
T(°C)
120
100
80
60
40
20
0
0
5
10
15
20
25
30
35
DP
n=10
s$_A$
poly(6-10)
s$_X$
glassy
T(°C)
170
140
110
80
50
20
-10
0
5
10
15
20
25
30
35
DP
n=11
s$_A$
poly(6-11)
s$_X$
glassy
T(°C)
170
140
110
80
50
20
-10
0
5
10
15
20
25
30
35
DP

Figure 28

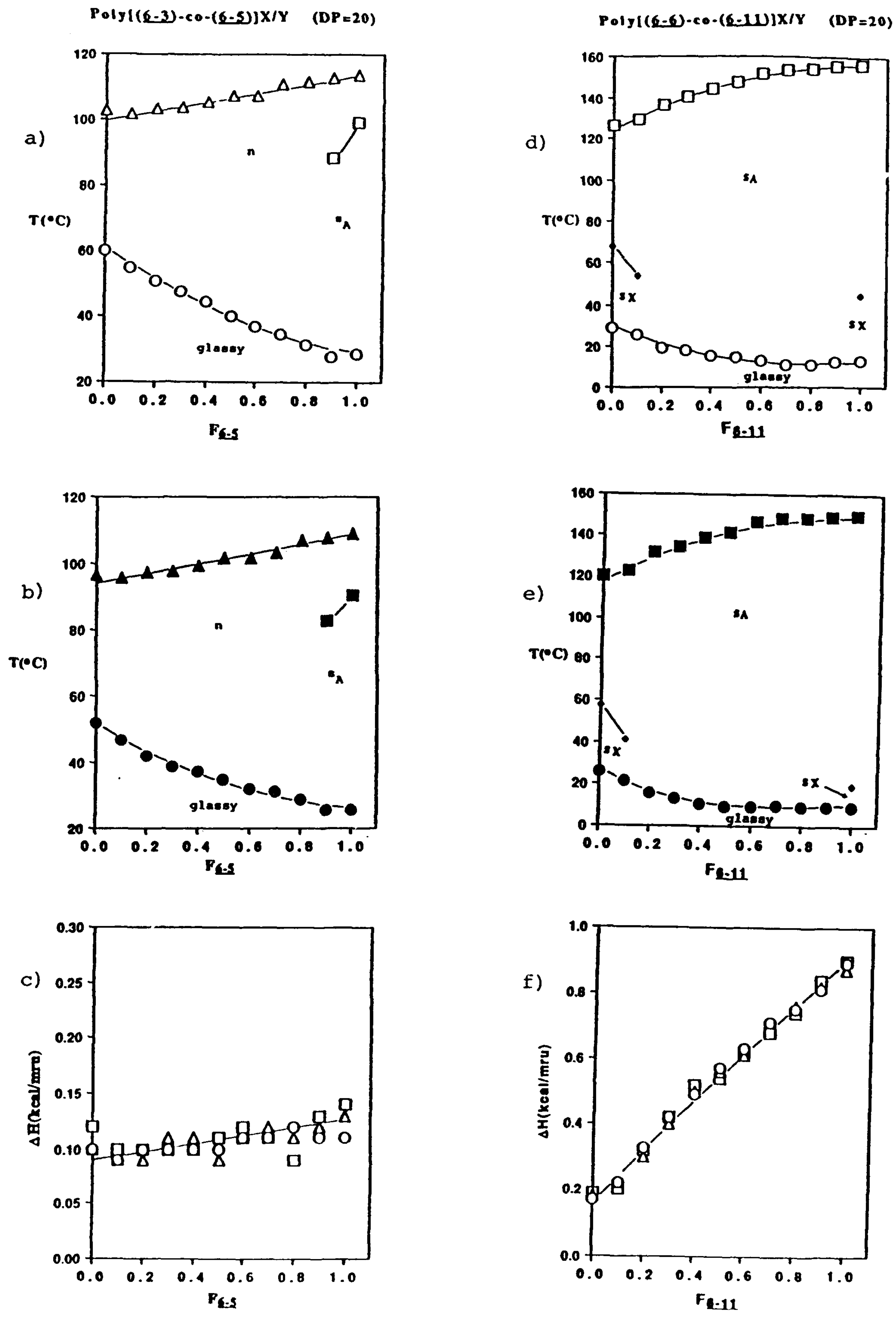

Poly[(6-3)-co-(6-5)]X/Y (DP=20)
Poly[(6-6)-co-(6-11)]X/Y (DP=20)
a)
b)
c)
d)
e)
f)
T(°C)
ΔH(kcal/mru)
F6-5
F6-11
n
sA
sX
glassy
0.0
0.2
0.4
0.6
0.8
1.0
20
40
60
80
100
120
140
160
0.00
0.05
0.10
0.15
0.20
0.25
0.30

Figure 29

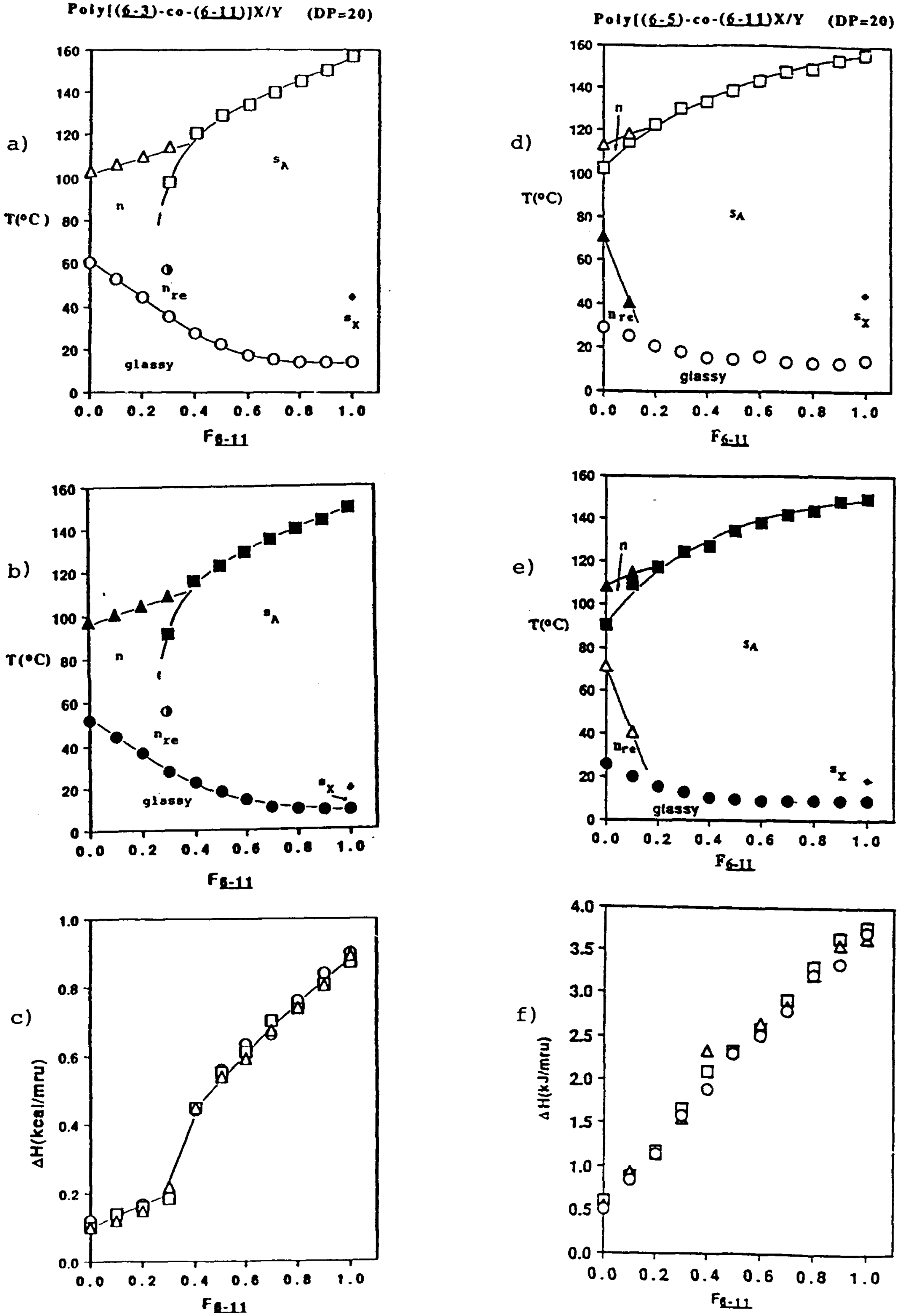

Poly[(6-3)-co-(6-11)]X/Y (DP=20)
Poly[(6-5)-co-(6-11)X/Y (DP=20)
a)
b)
c)
d)
e)
f)
T(°C)
n
s_A
n_{re}
s_X
glassy
F_{6-11}
ΔH(kcal/mru)
ΔH(kJ/mru)
0
20
40
60
80
100
120
140
160
0.0
0.2
0.4
0.6
0.8
1.0
0.5
1.5
2.0
2.5
3.0
3.5
4.0

Figure 30

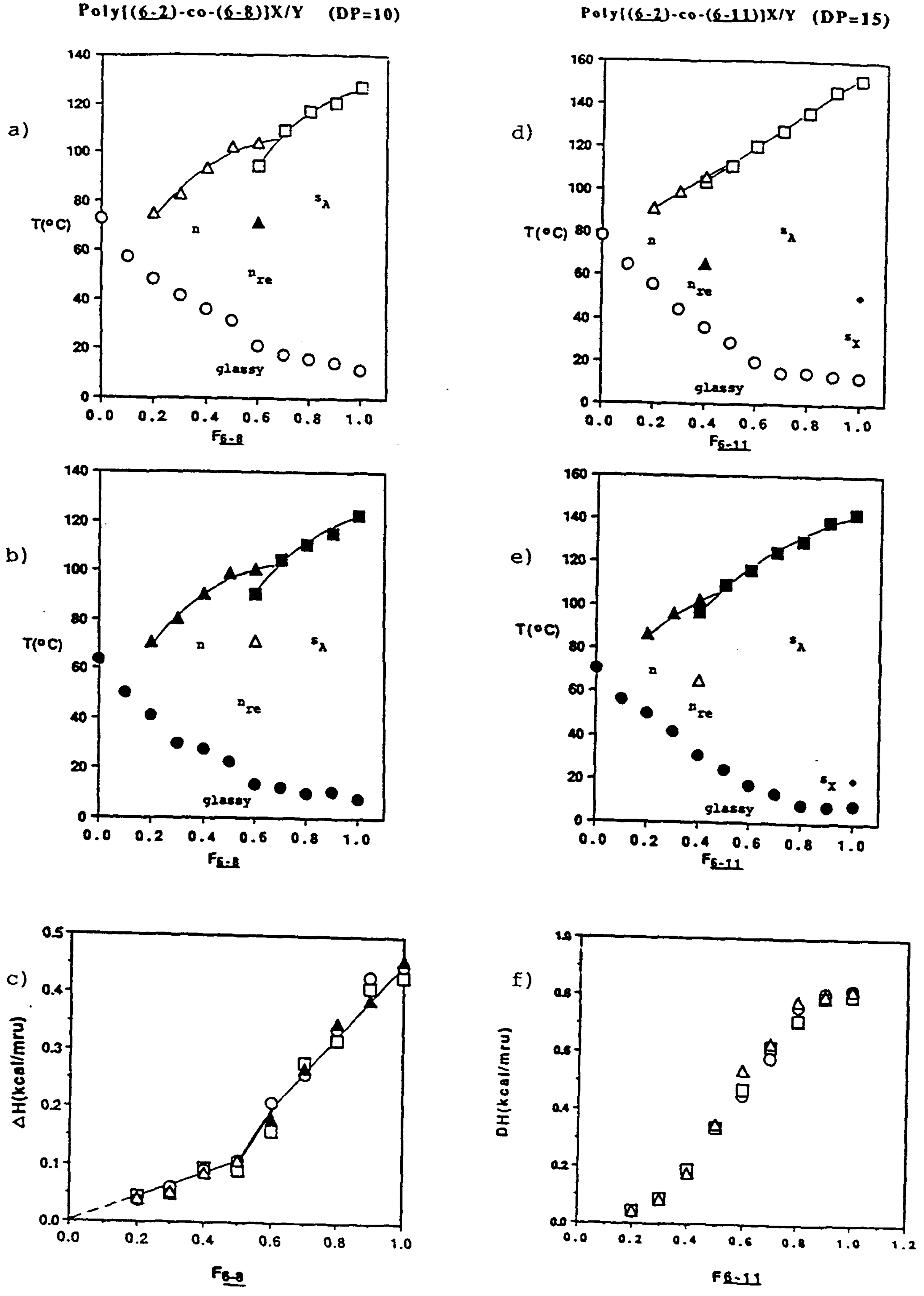

Poly[(6-2)-co-(6-8)]X/Y (DP=10)
Poly[(6-2)-co-(6-11)]X/Y (DP=15)
a)
b)
c)
d)
e)
f)
T(°C)
ΔH(kcal/mru)
DH(kcal/mru)
F6-8
F6-11
n
n_re
s_A
s_X
glassy
0.0
0.2
0.4
0.6
0.8
1.0
1.2
0
20
40
60
80
100
120
140
160
0.1
0.2
0.3
0.4
0.5

Figure 31

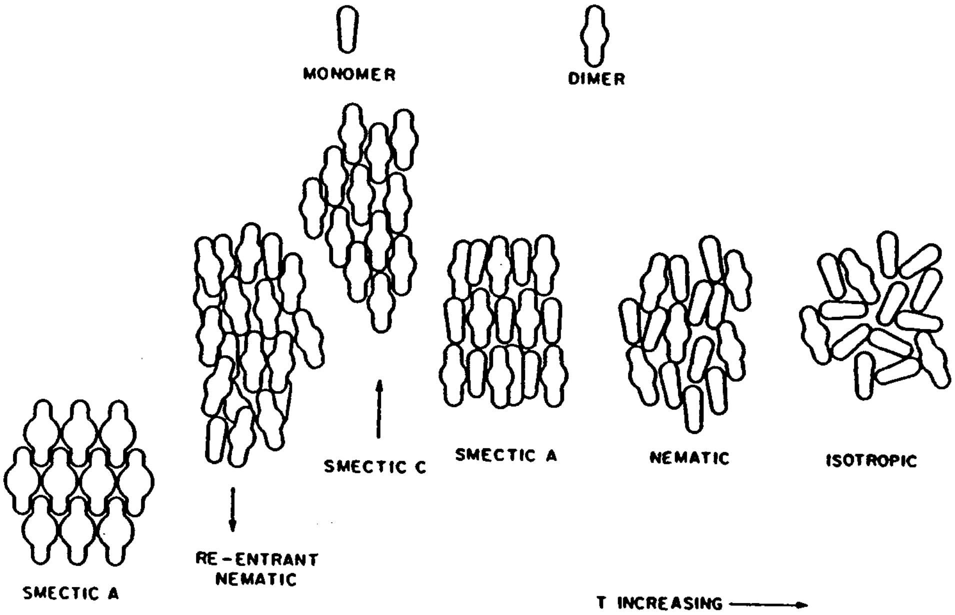

MONOMER
DIMER
SMECTIC A
RE-ENTRANT NEMATIC
SMECTIC C
SMECTIC A
NEMATIC
ISOTROPIC
T INCREASING ⟶

Figure 32

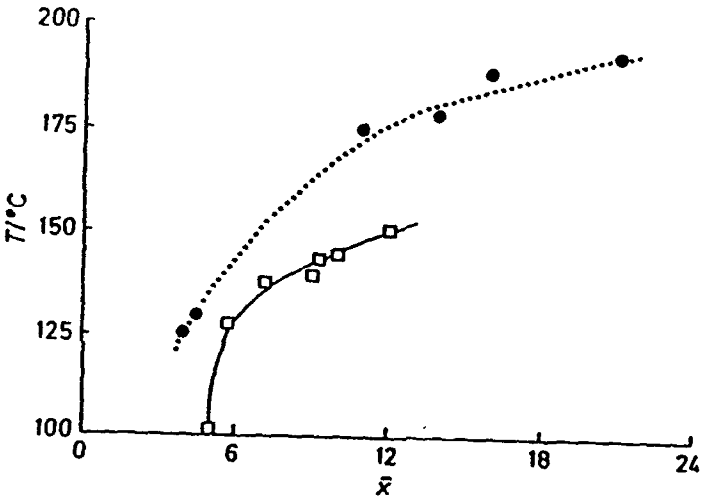
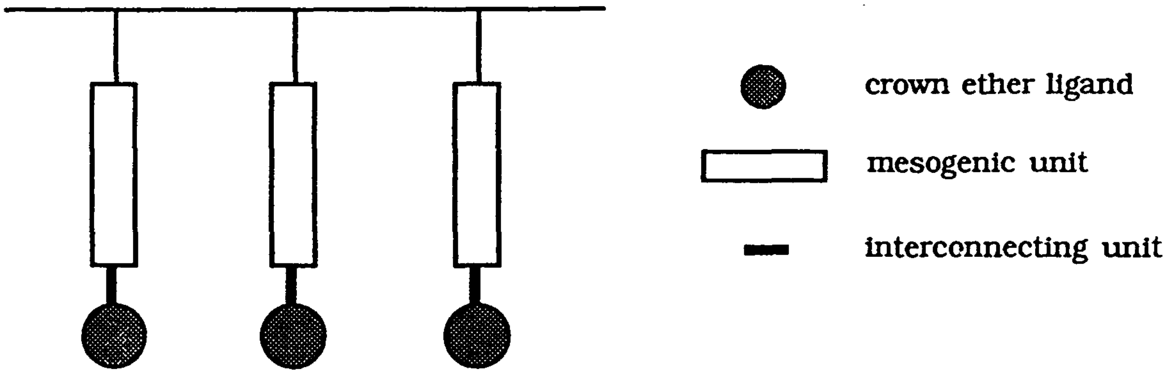


Figure 33

I. Main Chain Liquid Crystalline Polymers

II. Side Chain Liquid Crystalline Polymers

A. Crown ether ligand as part of the mesogenic unit



B. Crown ether ligand as part of the polymer backbone

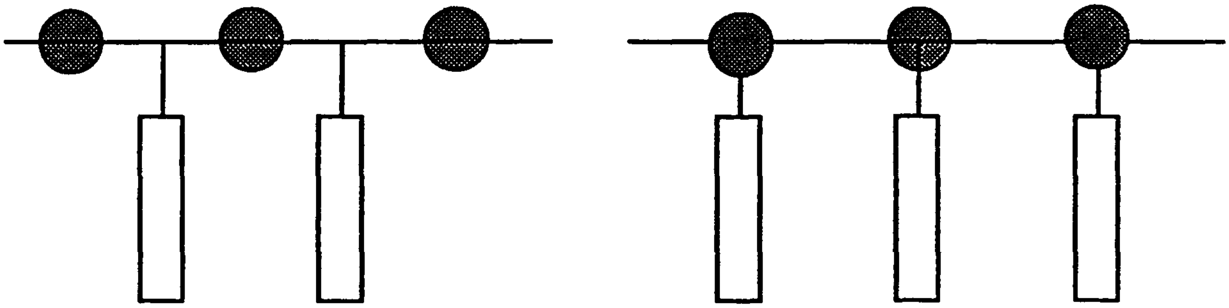


Figure 34

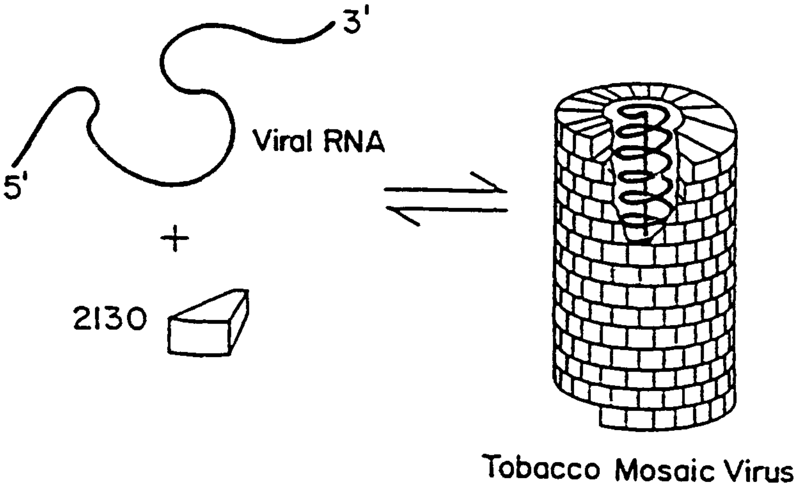


Figure 35

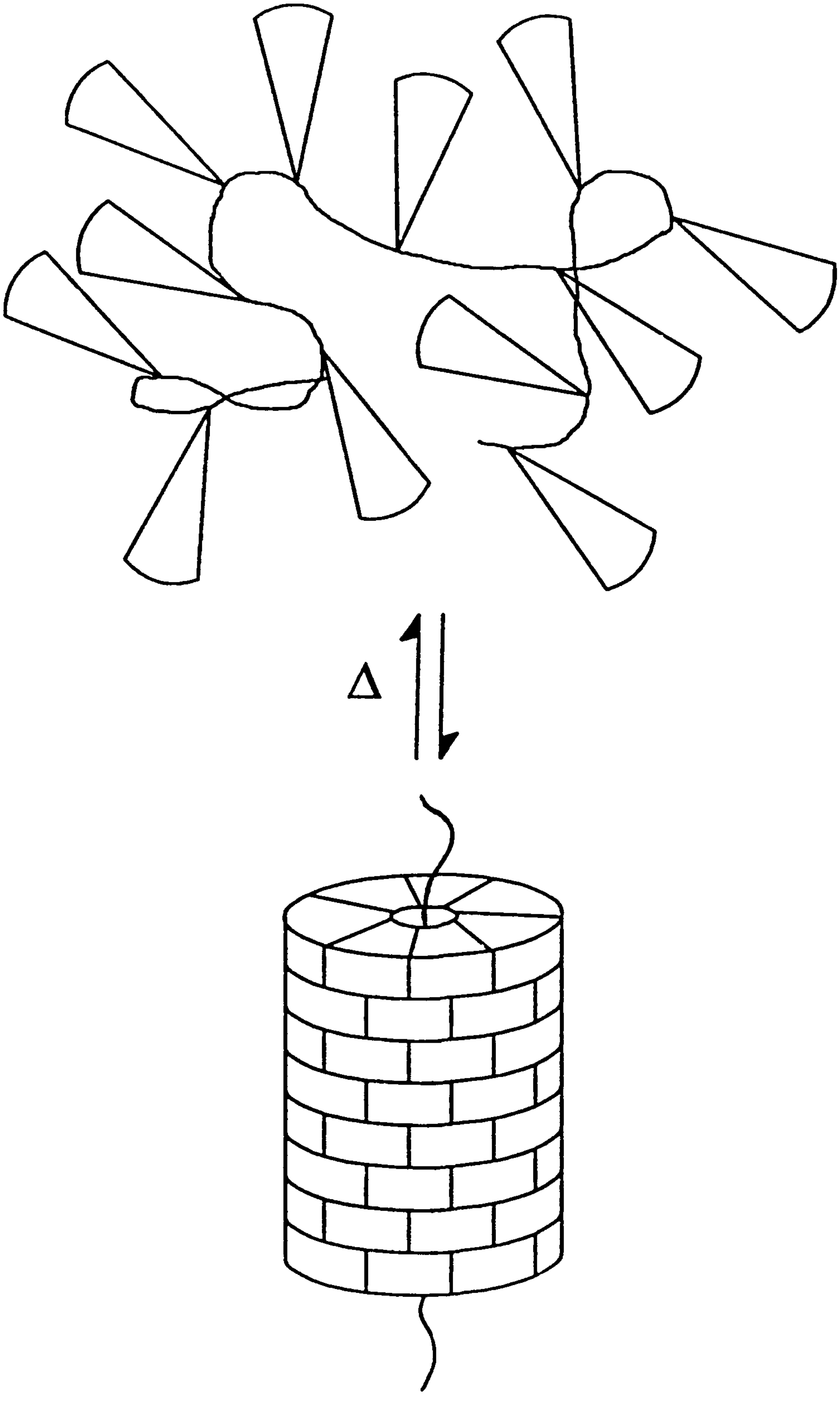
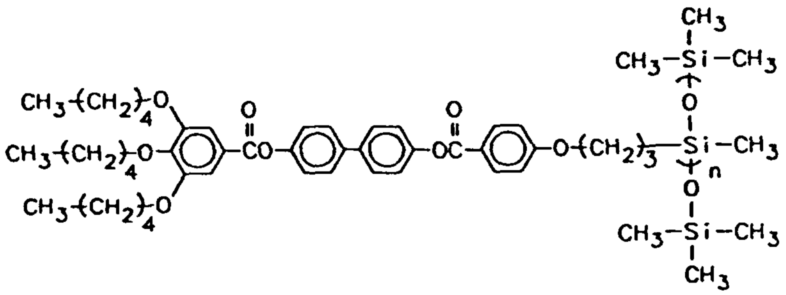
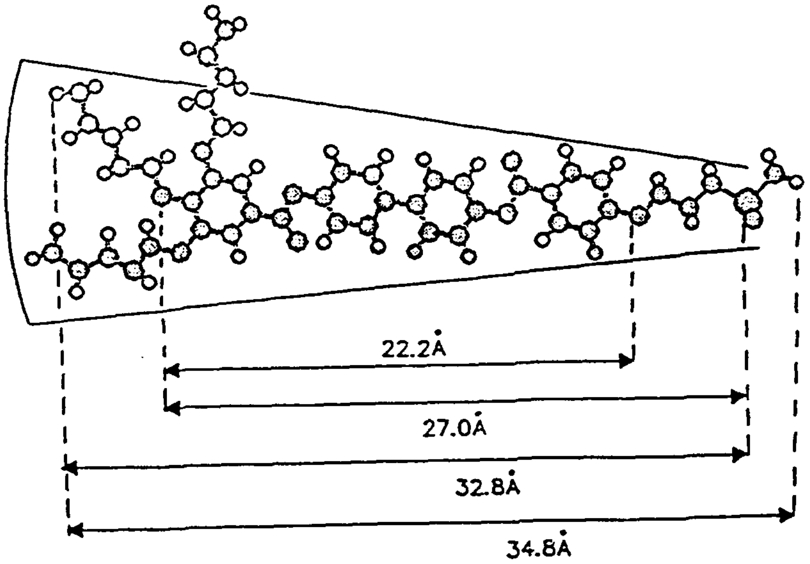
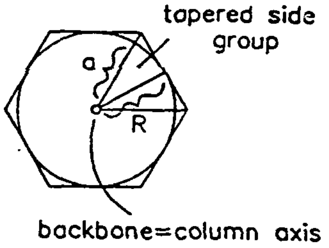


