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PREPARATION OF INORGANIC AND ORGANOMETALLIC POLYMERS WTIH CONTROLLED STRUCTURES

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Preparation of Inorganic and Organometallic Polymers with Controlled Structures

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Abstract: Preparative and mechanistic aspects of polysilanes and polyphosphazenes are reviewed based on the several synthetic methods developed in the author's laboratories. Polysilanes are prepared by sonochemical reductive coupling, modifications and ring opening polymerization. Polyphosphazenes are prepared by the catalyzed polycondensation of phosphoranimines and by the direct reaction of phosphonites and phosphinites with silyl azides. Various aspects of chemoselectivity, regioselectivity, stereoselectivity and supramolecular control in these reactions are discussed.

1. INTRODUCTION

Polymers have become the most important advanced materials not only because of their unique physical and chemical properties which are unmatched by other materials, but also due to their processability. Organic polymers can be extruded, injection molded, cast into thin films and spun into fibers. Metals and ceramics, the other two important classes of materials, have certain properties such as thermal stability or electrical conductivity superior to polymers but usually require processing by methods which utilize much more energy and are much more time consuming. Additionally, desirable geometries are more difficult to obtain for metals and ceramics than for polymers. Thus, the combination of the processability of organic polymers with thermal stability, resistance to chemicals and electronic conductivity of ceramics and metals is desirable. Inorganic and organometallic polymers (I&OMP) provide this possibility and, in addition, may exhibit new properties such as low temperature flexibility, photodegradability, or biocompatibility, which are often superior to parent materials: organic polymers, metals, and ceramics. I&OMP can be used as precursors to ceramics or to metals, but can be also applied as new advanced materials with very special applications ranging from space exploration through optics and electronics to medicine.

Properties of polymers depend on molecular weight. Mechanical and physical properties usually reach asymptotically limited values at molecular weights ranging from 20,000 to 100,000 g/mol. Some non-mechanical properties such as chemical reactivity or electron delocalization level off much earlier, often at the stage of oligomers. Polysilanes, which will be discussed in more detail in the next section, show strong electron delocalization which increases with polymerization degree[1,2]. As shown in Figure 1, delocalization in polysilanes reaches limited values at molecular weights in the range of 2,000 to 3,000 g/mol. Thus, only polymers above this limit possess uniform electronic properties. Some applications require thin polymer films and only polymers of molecular weight above certain limit (associated with the ability to entangle chains) may form films of the sufficient quality. These are just two examples showing how important the preparation of well-defined polymers may be. Polymers with controlled structure can be used as model compounds for the detailed structure-property correlations, they will enable more precise control of electronic and photochemical phenomena, they may also exhibit new phenomena typical for ordered materials, they may be used as block copolymers with strong tendency for microphase separation which may lead to various types of supramolecular structures.

Which elements of macromolecular structures can be controlled and how are they related to various types of selectivities known for chemical reactions?

1. <u>Chemoselectivity</u> defines a possibility for the formation of high molecular weight polymer with a controlled polymerization degree and low polydispersity. Some monomers contain either several functional groups or may participate in several competitive chemical reactions and chemoselectivity will define the "material" chain length. In chain reactions active centers should be sufficiently stable and selective. If the selectivity of propagation is 99%, polymers with degrees of polymerization about 100 may be obtained. However, synthesis of a polymer with molecular weight in the range of 1,000,000 g/mol (DP≅10,000) requires selectivities above 99.99%.

2. <u>Regioselectivity</u> determines the position of the attack of an active center at the functional group, resembling the direction of substitution in alkenes (Markovnikoff/ anti-Markovnikoff). This is an important factor in the ring-opening polymerization of the unsymmetrically substituted monomers. Regioselectivity determines proportion of head-head and head-tail structures. It is nearly impossible to control regioselectivity in condensation processes. Regioselectivity is very important in modification reactions.

3. <u>Stereoselectivity</u> influences the microstructure of polymer chains and affects tacticity of the final polymer. It can have a very strong impact on the mechanical and physical properties such as glass transition, melting point, modulus, and also on electron delocalization. Eventually, stereoselctivity may produce materials with optical activity, interesting for optoelectronic devices. Stereoselectivity may be related to the chiral or prochiral nature of a monomer (cyclics) or to the selective attack of the active center on the incoming monomer.