Figure 36







tail length=5 carbons

$d_0=46.5\text{Å}(\text{strong})=d^{hex}_{100}$
$d_1=26.5(\pm 0.5)\text{Å}(\text{weak})=d^{hex}_{110}$
$d_1/d_0=1.75\approx\sqrt{3}$

radius=$R=d_{100}/\sqrt{3}=27\text{Å}$
diameter=$2R=54\text{Å}$
$a=(2/\sqrt{3})R=31\text{Å}$

---

tail length=12 carbons

$d_0=57.4\text{Å}$ (strong)$=d^{hex}_{100}$
$d_1=33.3\text{Å}(\text{v.weak})=d^{hex}_{110}$
$d_2=28.5\text{Å}$ (v.weak)$=d^{hex}_{200}$.

radius=$R=33.5\text{Å}$ diameter=$2R=67\text{Å}$
fully extended conformation=42Å

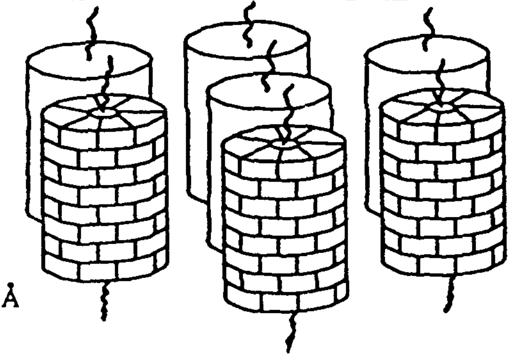
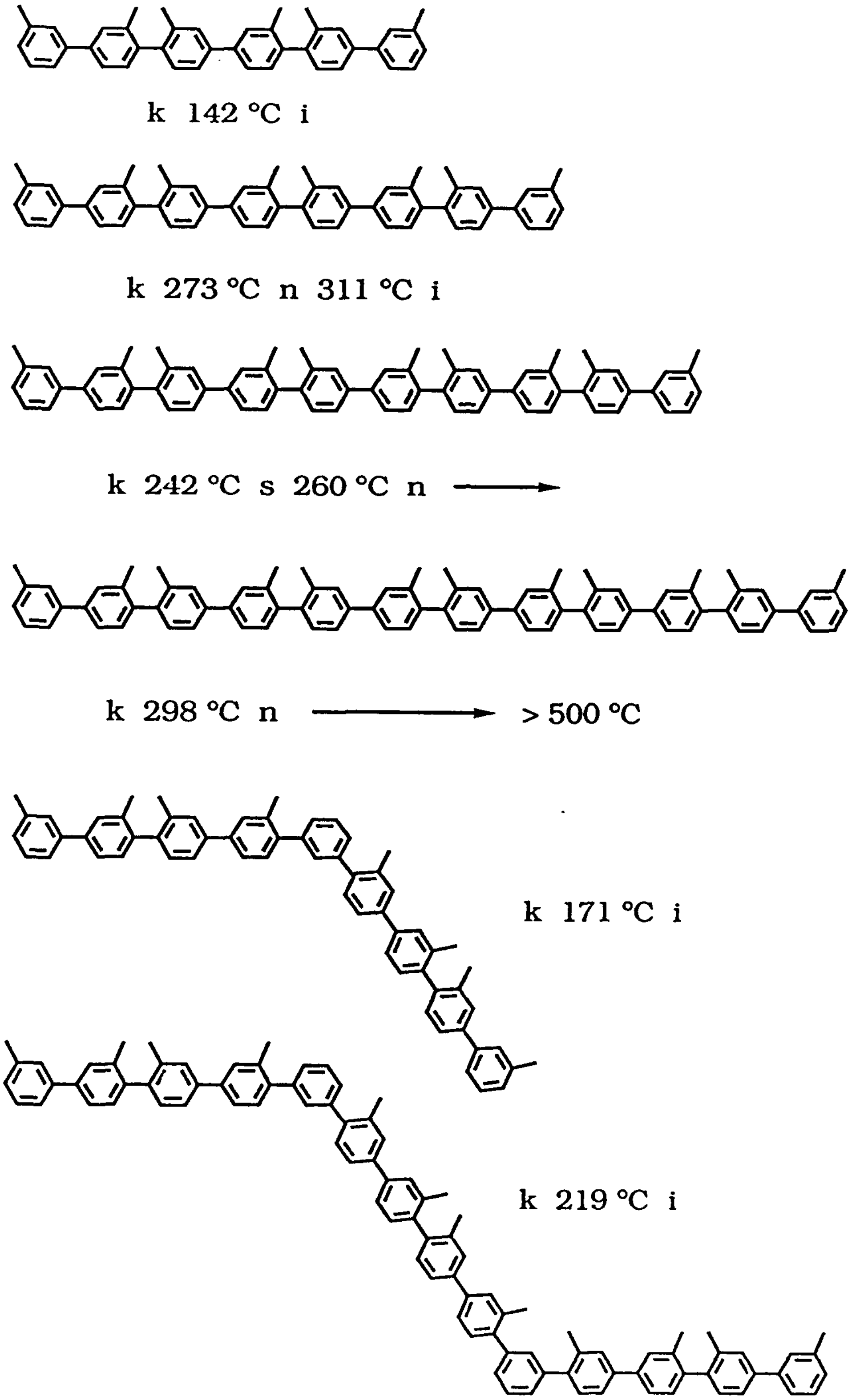


Figure 37



k 142 °C i

k 273 °C n 311 °C i

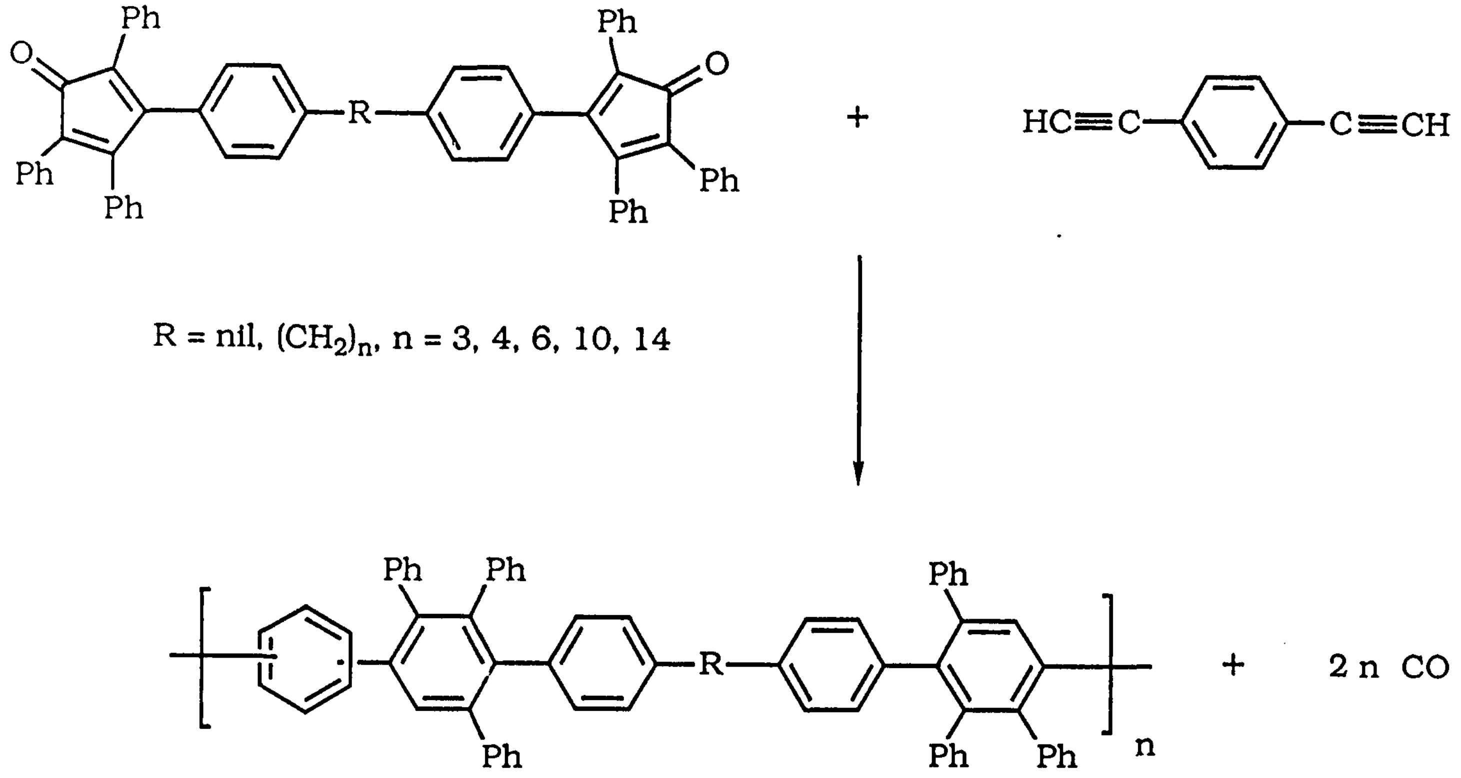
k 242 °C s 260 °C n ⟶

k 298 °C n ⟶ > 500 °C

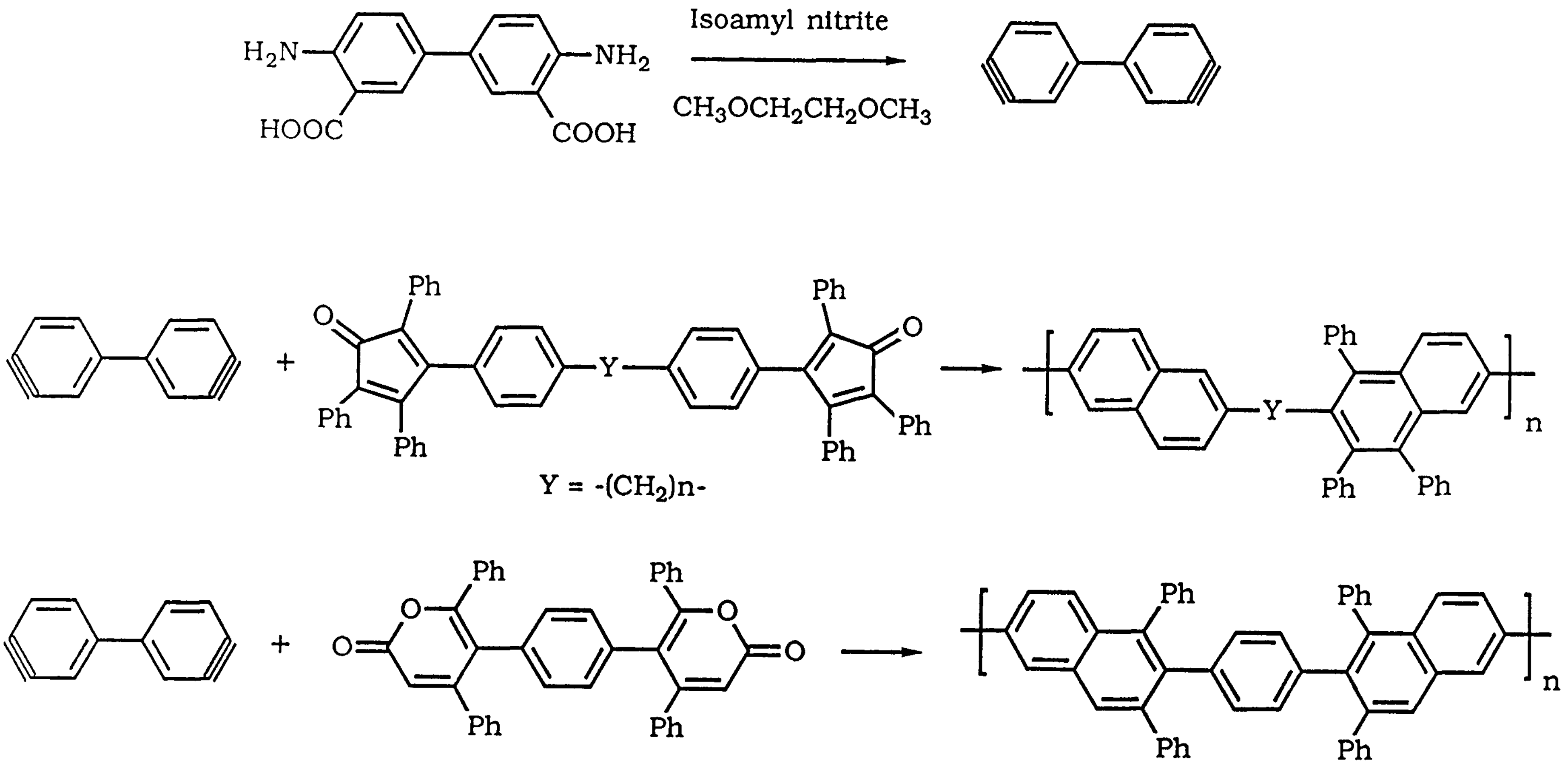
k 171 °C i

k 219 °C i

Scheme 1

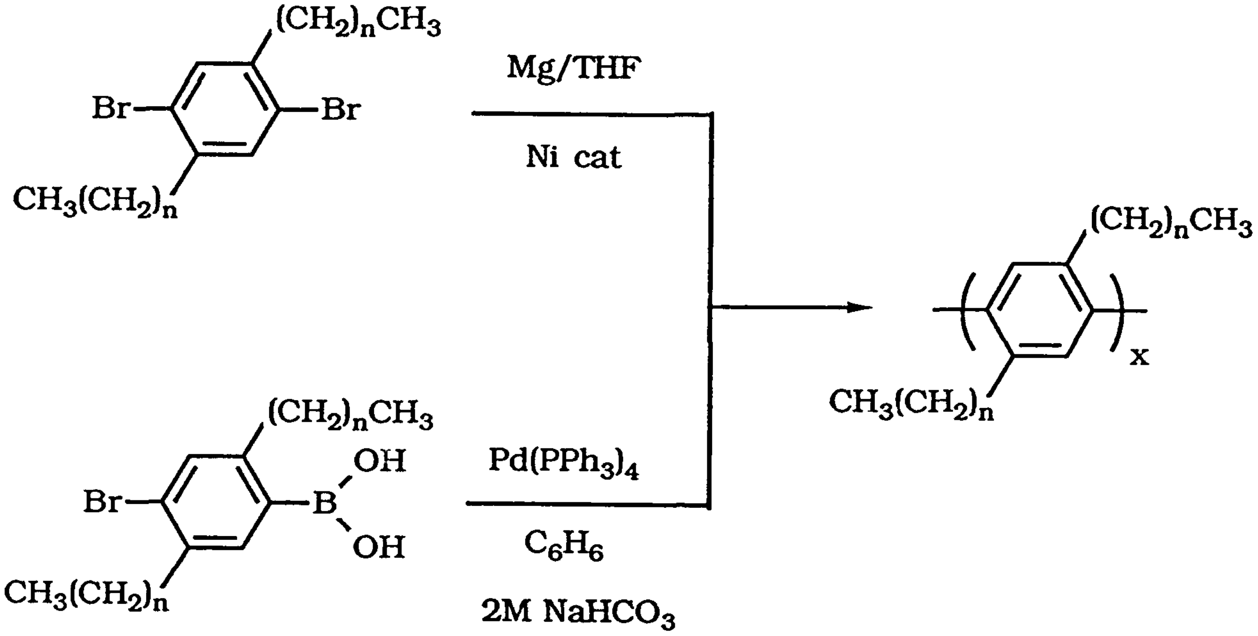

Ph
O
Ph
Ph
R
Ph
O
Ph
Ph
+
HC≡C
C≡CH
R = nil, (CH2)n, n = 3, 4, 6, 10, 14
Ph
Ph
Ph
R
Ph
Ph
Ph
n
+
2 n CO

Scheme 2

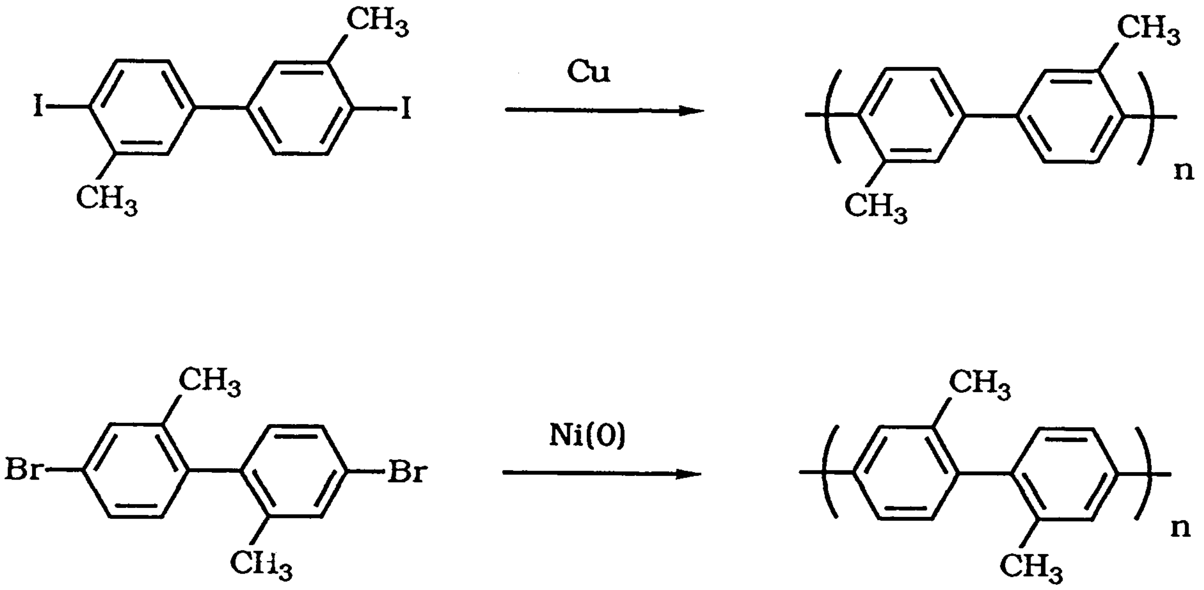


Isoamyl nitrite
$CH_3OCH_2CH_2OCH_3$
H_2N
NH_2
HOOC
COOH
Ph
O
Y
$Y = -(CH_2)n-$
n

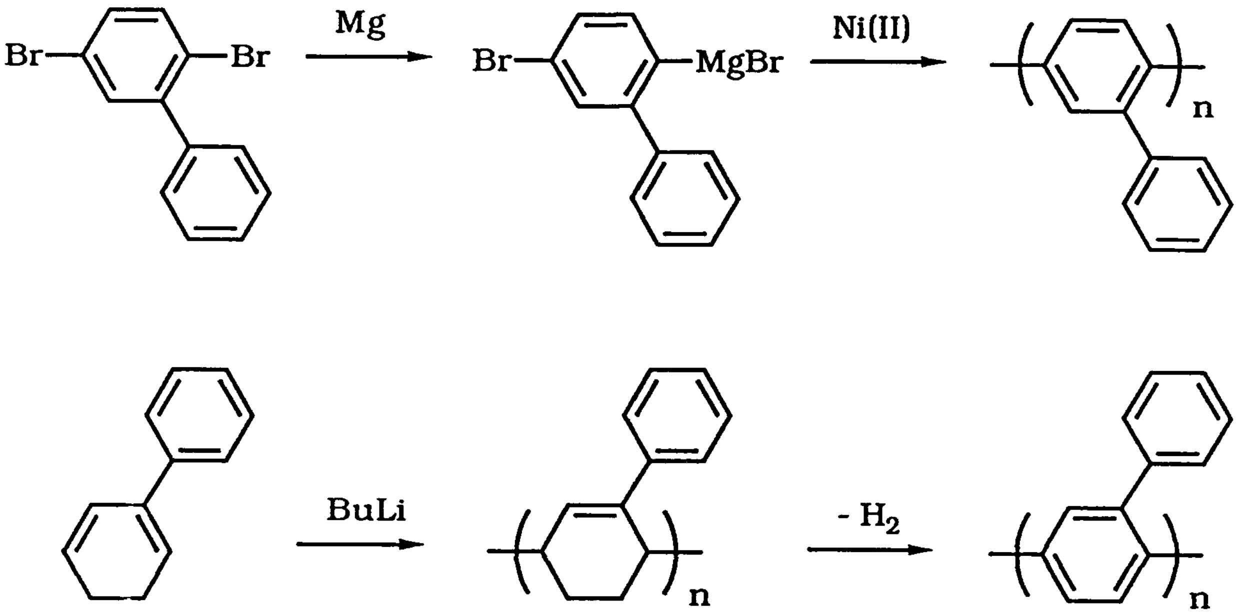
Scheme 3


(CH2)nCH3
Br
Br
CH3(CH2)n
Mg/THF
Ni cat
(CH2)nCH3
OH
B
OH
Br
CH3(CH2)n
Pd(PPh3)4
C6H6
2M NaHCO3
(CH2)nCH3
x
CH3(CH2)n