4. <u>Supramolecular control</u> is an important factor for inorganic/organic hybrid materials since they have a very strong tendency for microphase separation and formation of ordered structures. Inorganic and organometallic polymers have intrinsically build-in incompatibility between the inorganic backbone and organic substituents which leads to various types of mesophases and variety of crystalline modifications. Nearly all I&OMP exhibit a columnar

mesophase which at lower temperatures transforms to microcrystaline regular modifications with helical, transoidal and other structures. The correct design of substituents and formation of longer blocks leads to microphase separation and to new types of mesophases.

I&OMP are relatively new materials and there is only a scarce information on the degree of chemo-, regio-, stereo-, and supramolecular selectivities and there is a very little control of these factors. In a few recent articles new electronic properties of regular polymers was discussed. One can also imagine that properties of ceramic materials depend on the structure of preceramic polymers. Degree of crosslinking, degree of branching, length of chains between branching points may influence properties of ceramics. Block copolymers of two or more preceramic polymers may lead to microphase separation, formation of spheres, cyllinders, and lamellae with dimensions corresponding to the block size (i.e. tens of nm range). Conversion to ceramics may yield entirely new ceramic materials with molecularly engineered structures.

In this article several aspects of structural control will be given for inorganic and organometallic polymers with the strongest emphasis on polysilanes and polyphosphazenes which were studied in our laboratories. In this volume several authors discuss various aspects of improving structural control in various I&OMP and effect of the controlled structure on physical properties.

2. POLYSILANES

Polysilanes are relatively new materials which show a variety of exciting properties[1,3]. The majority of polysilanes are soluble in common organic solvents and can be processed by methods typical for organic polymers, including the formation of thin (<100 nm) films.

Interest in polysilanes originates in potential applications in microlithography and in optoelectronics. Polysilanes can be photodegraded very easily and used as self-developing positive photoresists with high contrast and good etching properties[4]. They can be used as very efficient photoconductors[5] and nonlinear optical materials[6]. Polysilanes have been already commercialized as preceramic polymers for production of β-SiC fibers[7]. Electronic and optical applications call for well-defined materials with good film-forming properties and uniform electron delocalization. As shown in Fig. 1, the delocalization of electrons, estimated by the absorption spectra, reaches constant values for polymers with molecular weights above 3,000 g/mol. Thus, it is synthetically important to produce monomodal high molecular weight polymers. Other aspects of molecular and supramolecular control in polysilanes are also essential. Polymers form various crystalline structures and a variety of mesophases which depend on external parameters such as solvent, temperature, pressure, and concentration but also on composition and microstructure. Thus, all aspects of structural control in polysilanes are very important. Four methods of controlling the structure of polysilanes will be discussed: sonochemical synthesis, ring-opening polymerization, modifications, and copolymerization. Each of them contributes to the control of chemoselectivity, regioselectivity, stereoselectivity and supramolecular structure to different degree.

2.1. SONOCHEMICAL SYNTHESIS

Reductive coupling of disubstituted dichlorosilanes with sodium in hydrocarbons (e.g. boiling toluene) is the main synthetic route to polysilanes due to availability of starting materials and a relatively simple preparative procedure. Polymerization, which is formally polycondensation, proceeds via a chain growth process because high polymer is formed at low conversion and is independent of ratio of chlorosilane to reducing agent[3]. However, polysilanes obtained in this process are accompanied by cyclic oligomers and usually have bimodal molecular weight distribution with a high ($M > 100,000$ g/mol) and a low molecular weight fraction ($M \cong 3,000$ g/mol) . The latters exhibit lower electron delocalization than high polymers and form films of poor quality. There were several attempts to improve the yield of the polymers and suppress formation of the low molecular weight fraction. Initially, various solvent additives[8] and, later, inverse addition[9] of sodium dispersion to monomers was proposed with limited success.

We postulated that the low molecular weight fraction can be formed via side reactions which might have a higher energy of activation than chain growth. In order to assure continuous regeneration of the sodium surface at temperatures below its melting point we applied ultrasound[10] which was able to clean the surface by cavitational erosion at ambient temperatures. Under such conditions, only high polymer was formed in addition to cyclics. Cyclics could be easily separated since they are soluble in isopropanol and ethyl alcohol. Surprisingly, we observed decrease of polydispersity with sonication time and also a decrease of molecular weights to limited value ($M \cong 100{,}000$ g/mol) which depended slightly on polymer concentration (cf. Fig. 2). Polymers with lower molecular weights, prepared in other experiments, could not be degraded by ultrasound. Thus, sonochemical synthesis at ambient temperatures has two aspects: the first is the absence of low molecular weight polymer by suppression of side reactions at lower temperatures; the second is selective mechanical degradation of high polymer by shear forces. This degradation is not random and only chains which can entangle intra- or intermolecularly can be cleaved by cavitational forces operating during sonication. This results in low polydispersities. Thus, two types of chemoselective processes (augmentation of chain growth and selective degradation of very high molecular weight polymers) operate during sonochemical reductive coupling at ambient temperatures.