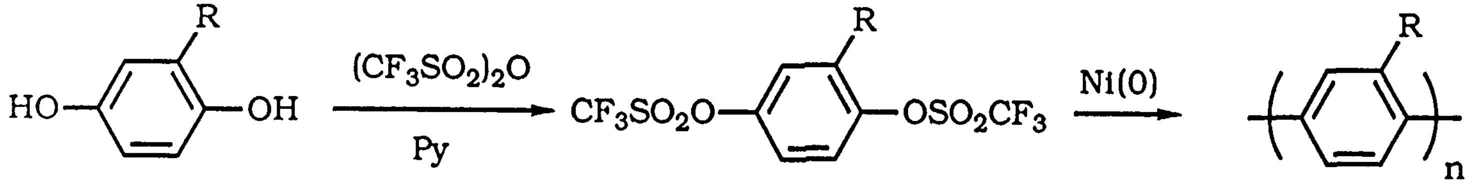
Scheme 4



Scheme 5

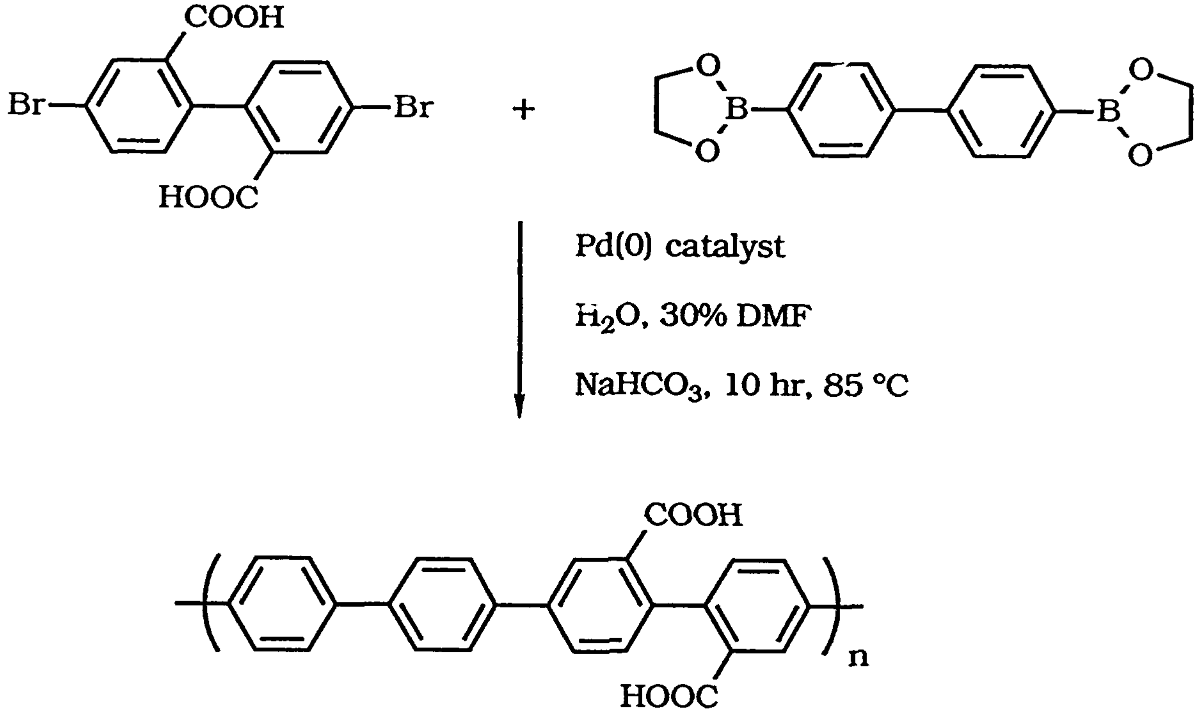


Scheme 6

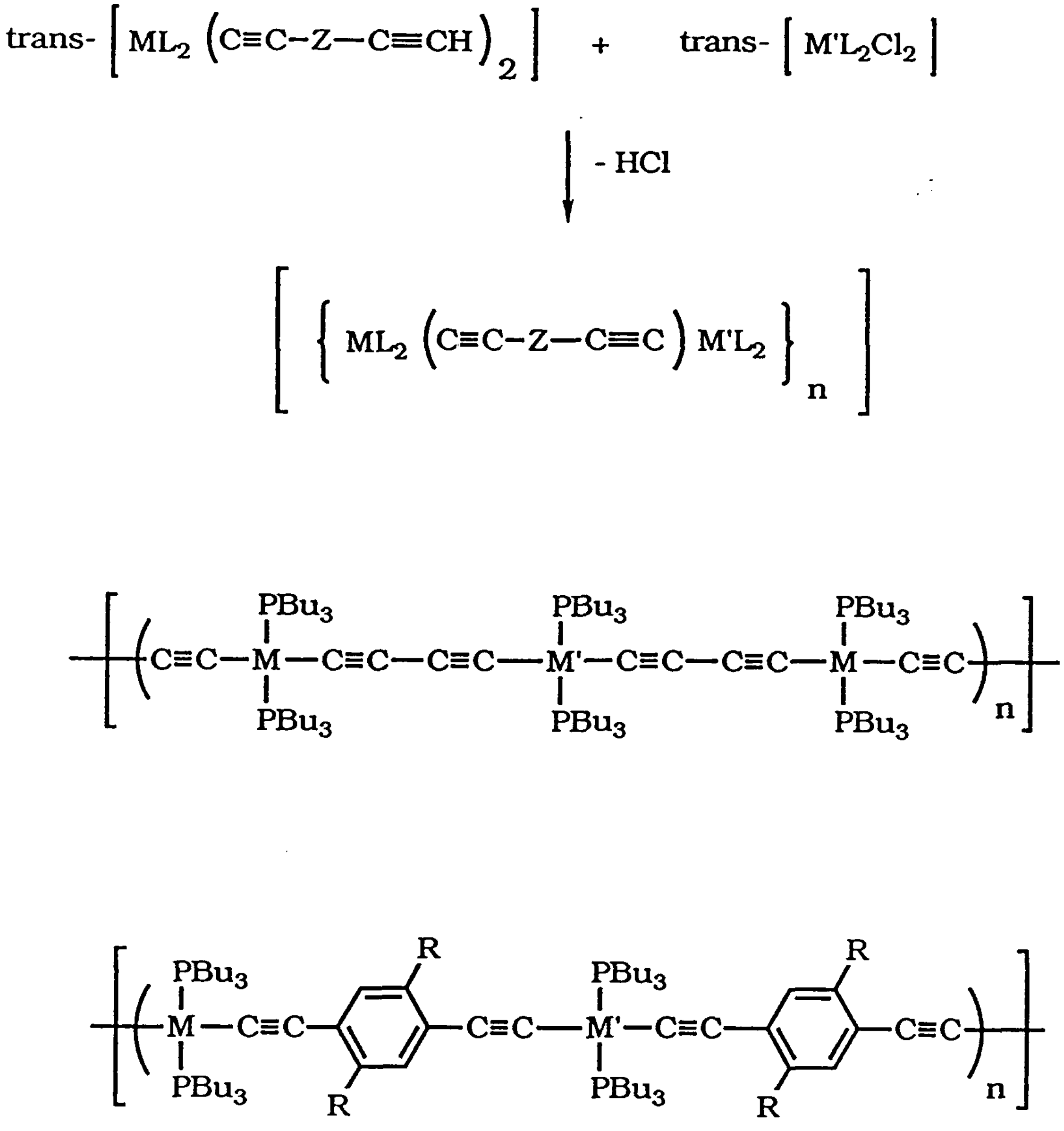


R = Ph, t-Bu, $-COOC_2H_5$ etc.

Scheme 7

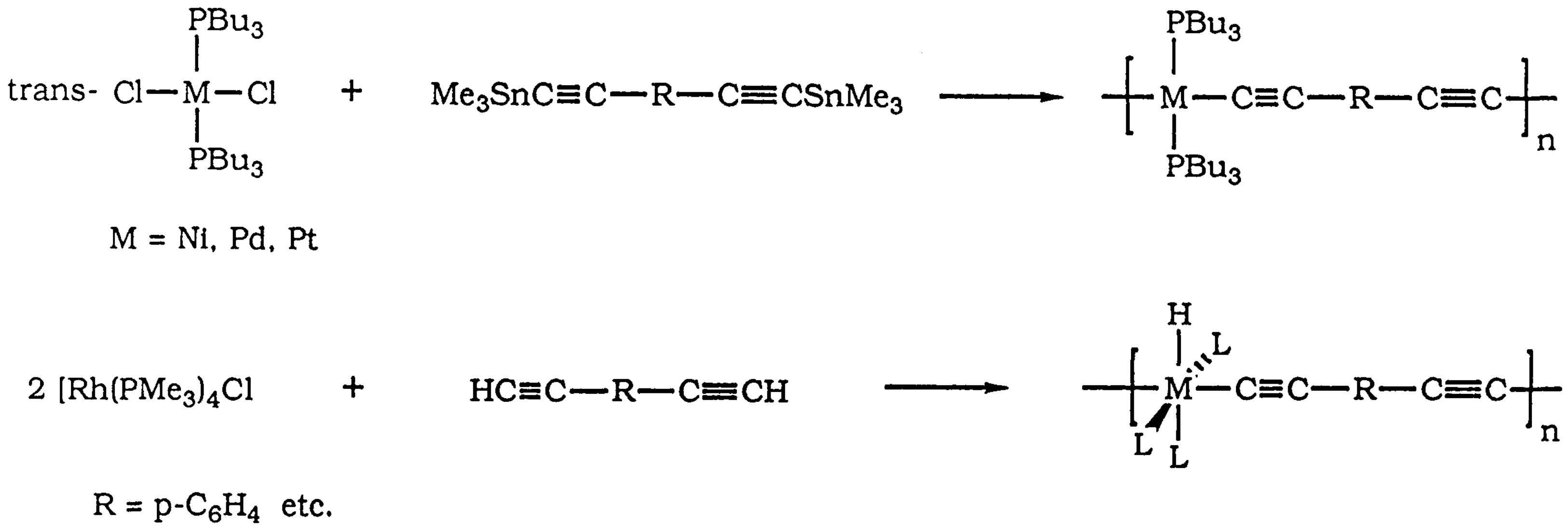

COOH
Br
Br
HOOC
+
O
B
O
B
O
O
Pd(0) catalyst
H2O, 30% DMF
NaHCO3, 10 hr, 85 °C
COOH
HOOC
n

Scheme 8



$R = H, CH_3, C_2H_5$

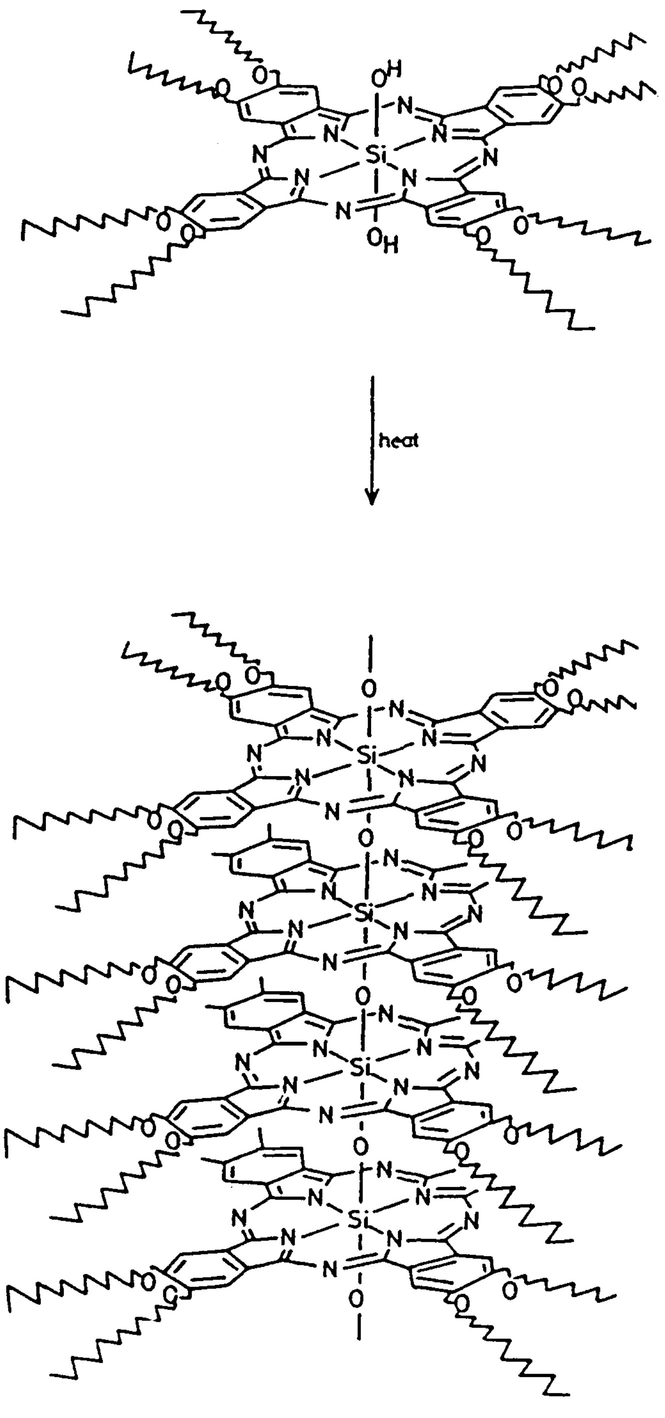
Scheme 9



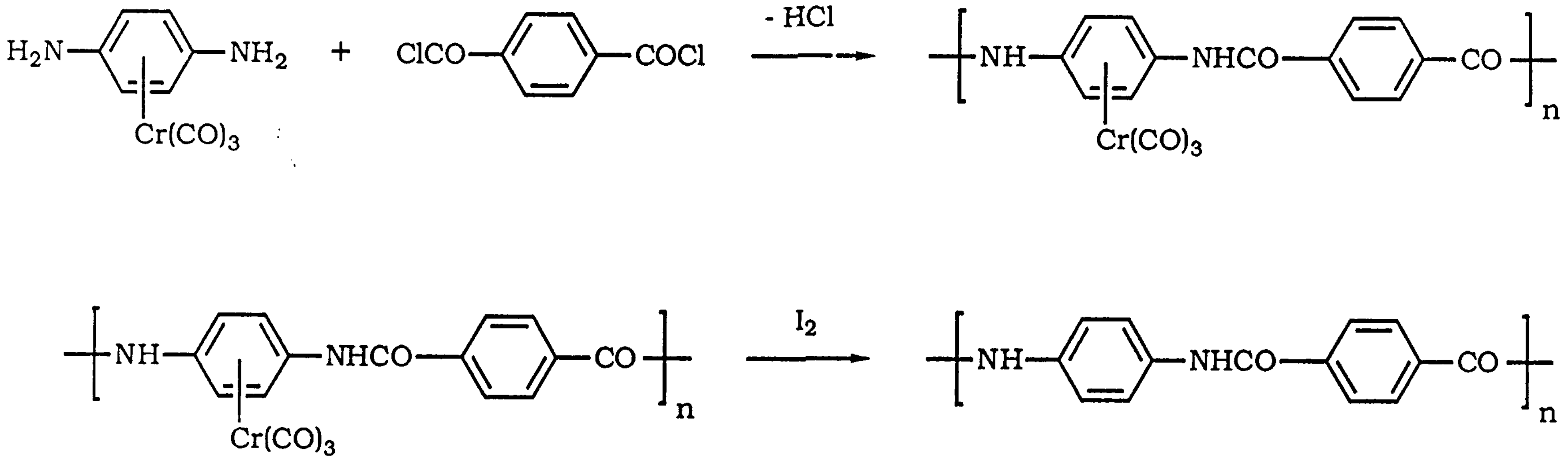
M = Ni, Pd, Pt

R = p-C_6H_4 etc.

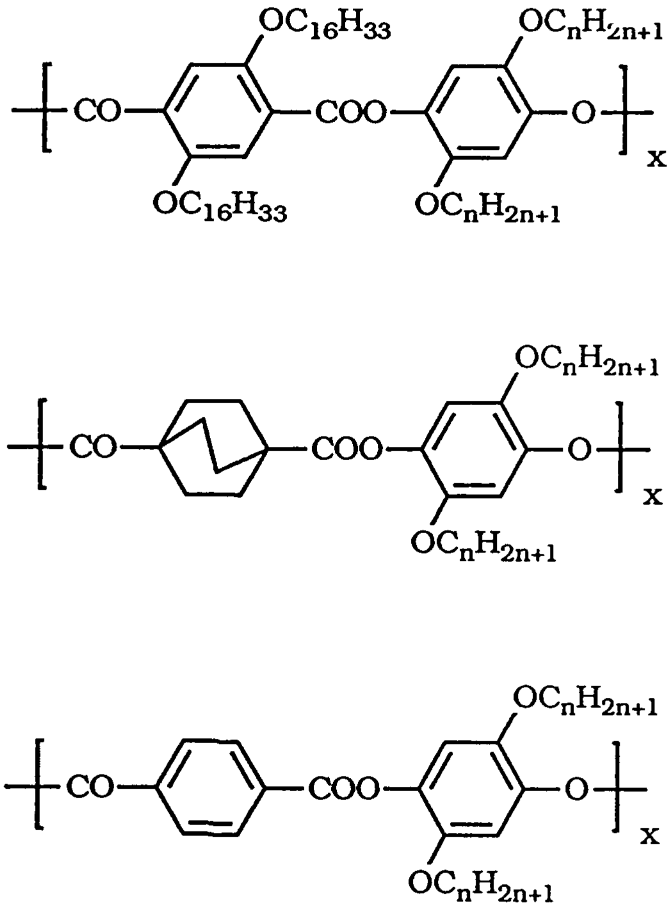
Scheme 10



Scheme 11



Scheme 12

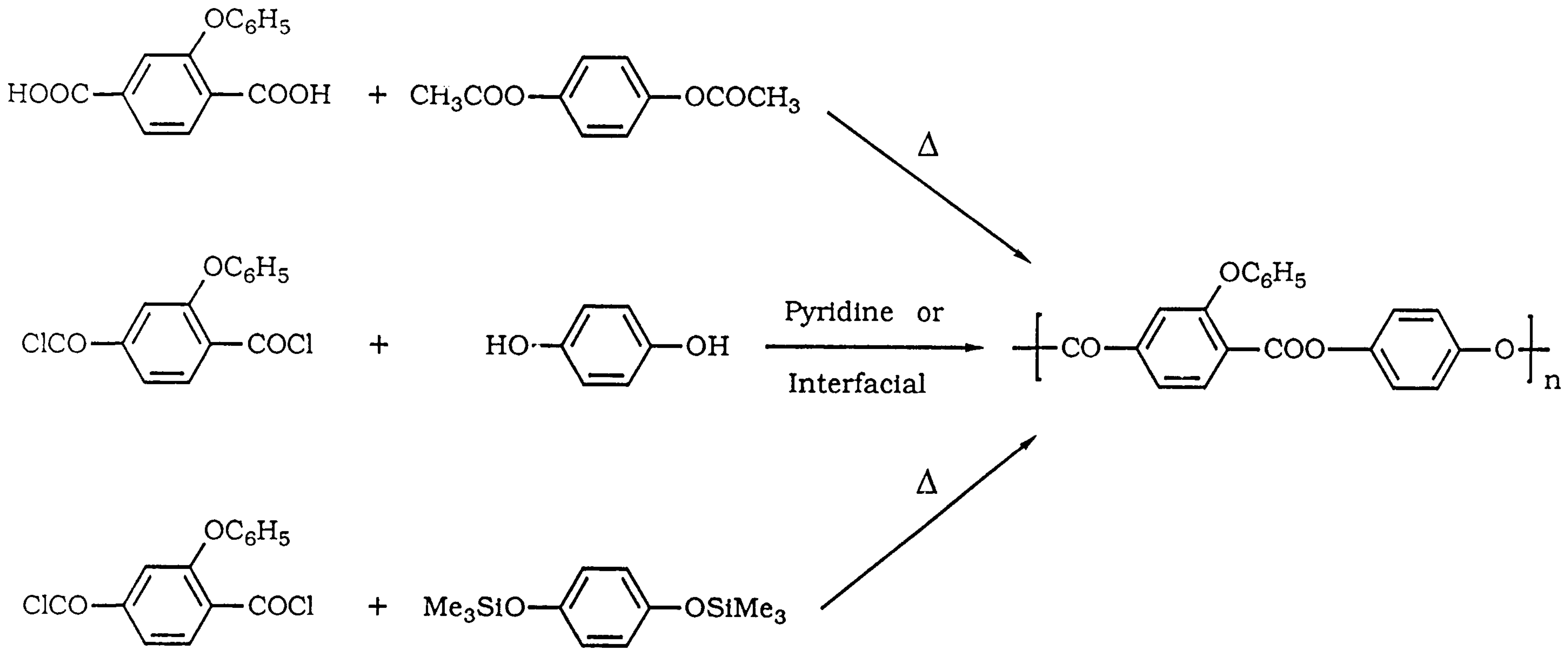


PTA16HQ-n

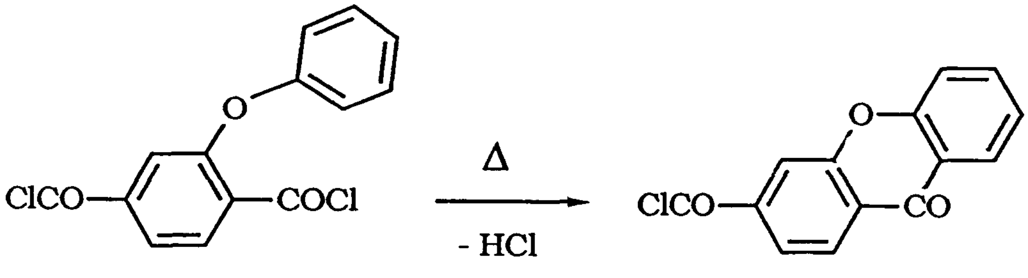
PBCOHQ-n

PTAHQ-n

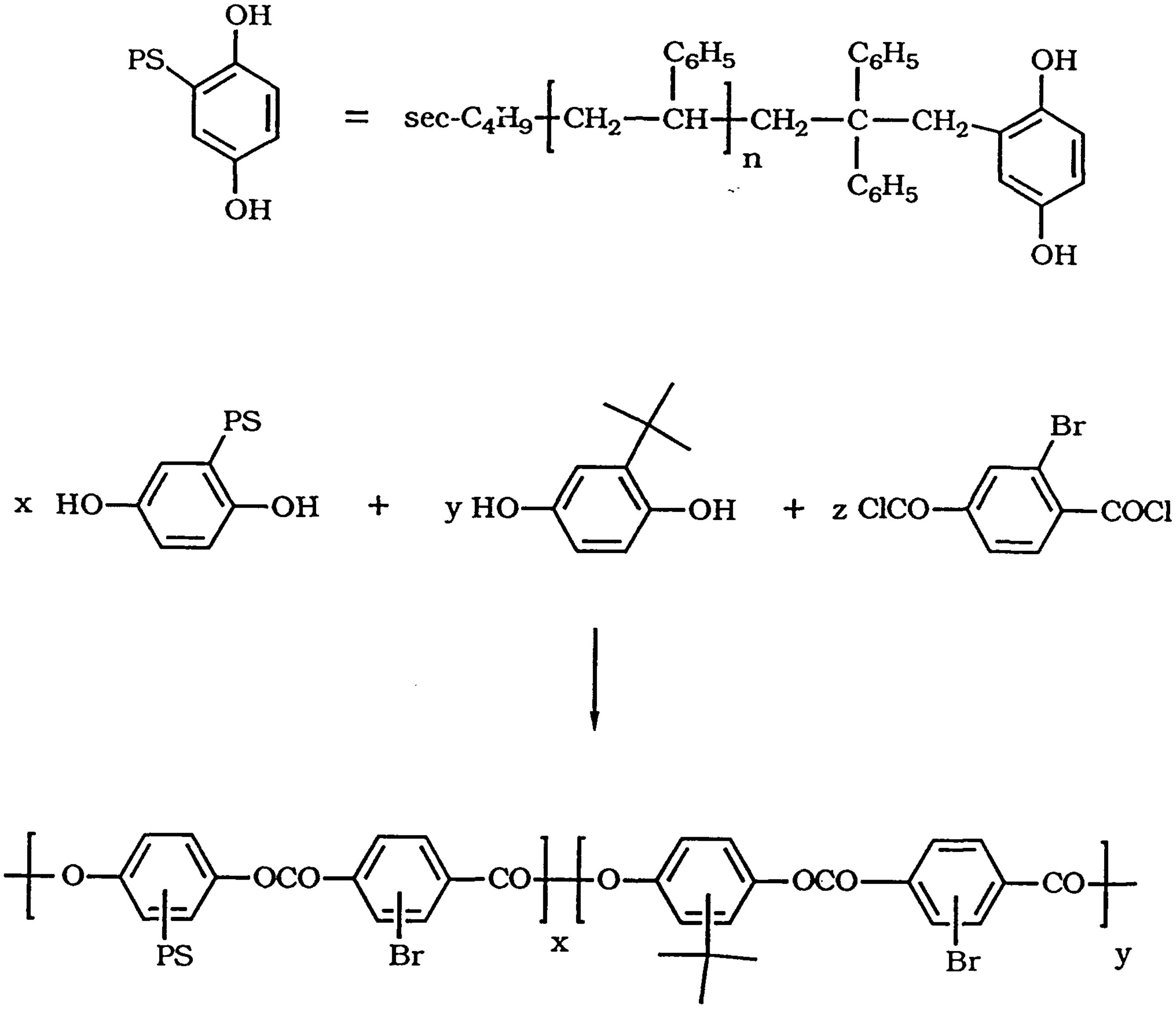
Scheme 13


HOOC
COOH
OC_6H_5
+
CH_3COO
$OCOCH_3$
Δ
ClCO
COCl
OC_6H_5
+
HO
OH
Pyridine or
Interfacial
ClCO
COCl
OC_6H_5
+
Me_3SiO
$OSiMe_3$
Δ
CO
COO
OC_6H_5
O
n

Scheme 14

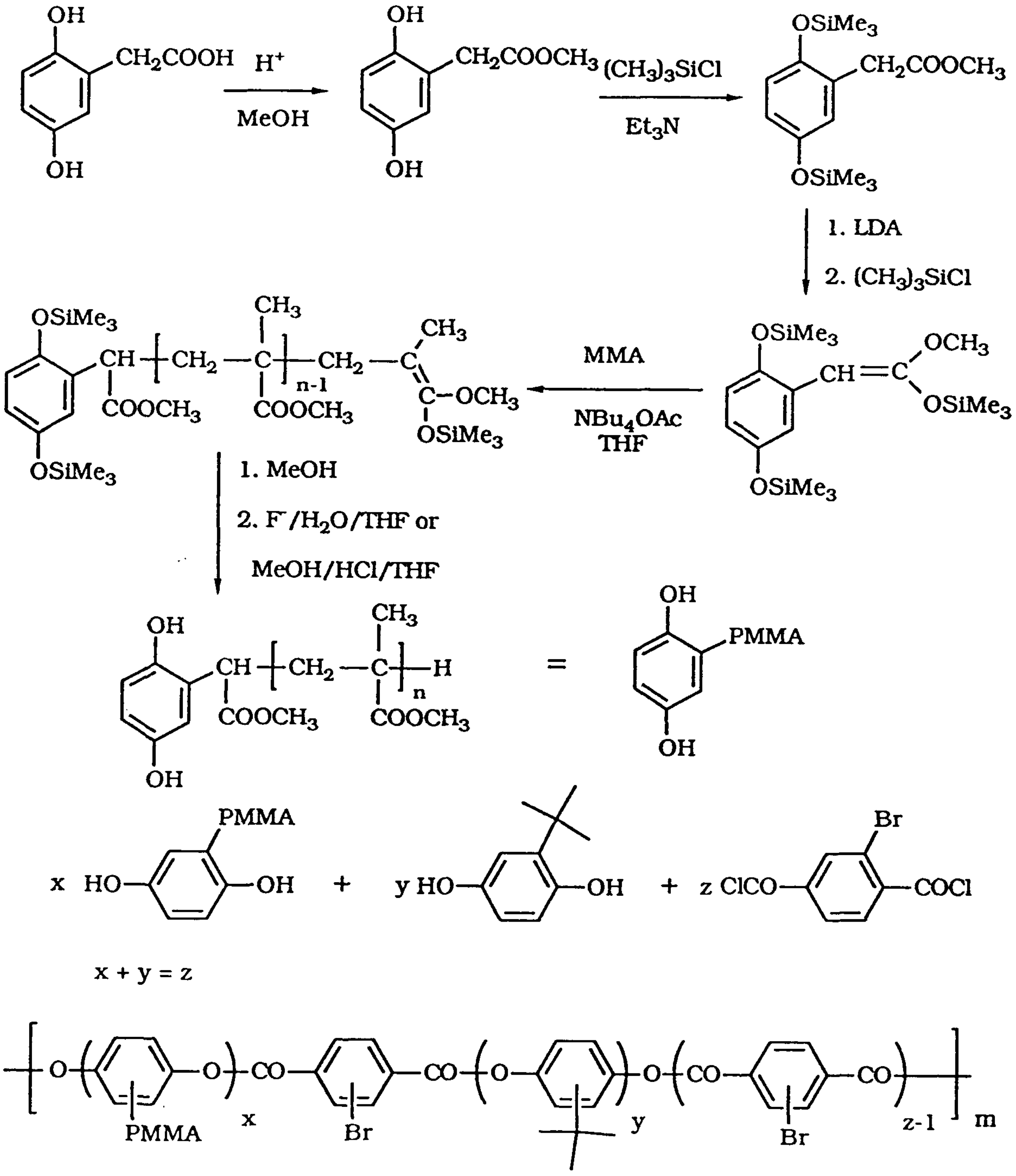


Scheme 15

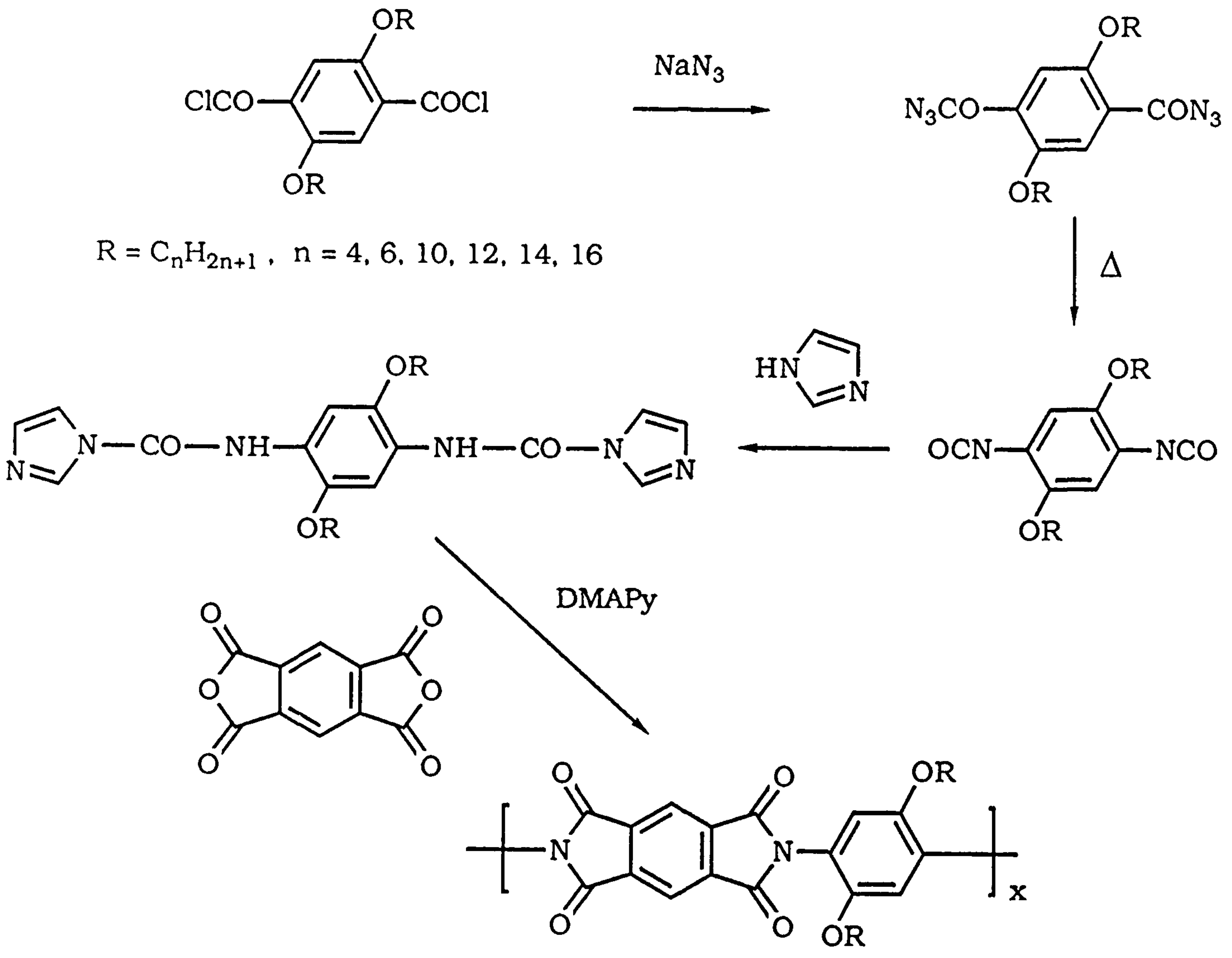


x + y = z

Scheme 16

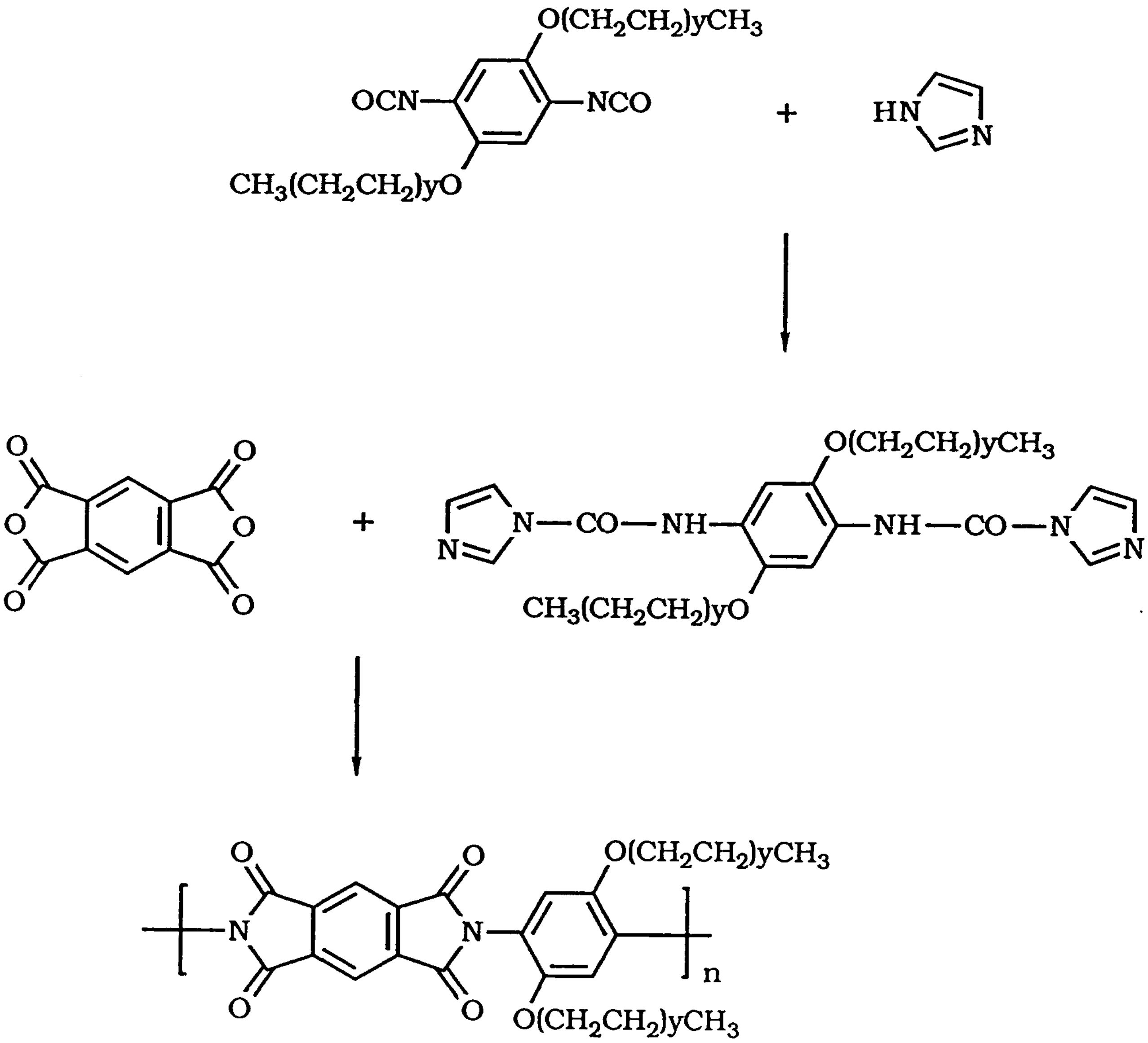

OH
CH2COOH
H+
MeOH
OH
CH2COOCH3
(CH3)3SiCl
Et3N
OSiMe3
CH2COOCH3
OSiMe3
1. LDA
2. (CH3)3SiCl
OSiMe3
OCH3
CH=C
OSiMe3
OSiMe3
MMA
NBu4OAc
THF
OSiMe3
CH3
CH
CH2
C
n-1
CH2
C
C-OCH3
COOCH3
COOCH3
OSiMe3
OSiMe3
1. MeOH
2. F-/H2O/THF or
MeOH/HCl/THF
OH
CH3
CH
CH2
C
H
n
COOCH3
COOCH3
OH
=
OH
PMMA
OH
PMMA
x HO
OH
+
y HO
OH
+
z ClCO
COCl
Br
x + y = z
O
O
CO
CO
O
O
CO
CO
PMMA
x
Br
y
Br
z-1
m

Scheme 17

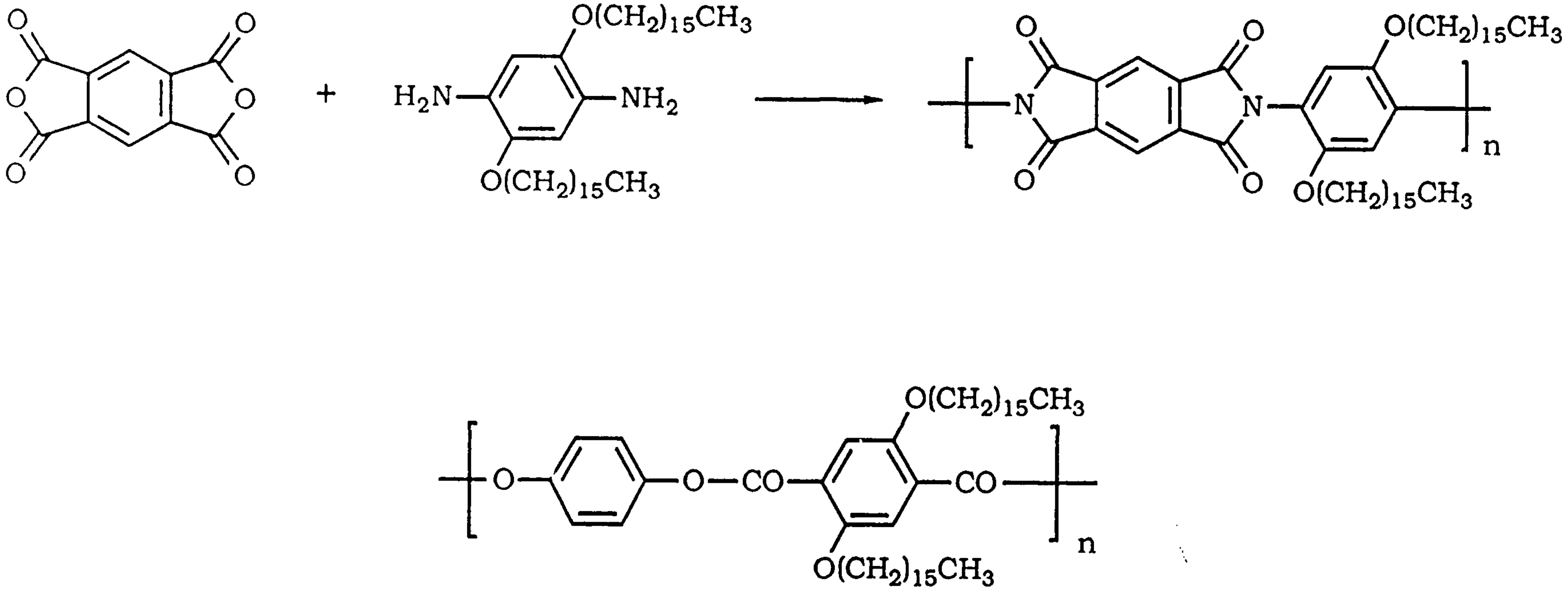


ClCO
COCl
OR
OR
$R = C_nH_{2n+1}$, n = 4, 6, 10, 12, 14, 16
NaN_3
N_3CO
CON_3
Δ
OCN
NCO
HN
N
NH—CO—N
N—CO—NH
DMAPy
O
N
x

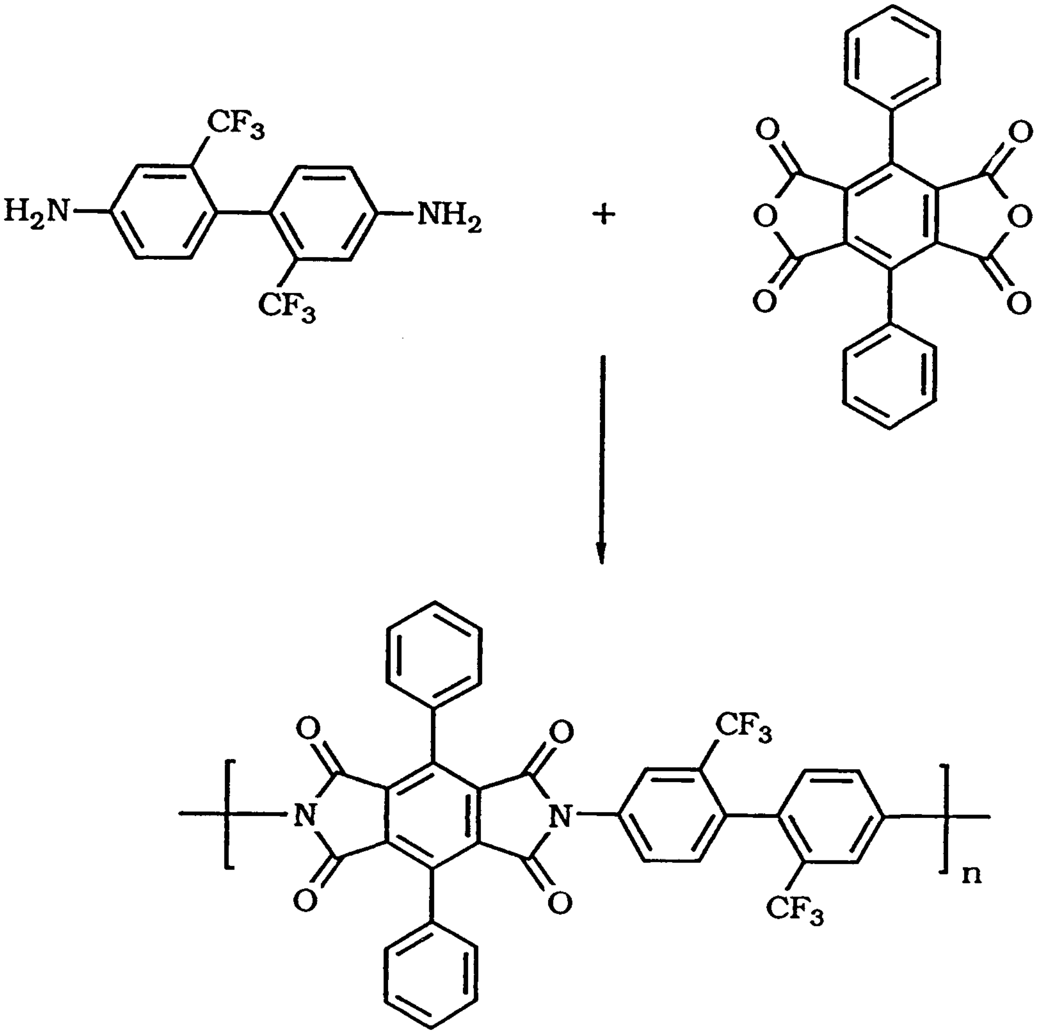
Scheme 18


O(CH2CH2)yCH3
OCN
NCO
CH3(CH2CH2)yO
+
HN
N
O
O
O
O
O
O
+
N
N—CO—NH
NH—CO—N
N
O(CH2CH2)yCH3
CH3(CH2CH2)yO
O
O
N
N
O
O
O(CH2CH2)yCH3
O(CH2CH2)yCH3
n

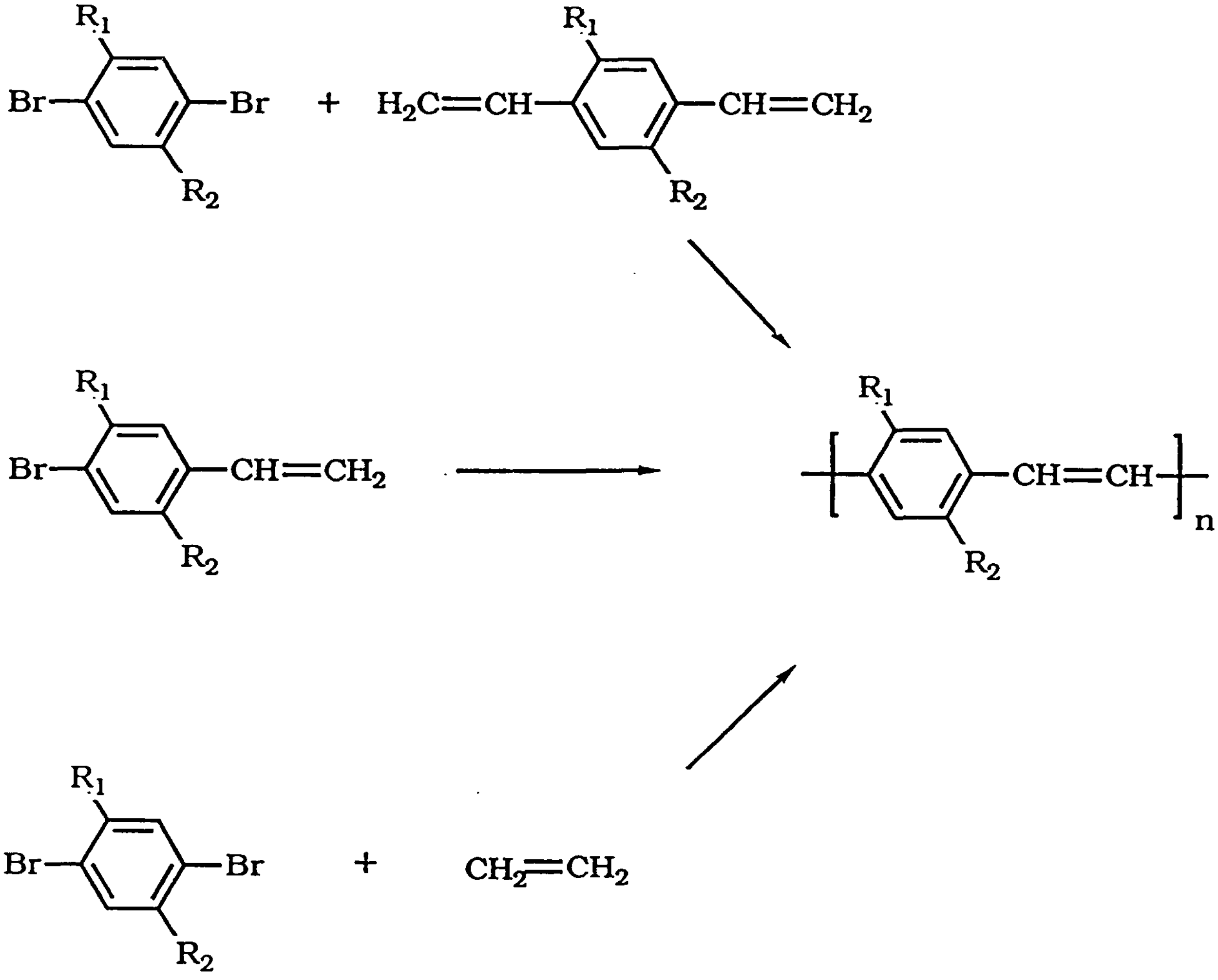
Scheme 19



Scheme 20

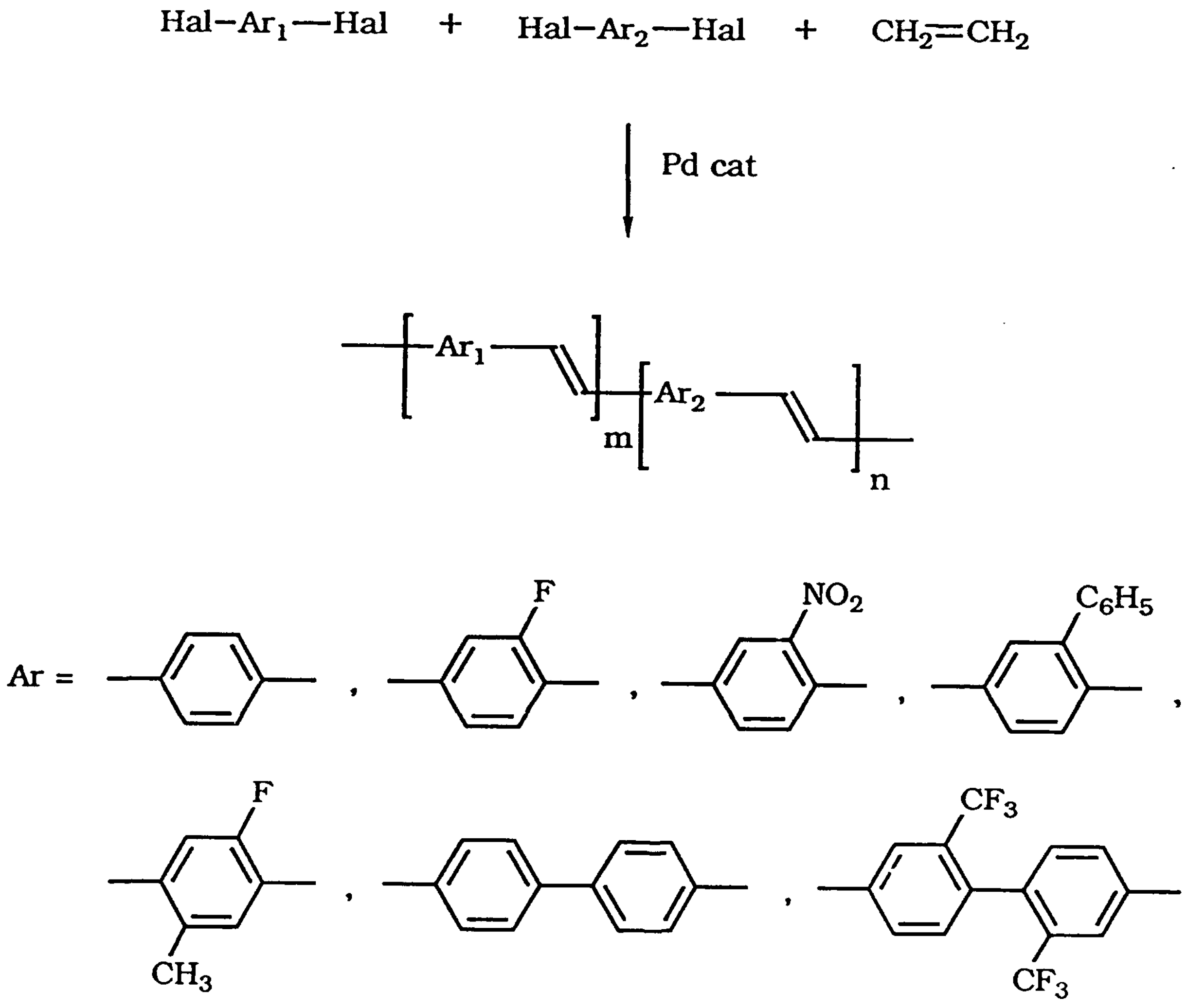


Scheme 21

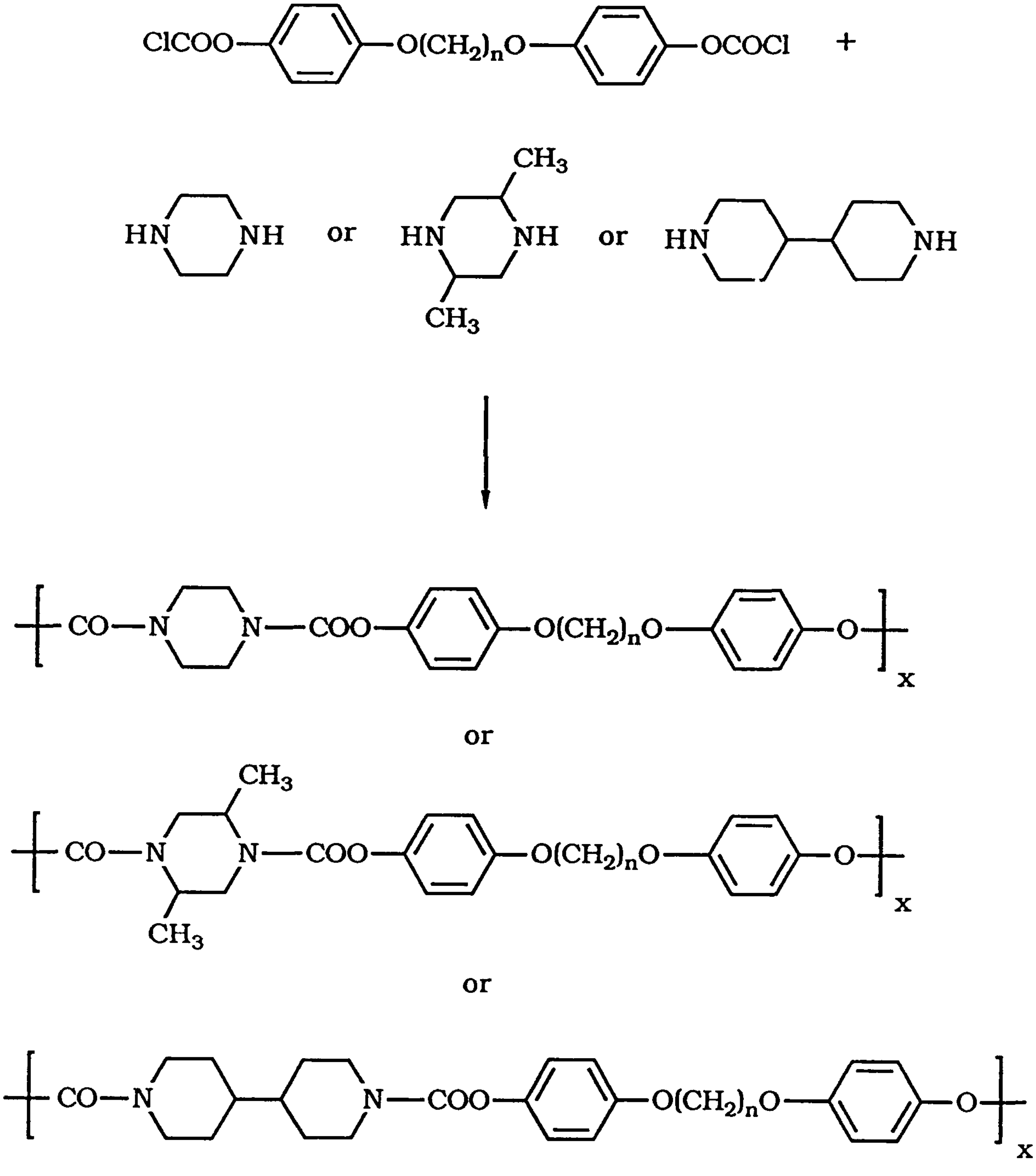


$R_1 = R_2 = H$; $R_1 = H$, $R_2 = CH_3$, CF_3 or C_6H_5 ; $R_1 = R_2 = CH_3$

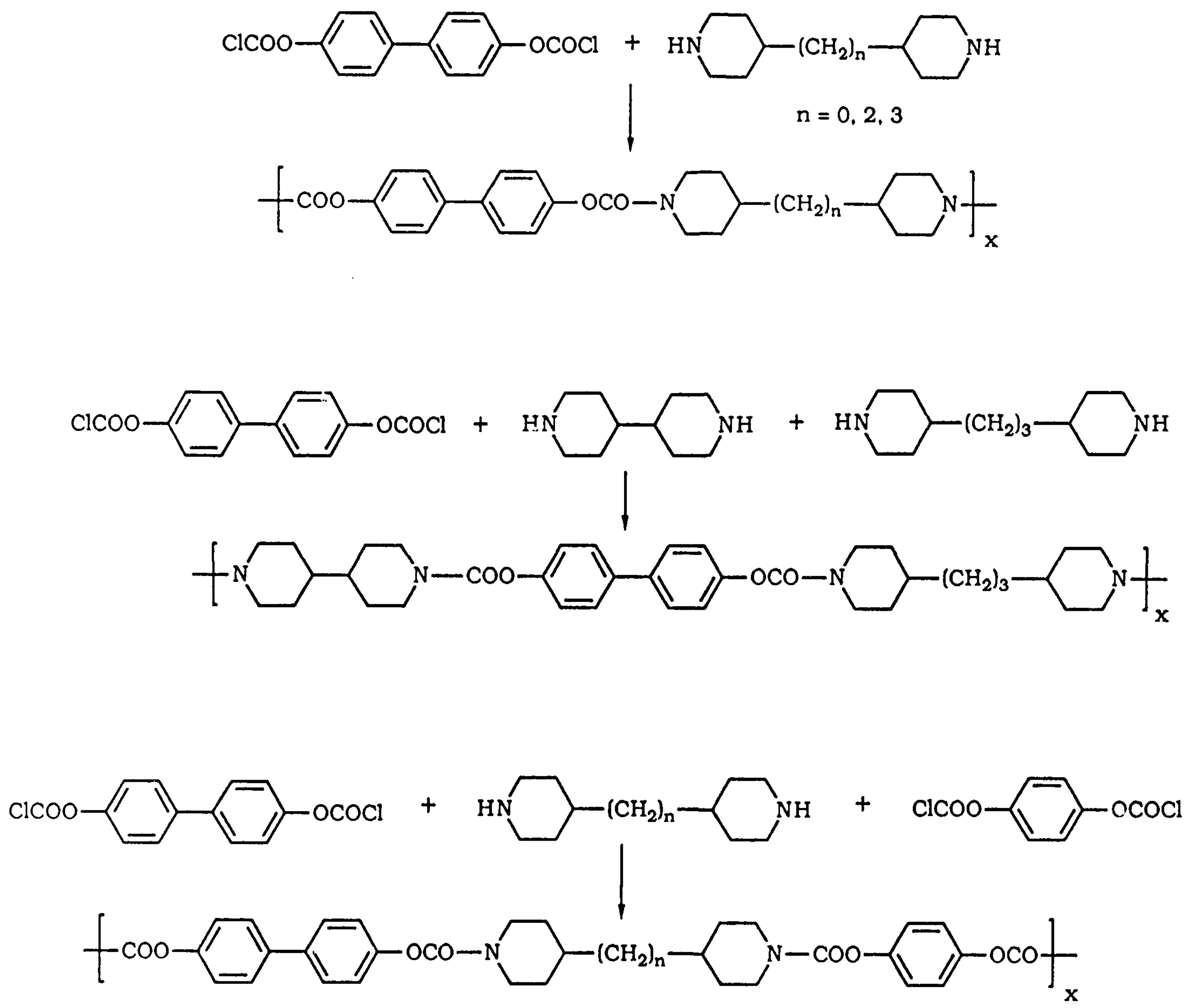
Scheme 22


Hal–Ar1—Hal + Hal–Ar2—Hal + CH2=CH2
Pd cat
Ar1
m
Ar2
n
Ar =
F
NO2
C6H5
F
CH3
CF3
CF3

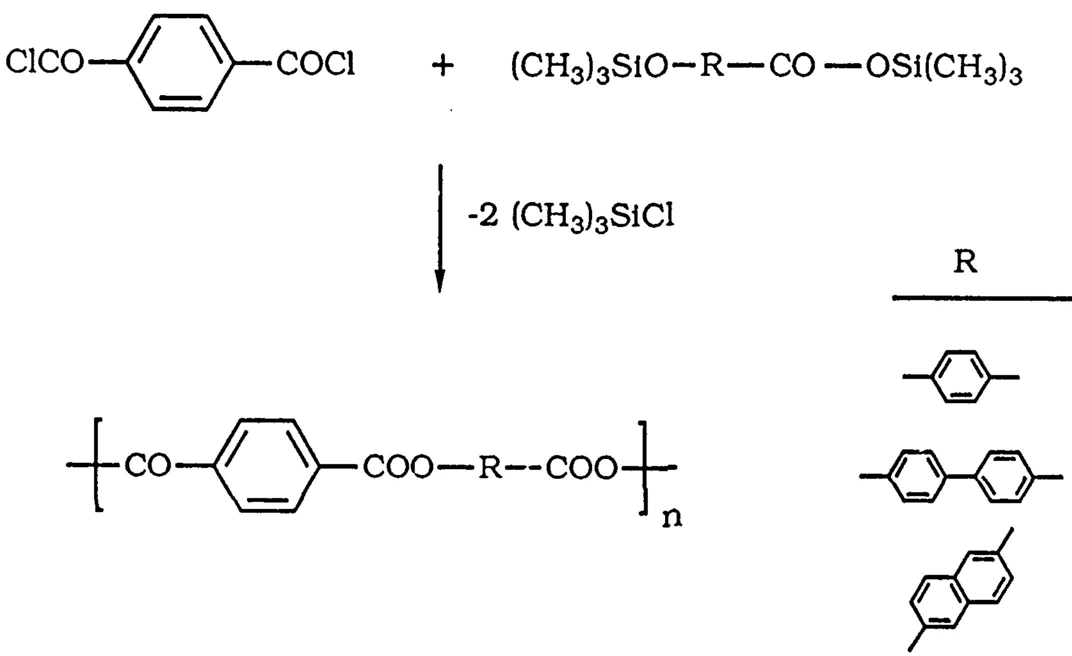
Scheme 23



Scheme 24

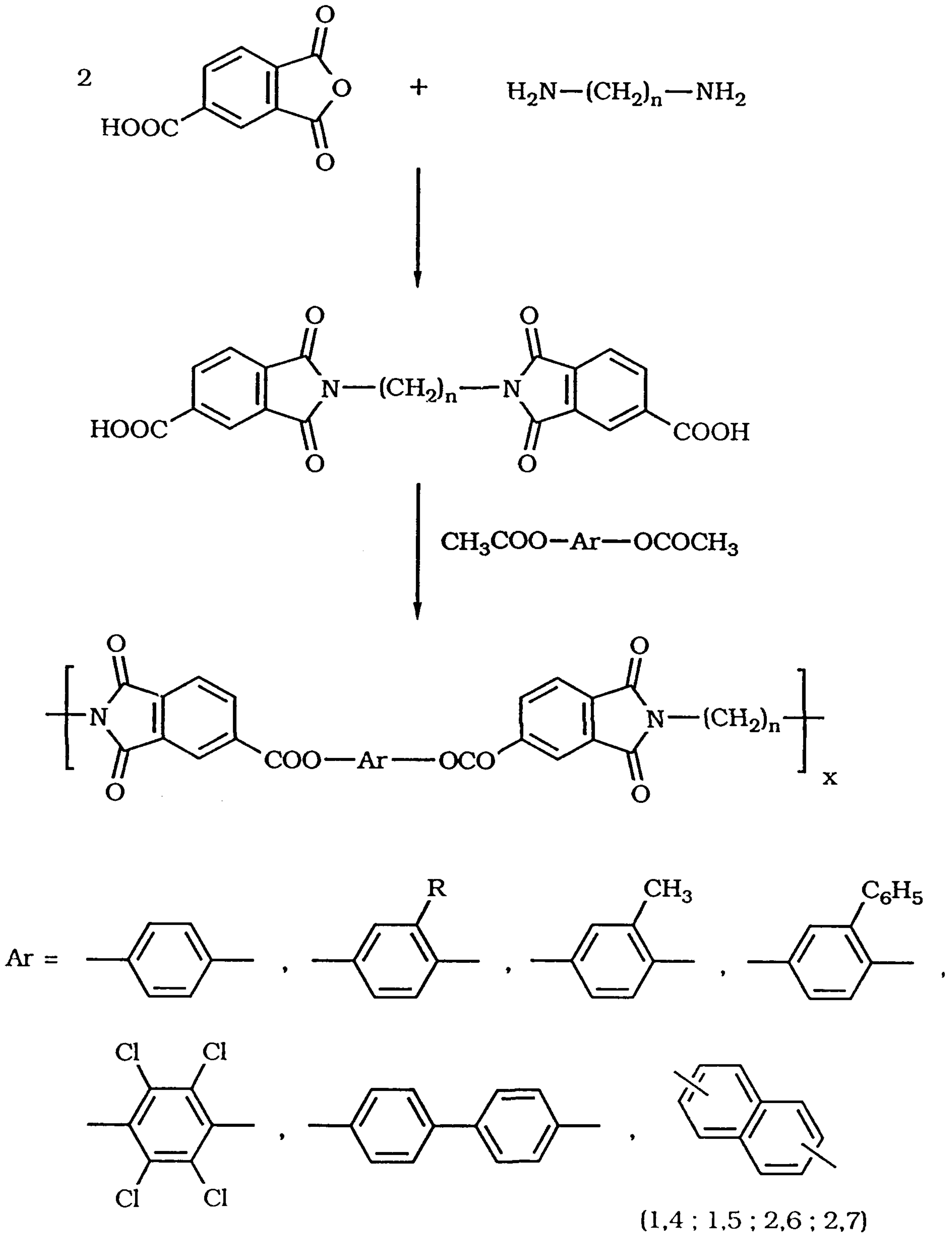

ClCOO
OCOCl
+
HN
$(CH_2)_n$
NH
n = 0, 2, 3
COO
OCO
N
x
ClCOO
OCOCl
+
HN
NH
+
HN
$(CH_2)_3$
NH
N
COO
OCO
N
$(CH_2)_3$
N
x
ClCOO
OCOCl
+
HN
$(CH_2)_n$
NH
+
ClCOO
OCOCl
COO
OCO
N
$(CH_2)_n$
N
COO
OCO
x

Scheme 25

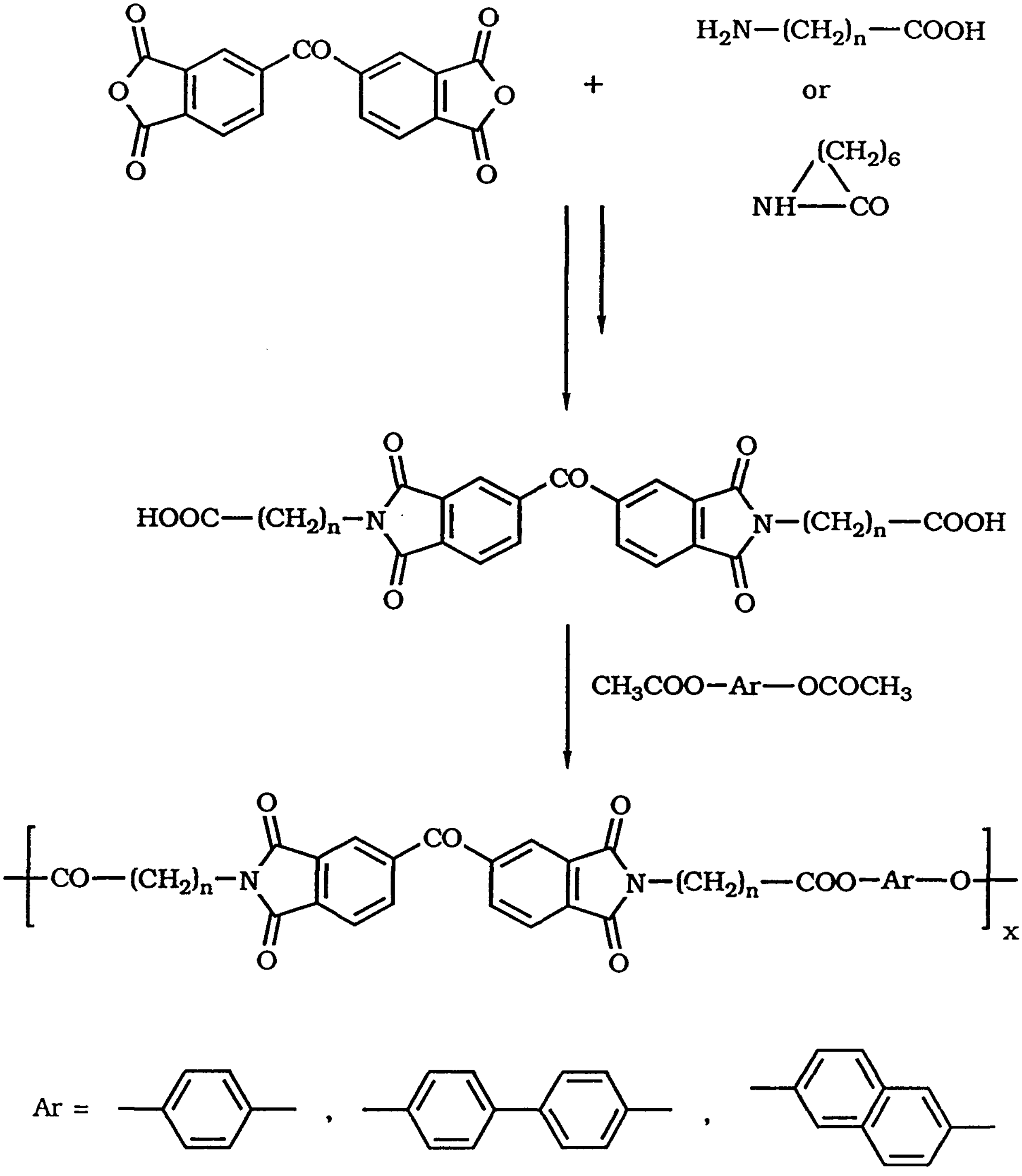


R	T_g(°C)	T_i(°C)
	136	360
	160	450
	162	440

Scheme 26

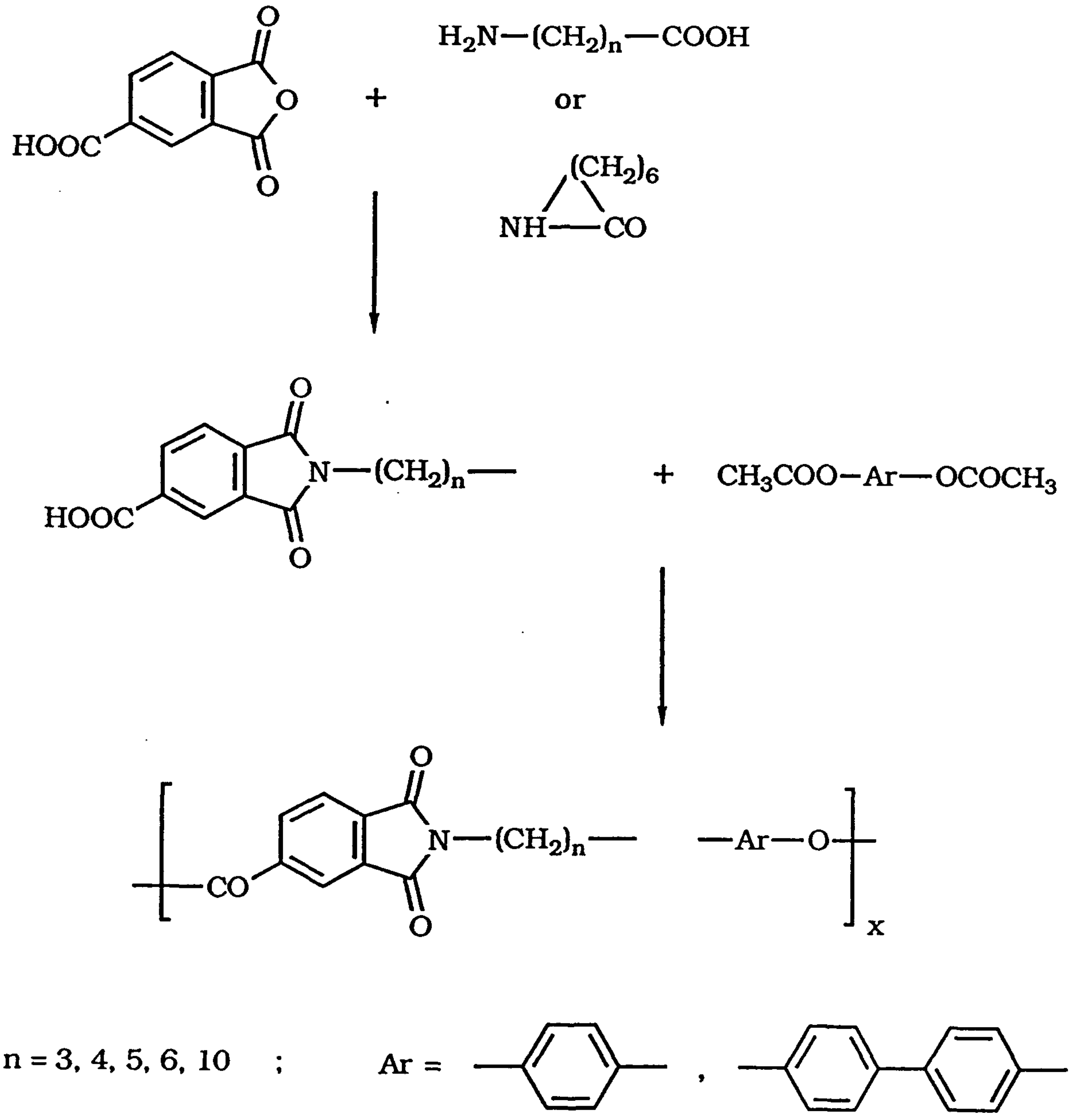

2
HOOC
+
H2N—(CH2)n—NH2
HOOC
N—(CH2)n—N
COOH
CH3COO—Ar—OCOCH3
N
COO—Ar—OCO
N—(CH2)n
x
Ar =
R
CH3
C6H5
Cl
Cl
Cl
Cl
(1,4 ; 1,5 ; 2,6 ; 2,7)

Scheme 27

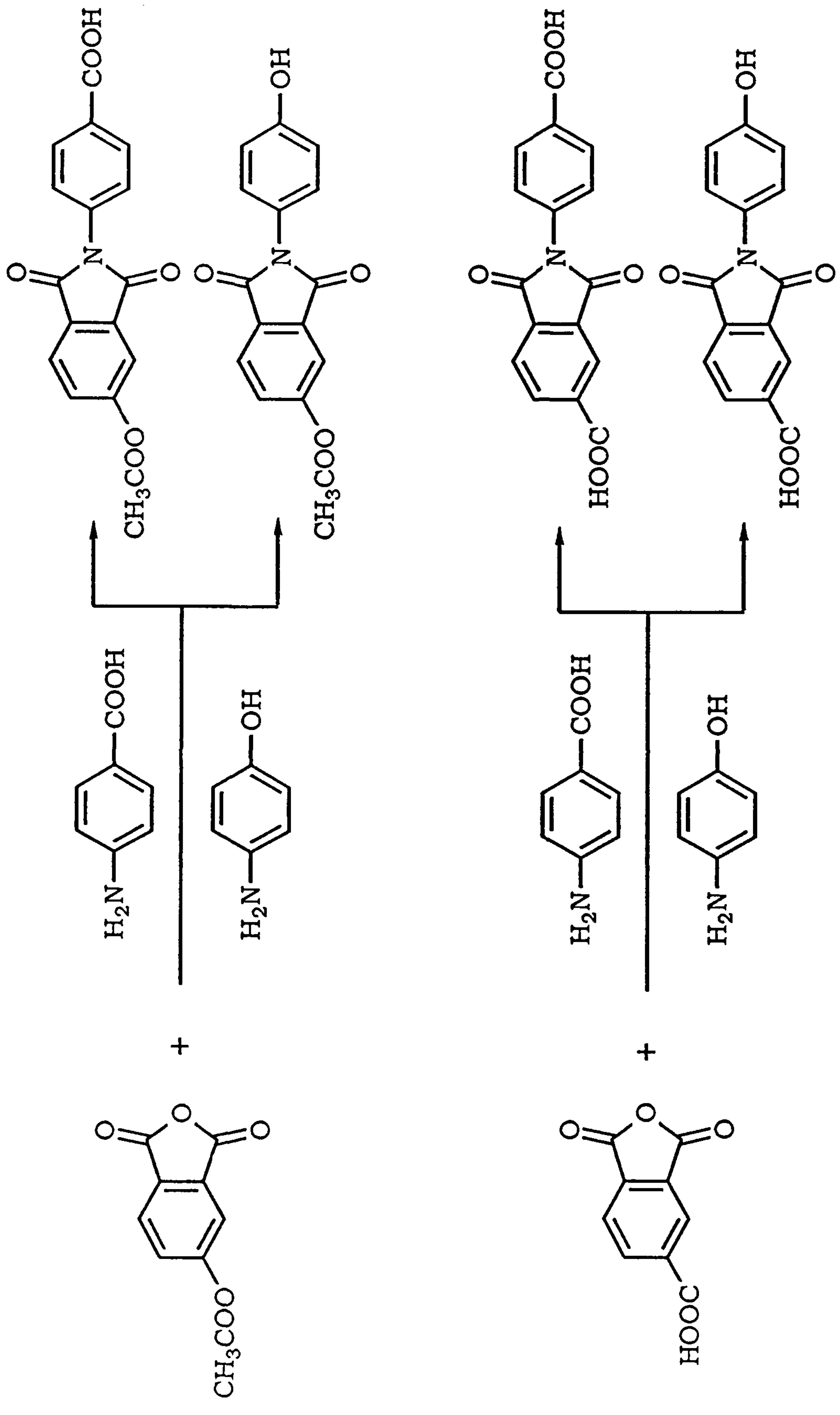


n = 3, 4, 5, 6, 10, 11

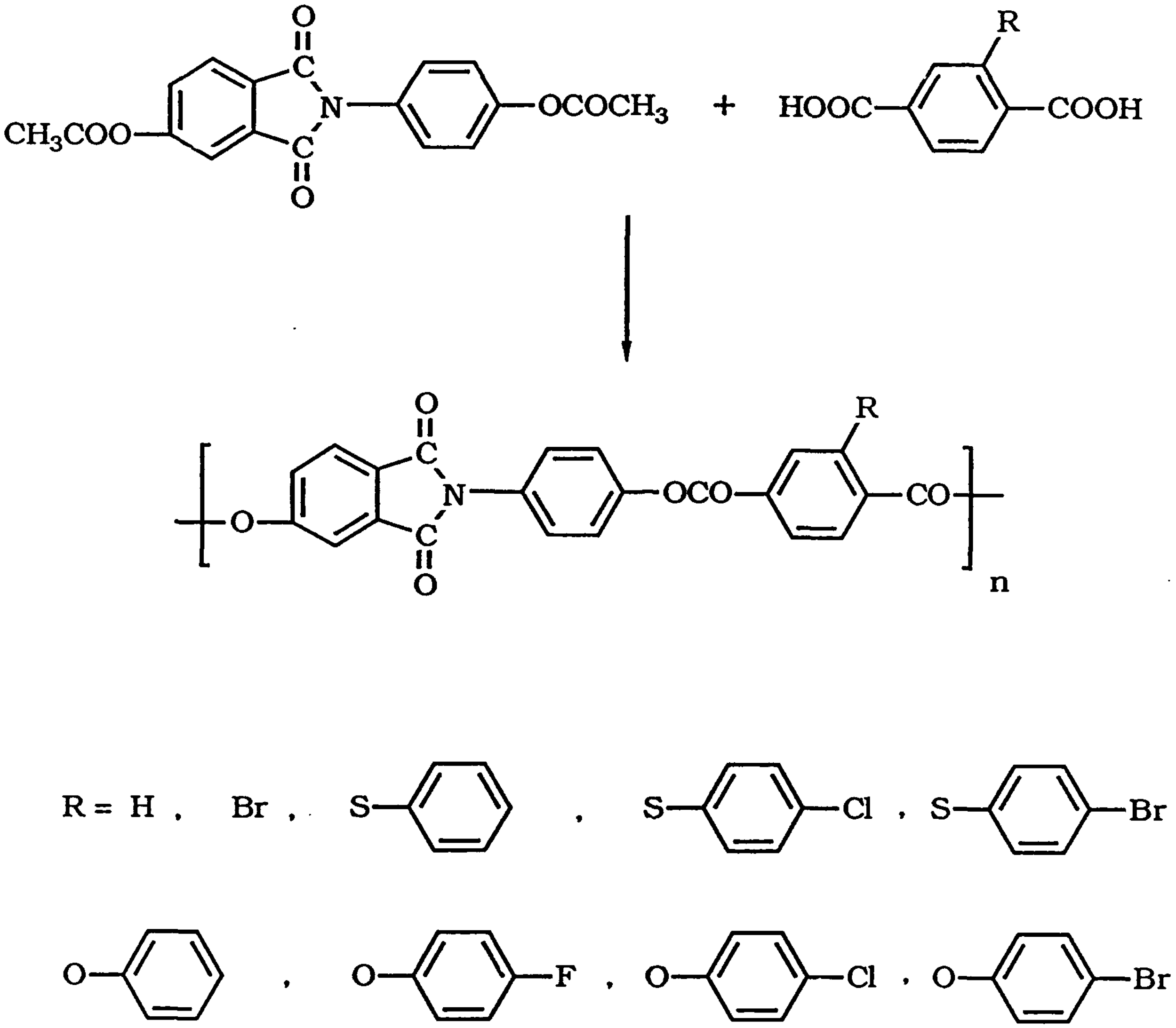
Scheme 28


HOOC
O
O
O
+
$H_2N-(CH_2)_n-COOH$
or
$(CH_2)_6$
NH
CO
HOOC
O
N
$(CH_2)_n$
O
+
$CH_3COO-Ar-OCOCH_3$
CO
O
N
$(CH_2)_n$
O
Ar
O
x
n = 3, 4, 5, 6, 10 ;
Ar =

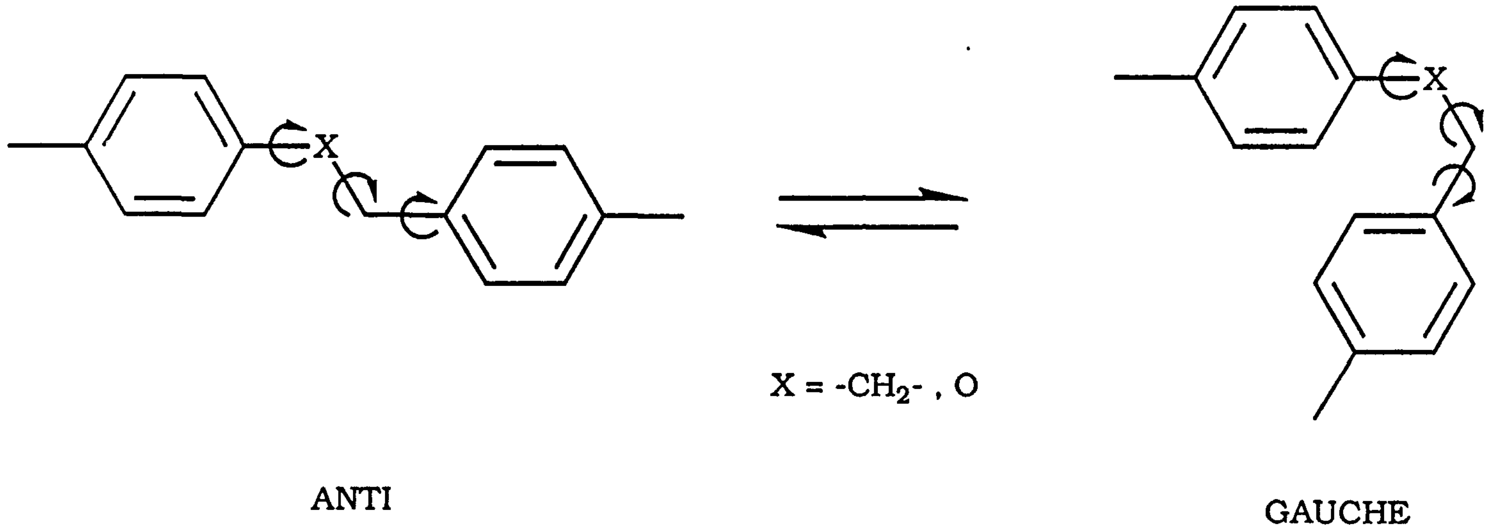
Scheme 29



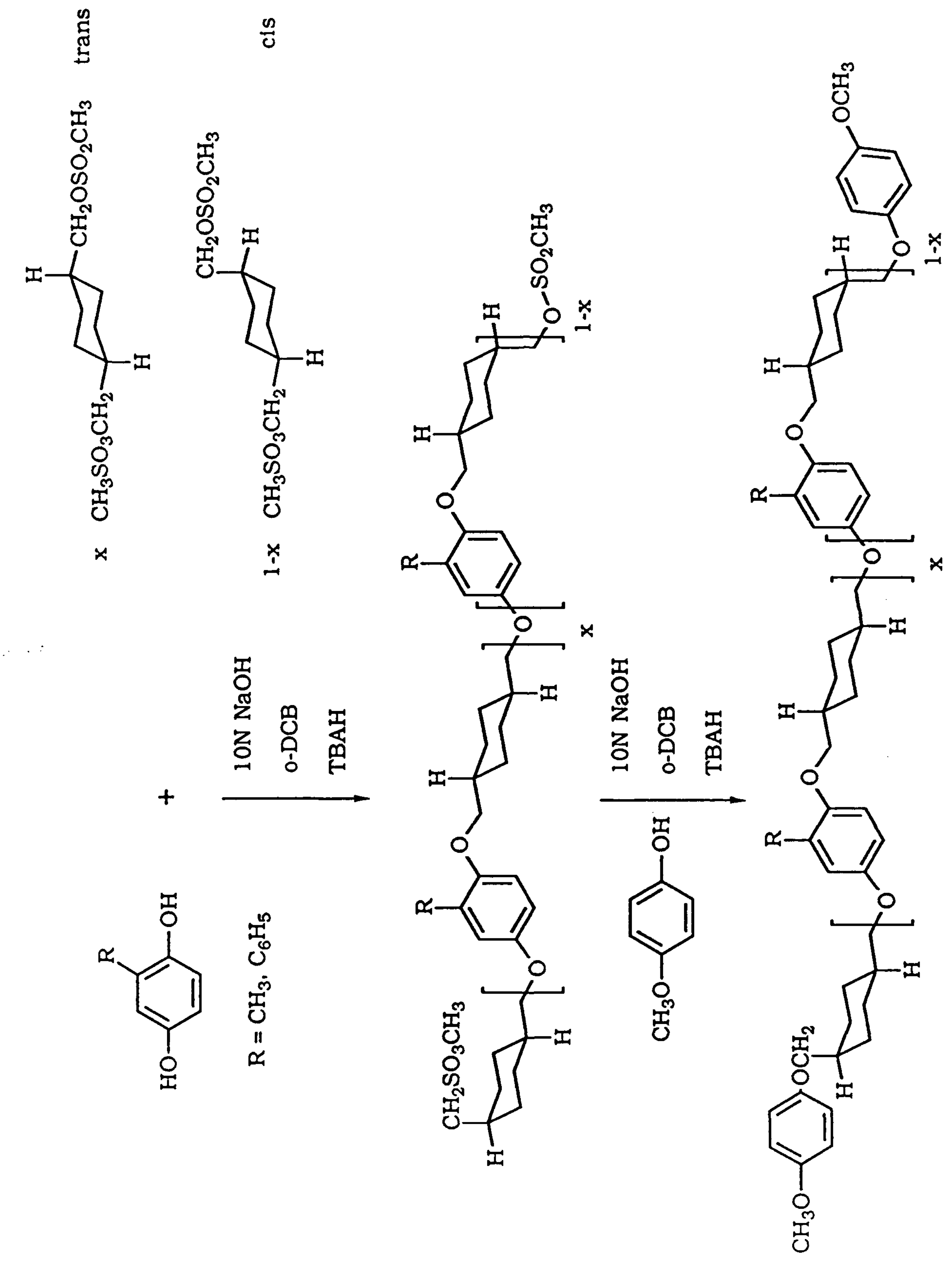
Scheme 30



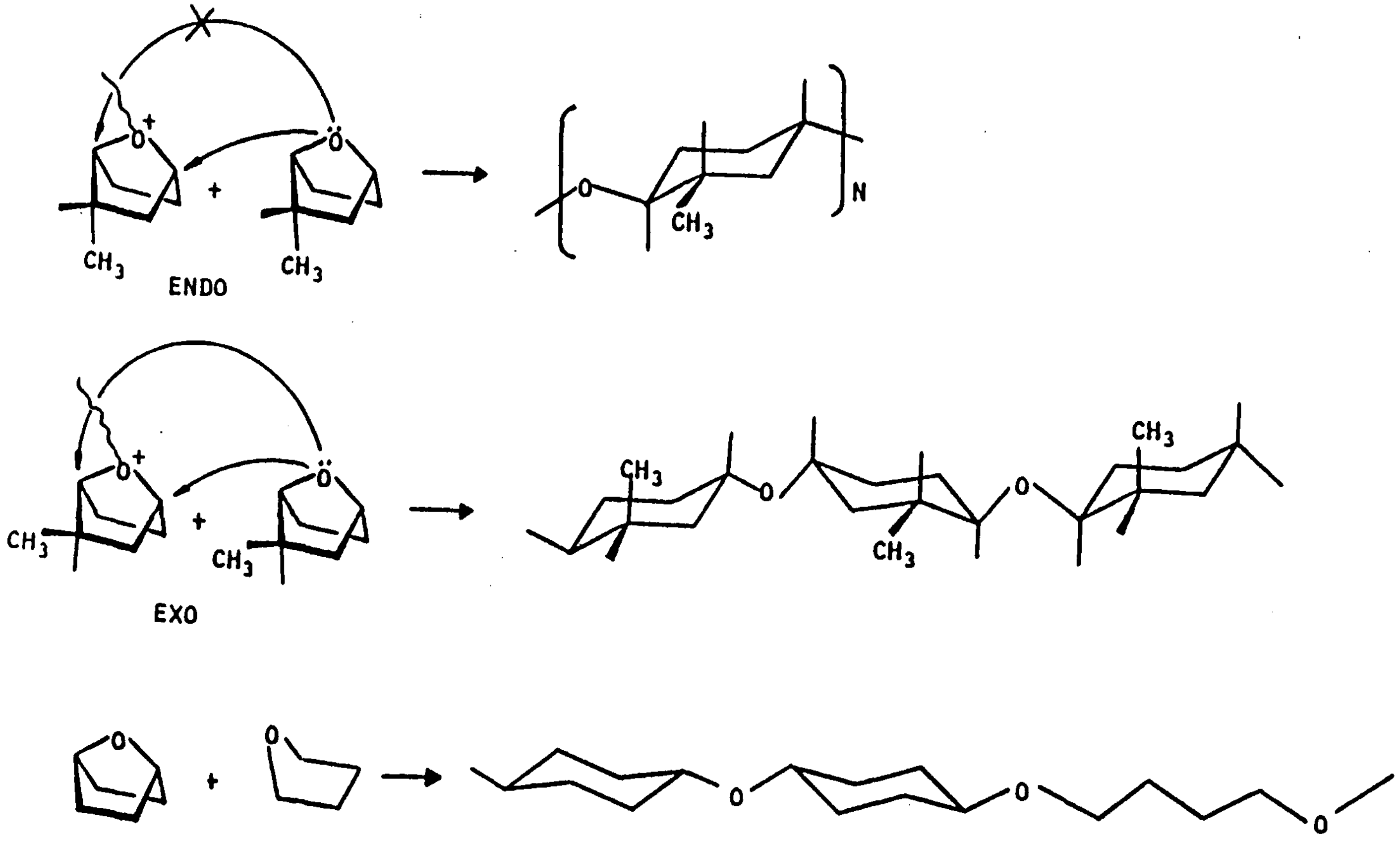
Scheme 31



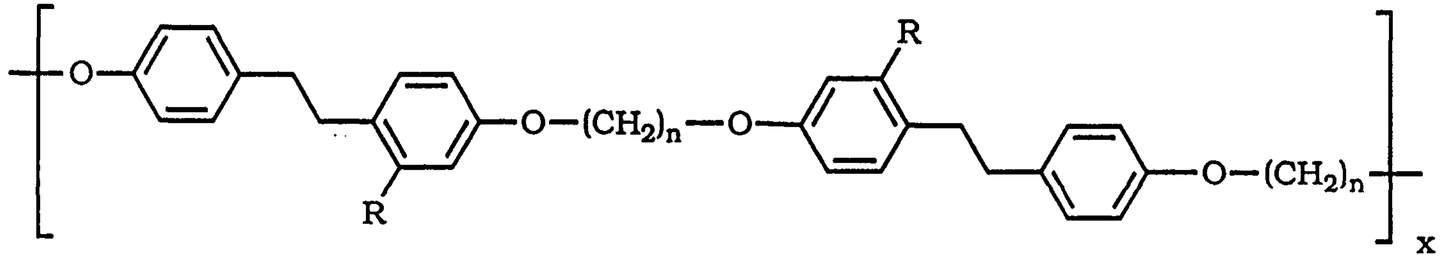
Scheme 32


R
HO
OH
R = CH3, C6H5
+
x
CH3SO3CH2
CH2OSO2CH3
H
trans
1-x
cis
10N NaOH
o-DCB
TBAH
CH2SO3CH3
O
SO2CH3
1-x
CH3O
OCH2
OCH3
OH

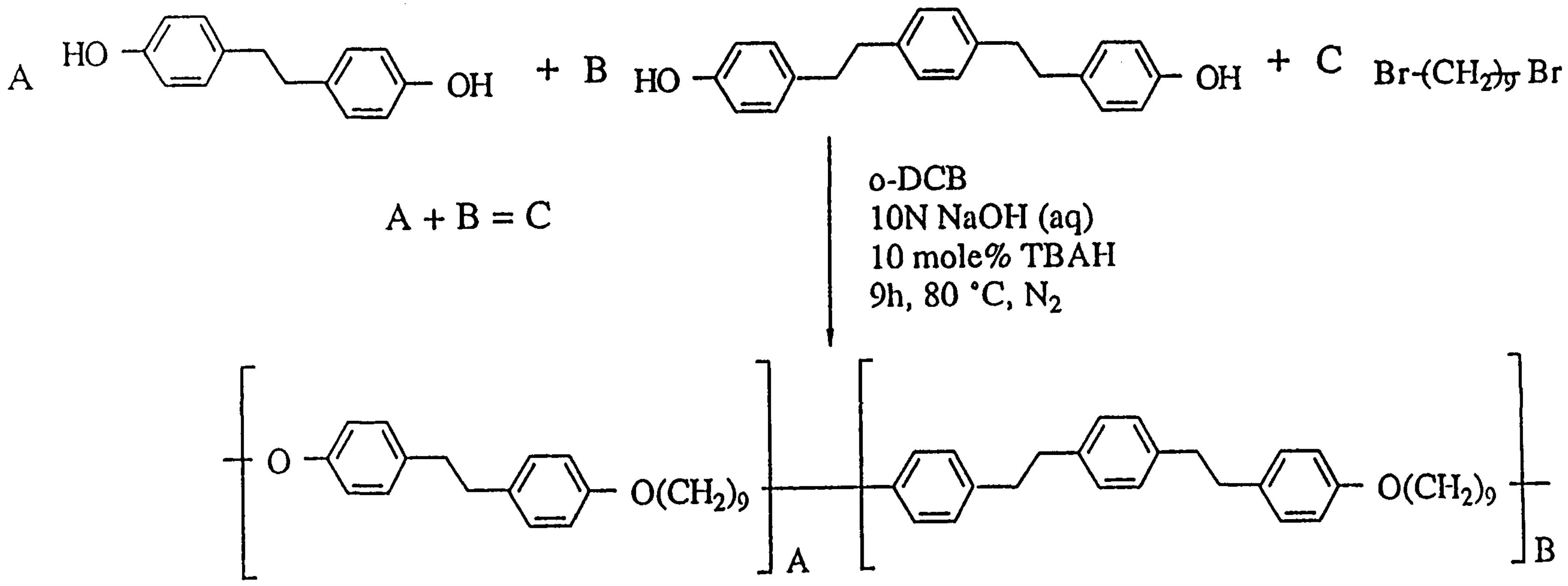
Scheme 33



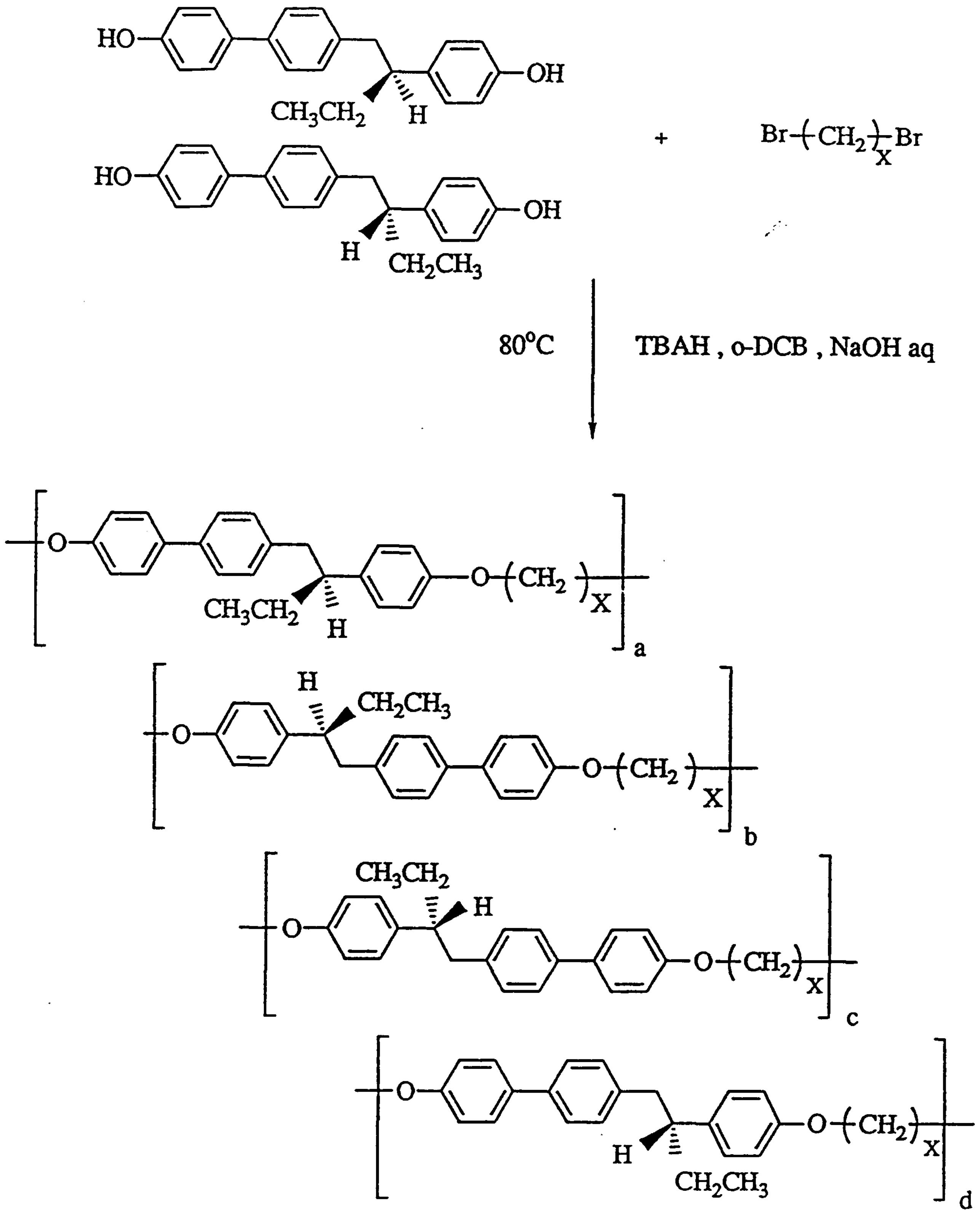
Scheme 34



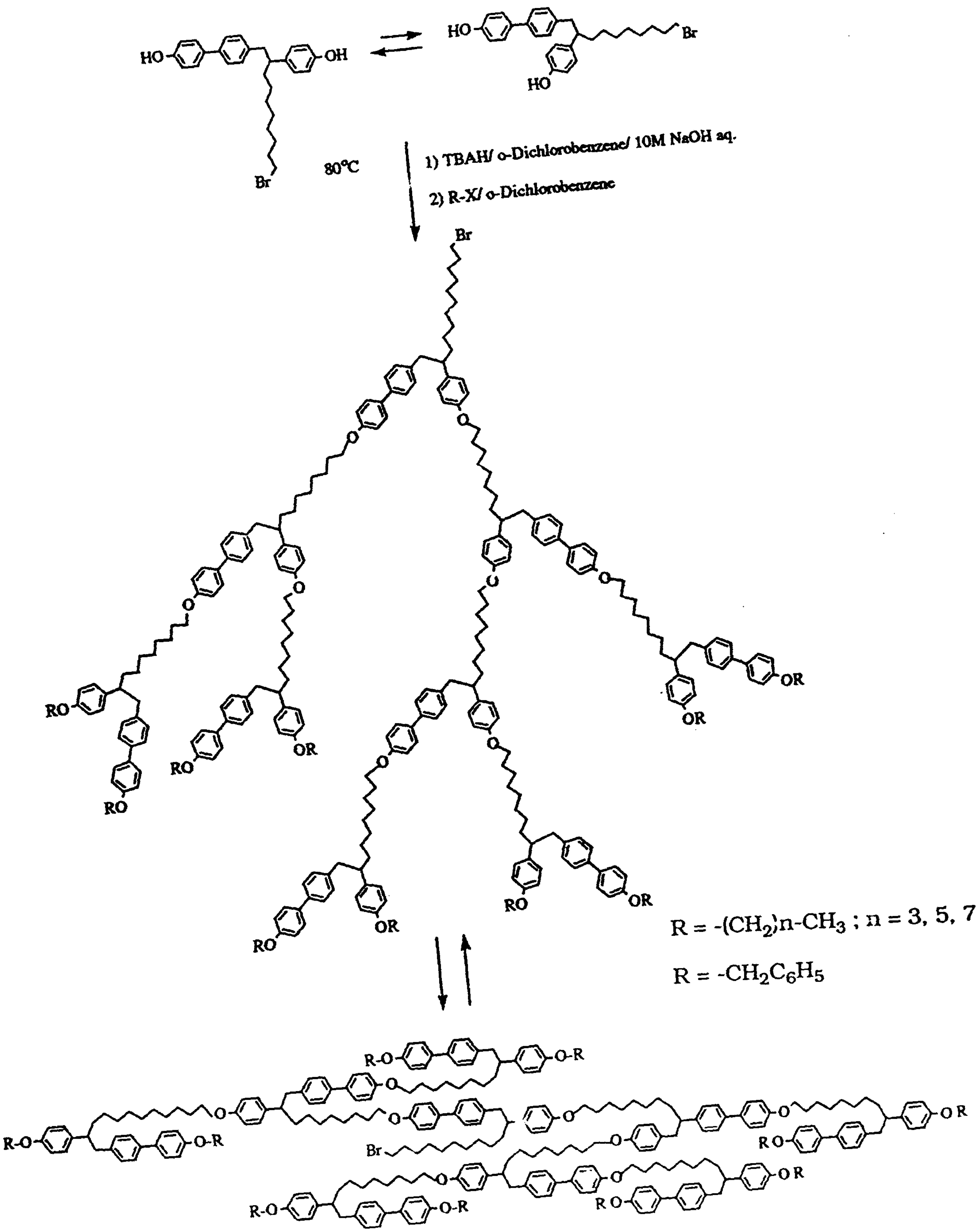
Scheme 35


A
HO
OH
+
B
HO
OH
+
C
Br-(CH2)9-Br
A + B = C
o-DCB
10N NaOH (aq)
10 mole% TBAH
9h, 80 °C, N2
O
O(CH2)9
A
O(CH2)9
B

Scheme 36

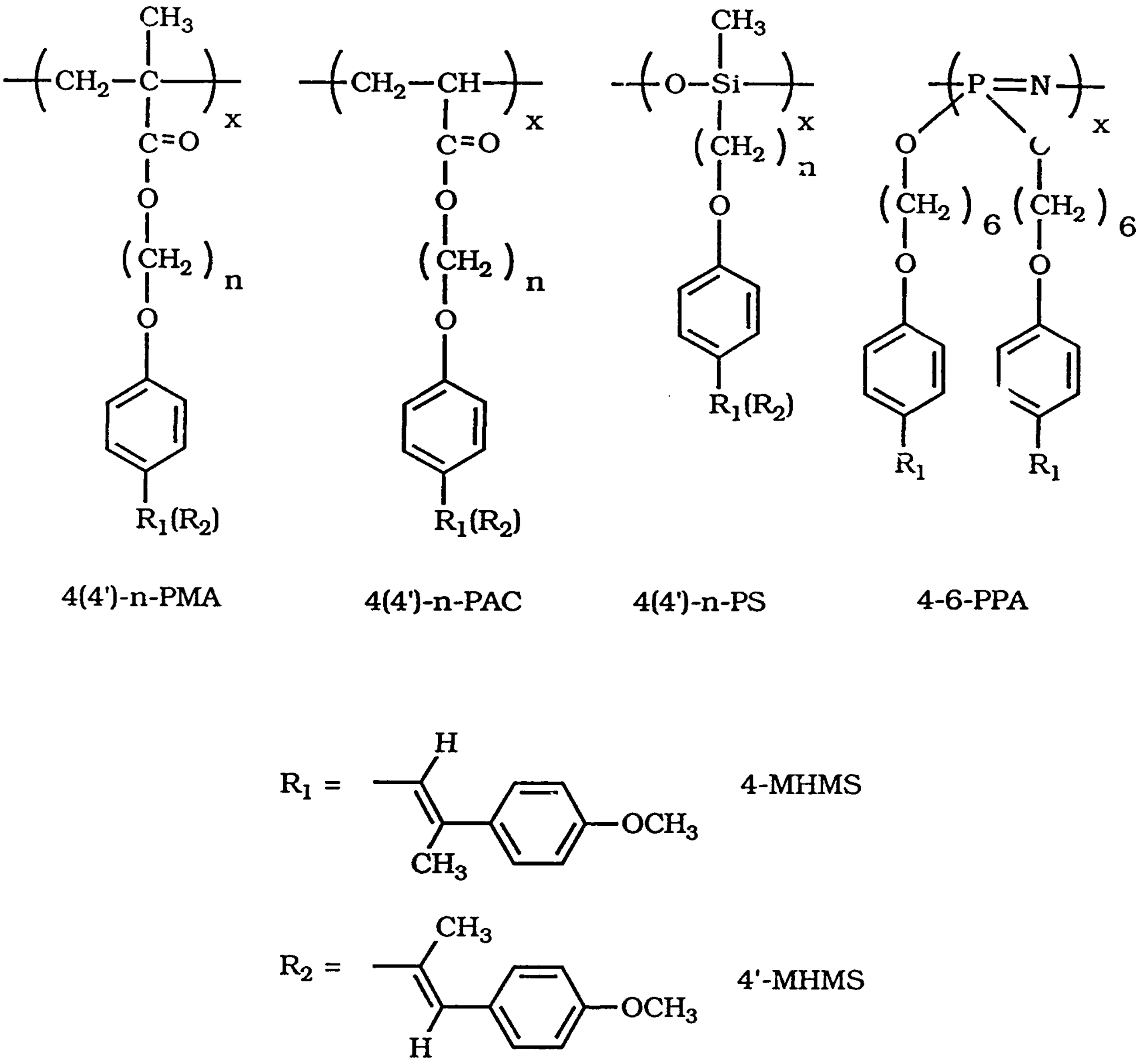

HO
OH
CH3CH2
H
HO
OH
H
CH2CH3
+
Br-(CH2)X-Br
80°C
TBAH , o-DCB , NaOH aq
O
O-(CH2)X
CH3CH2
H
a
O
H
CH2CH3
O-(CH2)X
b
CH3CH2
H
O
O-(CH2)X
c
O
O-(CH2)X
H
CH2CH3
d

Scheme 37



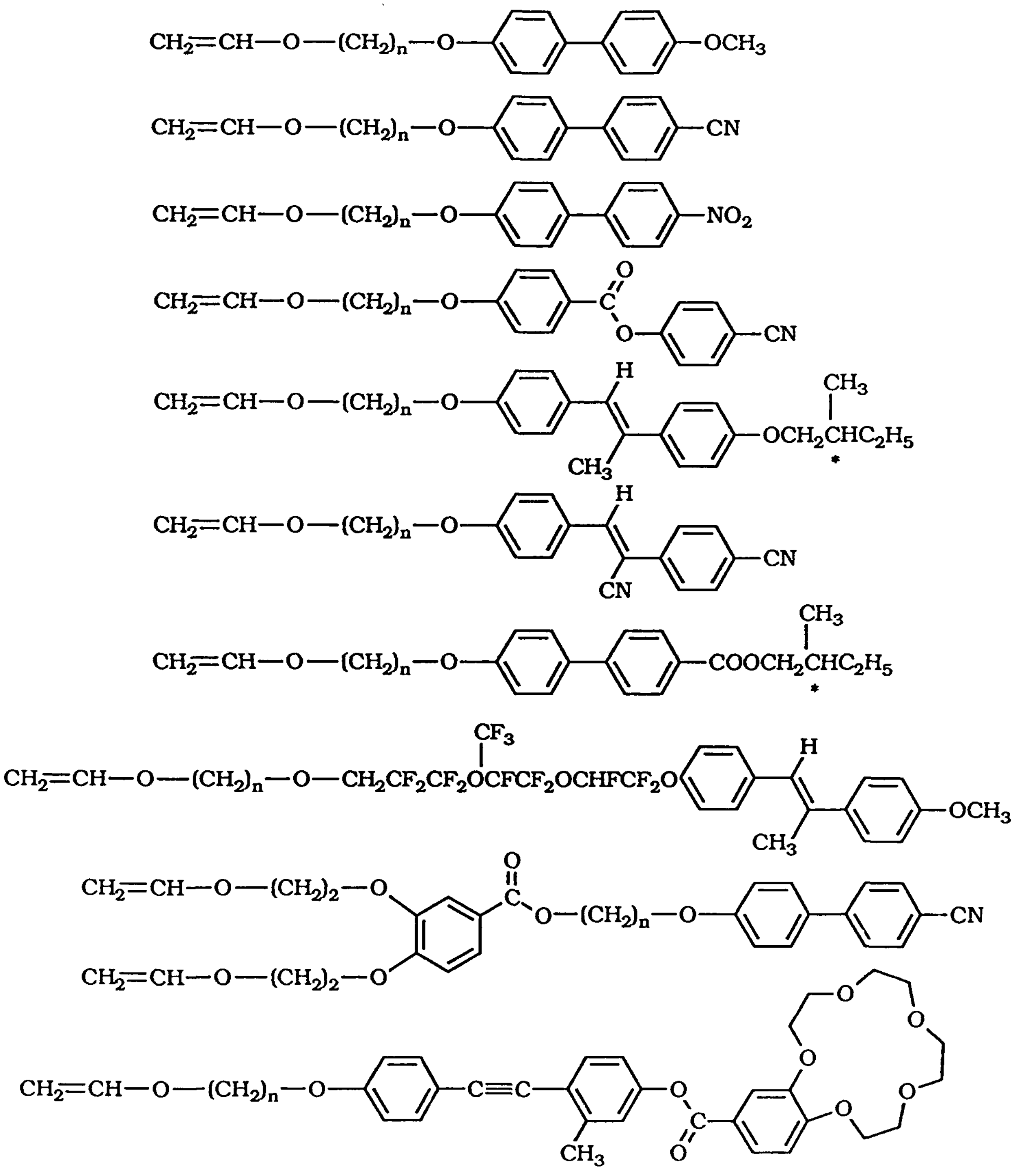
$R = -(CH_2)_n-CH_3$; n = 3, 5, 7

$R = -CH_2C_6H_5$

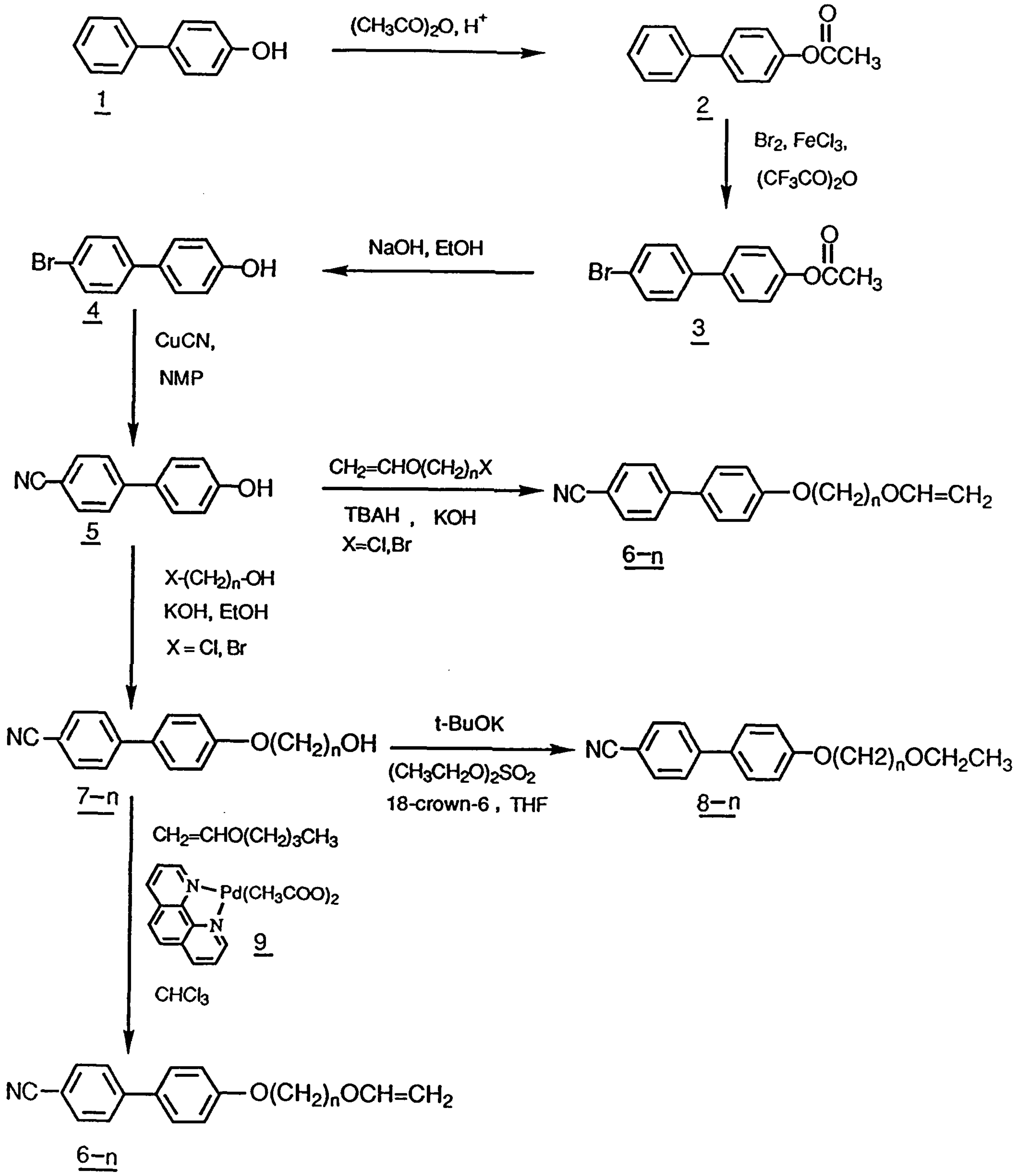


n = 3, 6, 8, 11

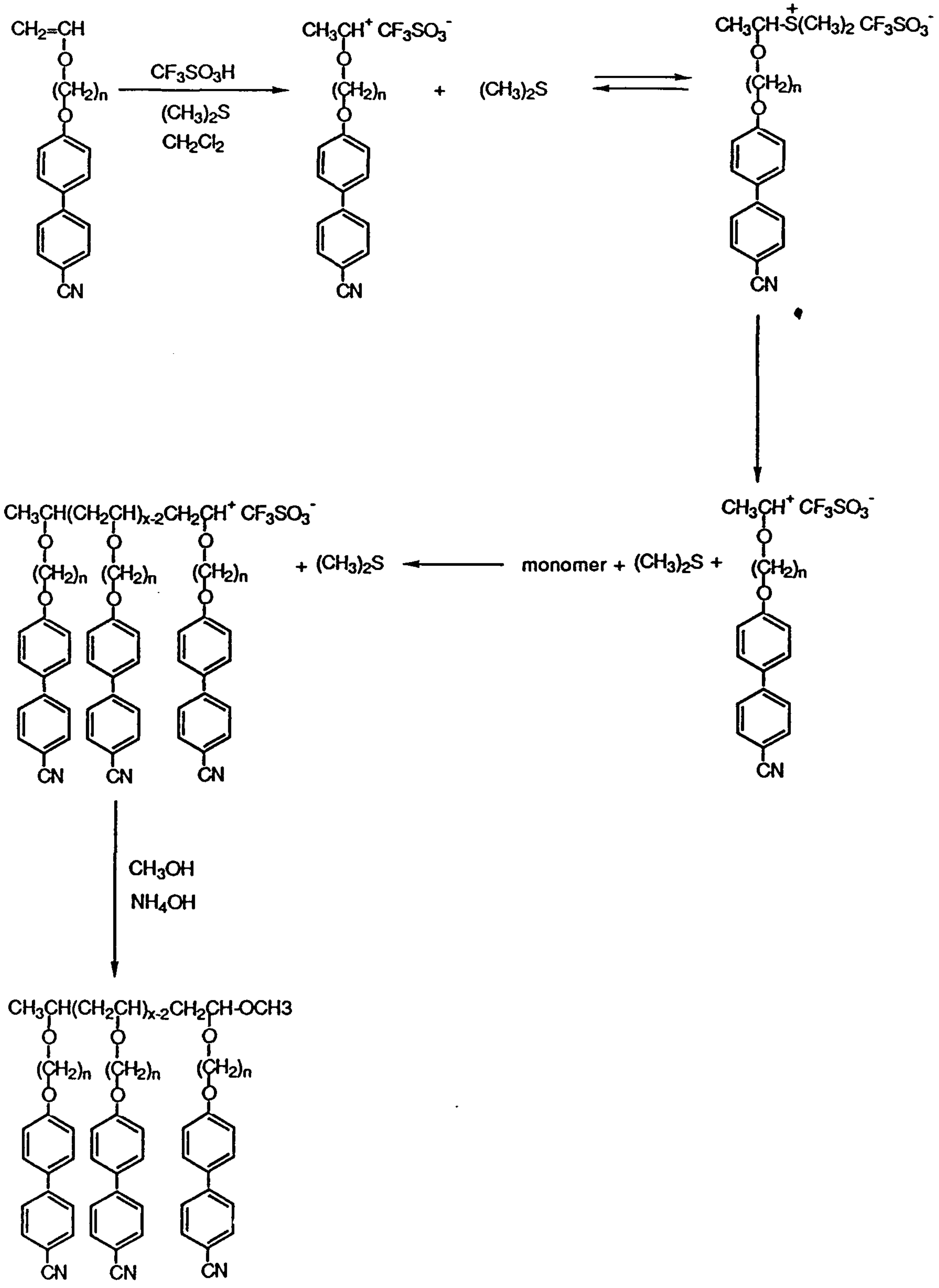
Scheme 39



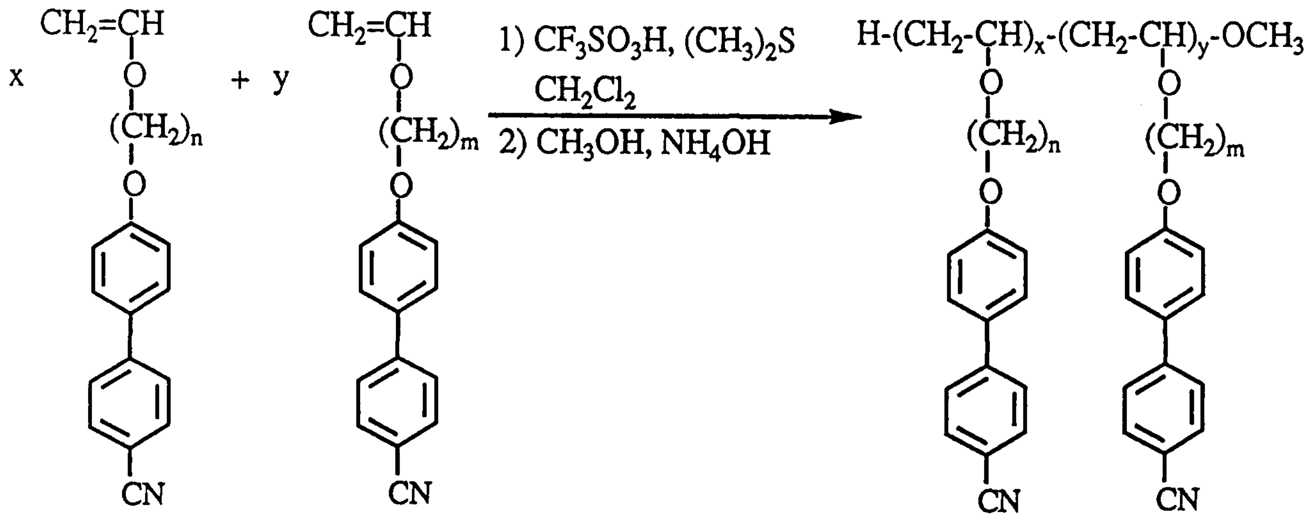
Scheme 40


1
(CH3CO)2O, H+
2
Br2, FeCl3,
(CF3CO)2O
3
NaOH, EtOH
4
CuCN,
NMP
5
CH2=CHO(CH2)nX
TBAH , KOH
X=Cl,Br
6–n
X-(CH2)n-OH
KOH, EtOH
X = Cl, Br
7–n
t-BuOK
(CH3CH2O)2SO2
18-crown-6 , THF
8–n
CH2=CHO(CH2)3CH3
Pd(CH3COO)2
9
CHCl3
6–n

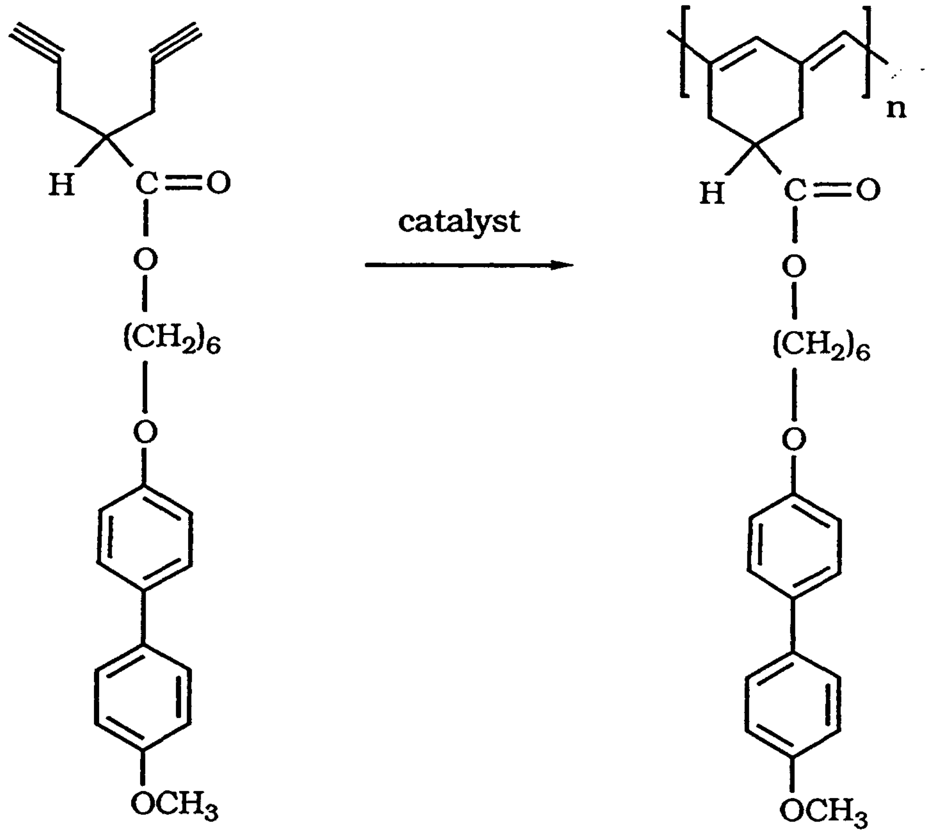
Scheme 41


CH2=CH
O
(CH2)n
O
CN
CF3SO3H
(CH3)2S
CH2Cl2
CH3CH+ CF3SO3-
(CH2)n
CN
+
(CH3)2S
CH3CH-S+(CH3)2 CF3SO3-
(CH2)n
CN
CH3CH+ CF3SO3-
monomer + (CH3)2S +
+ (CH3)2S
CH3CH(CH2CH)x-2CH2CH+ CF3SO3-
(CH2)n
CN
CH3OH
NH4OH
CH3CH(CH2CH)x-2CH2CH-OCH3
(CH2)n
CN

Scheme 42


x
+ y
1) CF3SO3H, (CH3)2S
CH2Cl2
2) CH3OH, NH4OH
H-(CH2-CH)x-(CH2-CH)y-OCH3
(CH2)n
(CH2)m
CN

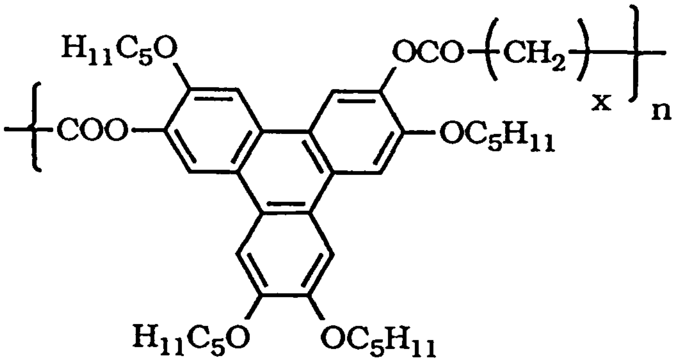
Scheme 43



k 76 °C s 106 °C i

k 92 °C s 105 °C i

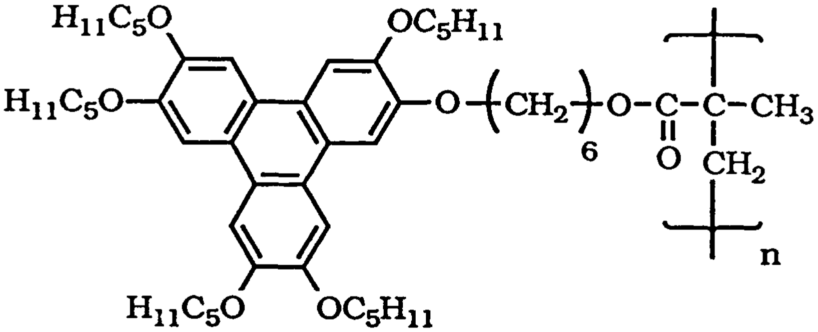
Scheme 44



x=10 g 50 °C D_{ho} 195 °C i $\xrightarrow[\text{0.25 mole}]{\text{TNF}}$ g 50 °C D_{ho} 246 °C i

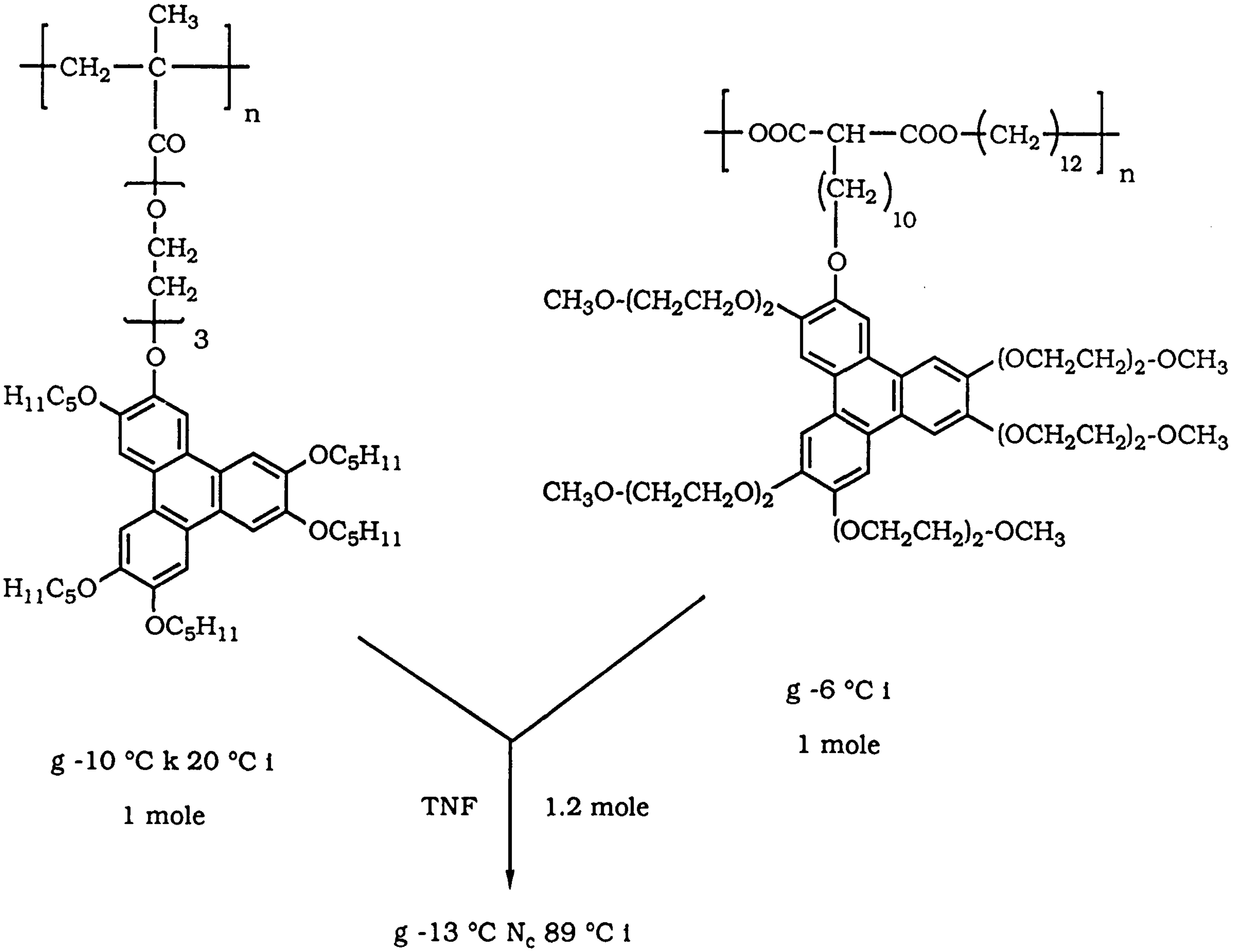
x=20 g 35 °C i $\xrightarrow[\text{0.30 mole}]{\text{TNF}}$ g 22 °C D_{ho} 83 °C i

Scheme 45

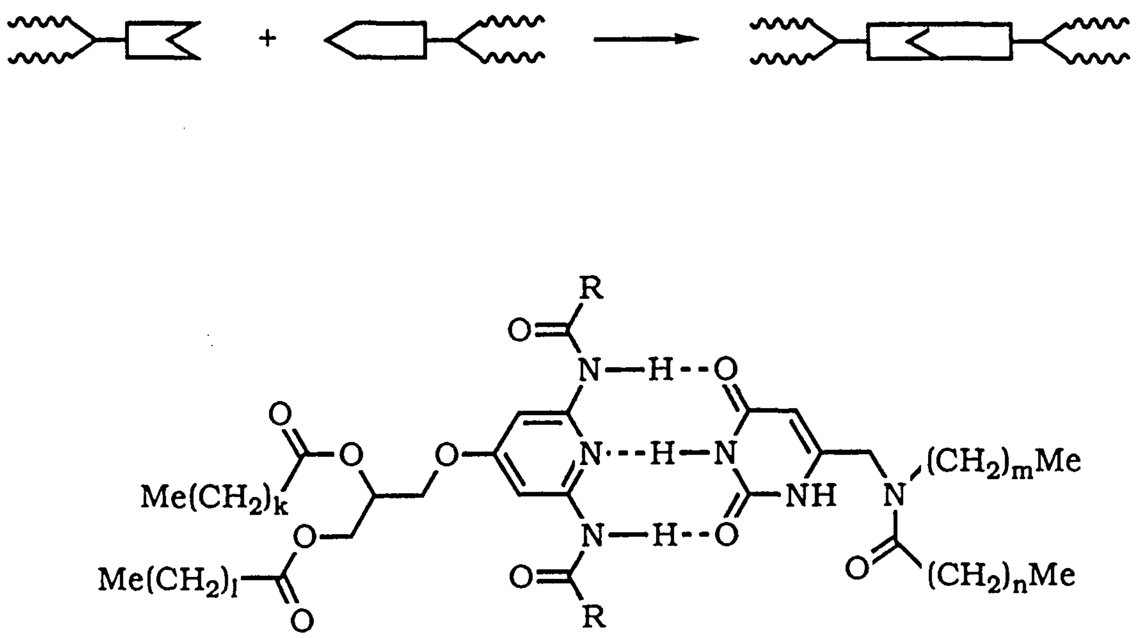


$$g\ 30\ ^{\circ}C\ i \xrightarrow[0.25\ \text{mole}]{\text{TNF}} g\ 50\ ^{\circ}C\ N_c\ 170\ ^{\circ}C\ i$$

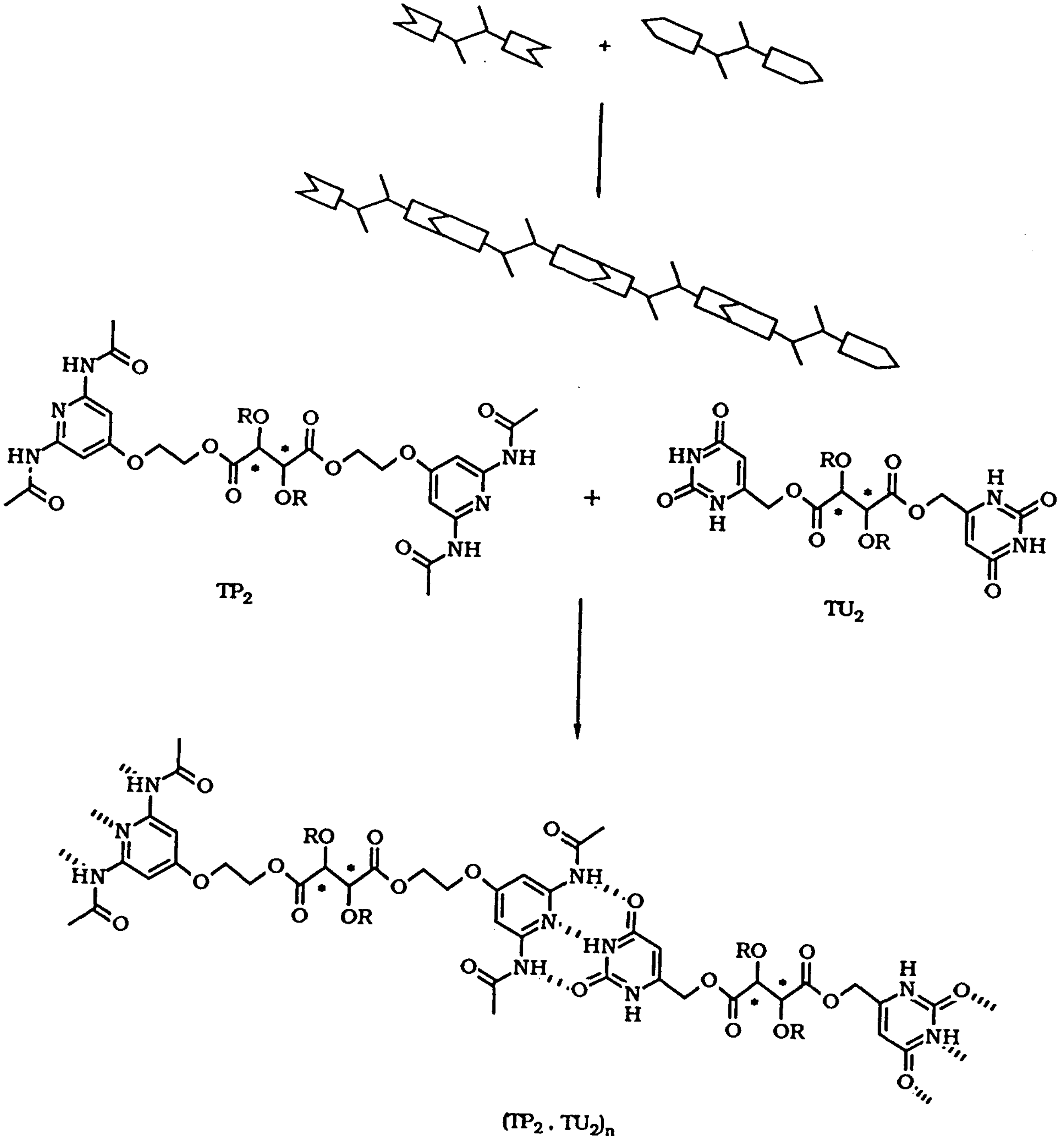
Scheme 46



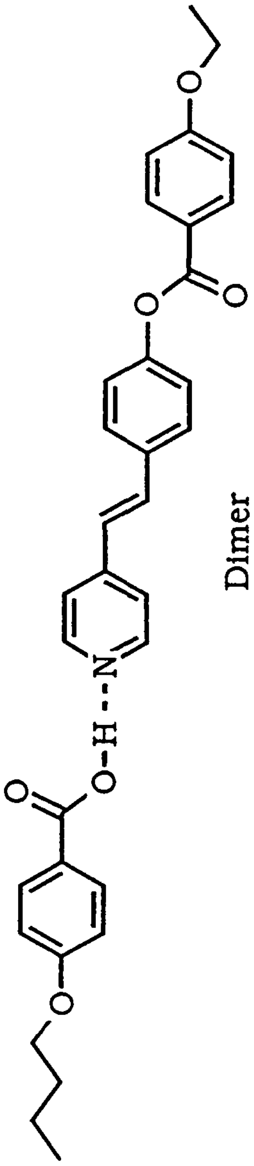
Scheme 47



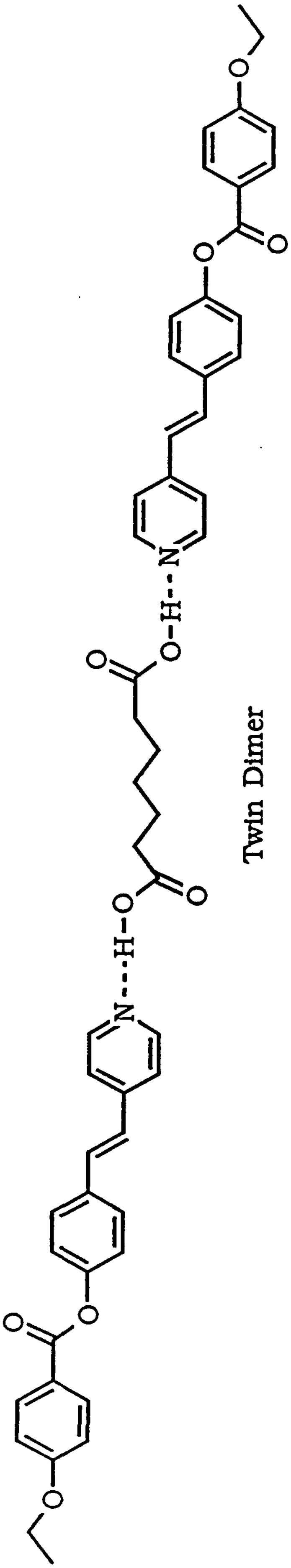
Scheme 48



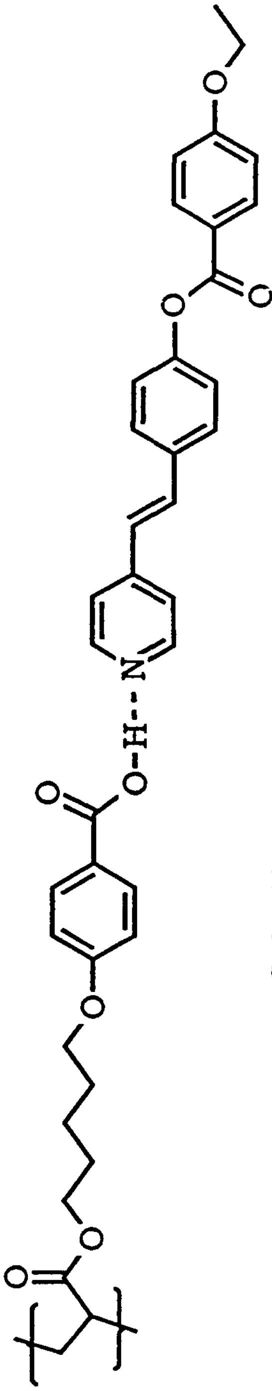
Scheme 49



Dimer



Twin Dimer



Side Chain Liquid Crystalline Polymer

Scheme 50

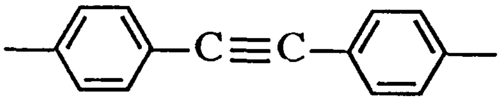
$$F_1 = \left\{ 1 - \frac{\Delta H_1^o T_2 (T-T_1)}{\Delta H_2^o T_1 (T-T_2)} \right\}^{-1}$$ equation (1)

$$A = \frac{\Delta H_1^o T_2}{\Delta H_2^o T_1}$$ equation (2)

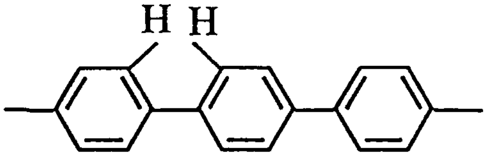
$$dG = VdP - SdT$$ equation (3)

$$T = \sum_{i=1}^{n} x_n T(n)$$ equation (4)

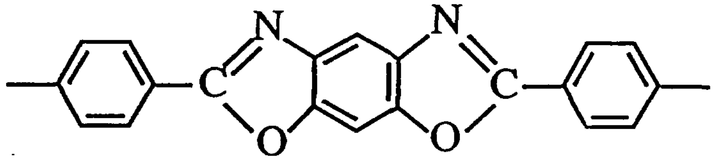
$$\Delta H = \sum_{i=1}^{n} x_n \Delta H(n)$$ equation (5)



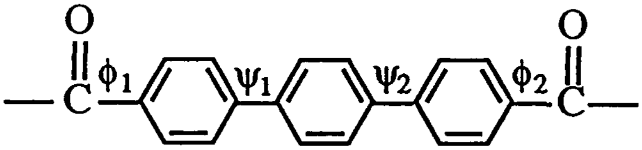
(1)



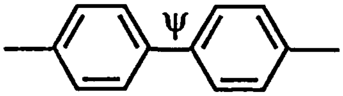
(2)



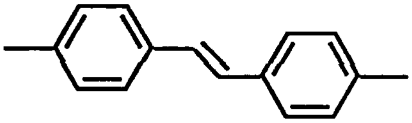
(3)



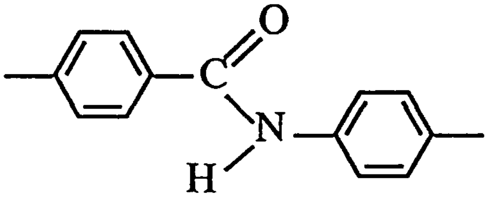
(4)



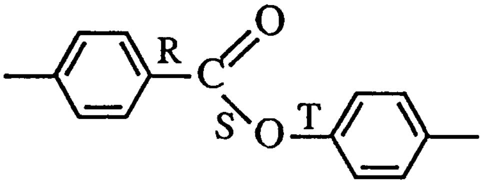
(5)



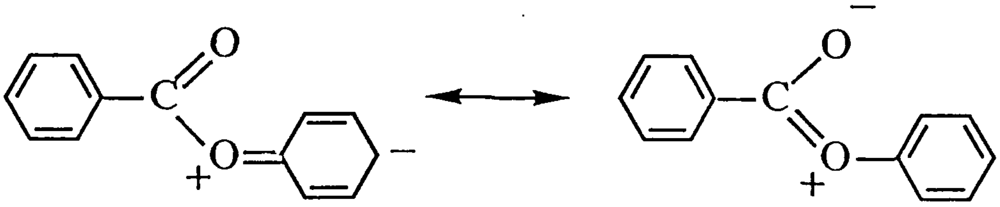
(6)



(7)

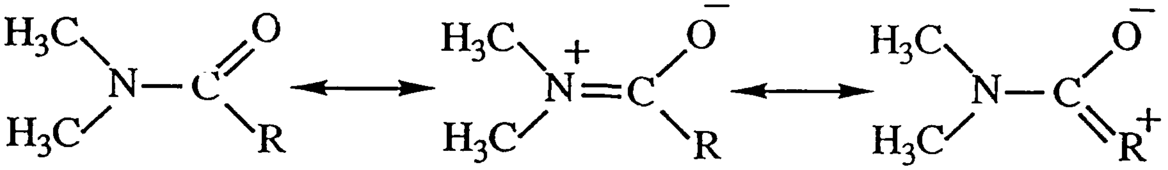


(8)

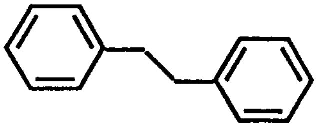


(9)

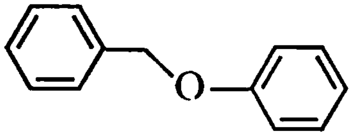
(10)



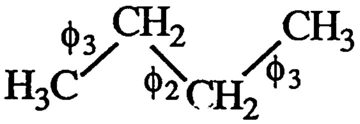
(11) (12) (13)



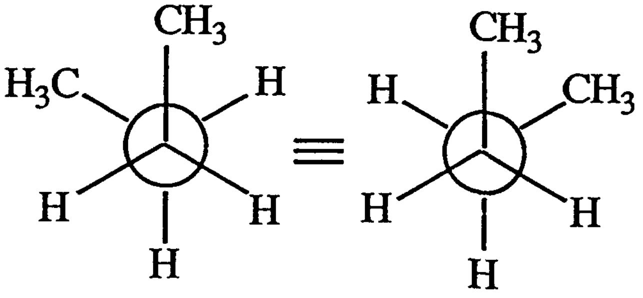
(14)



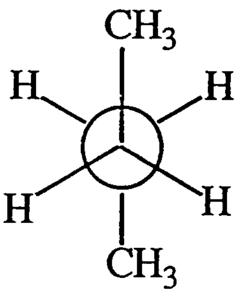
(15)



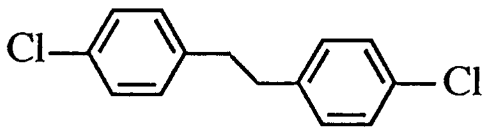
(16)



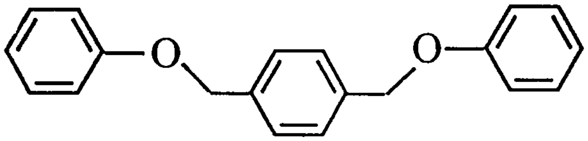
(17) (18)



(19)



(20)



(21)