The proper choice of the reaction solvent is also extremely important. Polymerization of methylphenyldichlorosilane with sodium in diglyme or THF leads exclusively to the formation of cycles[11]. Poly(methylphenylsilylene) dissolved in THF is degraded in less than five minutes in the presence of potassium to the corresponding cyclopentasilanes. Thus, any polymer formed *in situ* during reductive coupling in etheral solvents is immediately degraded to cyclic oligomers due to very low chemoselectivity in this medium.

2.3. RING-OPENING POLYMERIZATION

As discussed in the previous section cyclosilanes are the true thermodynamic products of the reductive coupling, whereas a linear polysilane is a kinetic product which decomposes to cyclics under appropriate conditions. Therefore, the majority of known cyclosilanes are non-polymerizable. Some of them have potential ring strain (e.g. four membered ring in octaphenylcyclotetrasilane) but they are stable and can not be polymerized due to presence of two bulky substituents on each silicon atom. The large steric crowdening in the hypothetical open chain polymer overcompensates the angular strain. Thus, reductive coupling usually do not provide polymerizable cyclics.

In order to make monomers useful for the ring-opening process we decided to use a skeleton of a potentially strained ring and replace bulky phenyl substituents by smaller methyl groups leaving the ring intact[12].

Action of trifluoromethanesulfonic acid on octaphenylcyclotetrasilane provides tetratriflate derivative with one triflate group on each silicon atom. Subsequently, these triflate groups are replaced by either methyl lithium at low temperatures or by methylmagnesium bromide at ambient temperatures to provide 1,2,3,4-tetramethyl-1,2,3,4-tetraphenylcyclotetrasilane. As shown in Fig. 3, there are three isomers of the resulting cyclic monomer, "all-cis" isomer is probably too strained and is not observed under this reaction conditions.

Polymerization proceeds by the attack of a nucleophilic initiator (e.g. n-butyl lithium) on the electropositive silicon atom in the strained monomer leading to the ring cleavage and to the formation of silyl anion. Silyl anions may propagate by attack at the Si atom in the strained monomer and may also attack a Si atom in its own chain. The latter back-biting reaction will result in the formation of strainless cyclic oligomers (cf. Eq. 1).

The former reaction is favored by enthalpy (ring strain), whereas the latter by entropy (unimolecular process). In real systems therelative contributions of these two factors depend on time, concentration, solvent, temperature, counterion, and the substituents on the silicon.

In less polar solvents, such as benzene and toluene, linear polymers are formed and degradation is much less favored. In pure THF very rapid isomerization of cyclotetrasilane to cyclopentasilane is found. In equimolar mixtures of benzene and THF, polymerization carried out with 1 mol% of BuLi as initiator is completed within 30 minutes but after 1 hour degradation becomes significant and polymer is converted to cycles within 2 hours. Thus, again solvent plays a very important role in determining the chemoselectivity of propagation. Reactions are usually run at relatively low monomer and initiator concentrations and minute amounts of impurities may be responsible for transfer reactions. As shown in Figure 4, molecular weights follow [Monomer]/[Initiator] ratio up to the value of 50 ($[\mathrm{BuLi}]_0=4\times10^{-3}$ mol/L) and then deviate from linearity expected for transferless and terminationless process. Higher polymers ($M \cong 100{,}000$ g/mol) were obtained at lower temperatures.

One of the main advantages of ring-opening polymerization is the possibility of control of microstructure. Assuming that the propagation and attack of the silyl anion on the Si atom in the ring proceeds with retention of configuration, at least three stereogenic centers must be controlled because of the retention of configuration at the other two Si atoms. It is difficult to estimate the proportion of racemization at the negatively charged Si-anion since it may be influenced by counterion, solvent and also by configuration of penultimate substituents in the chain. Ring-opening polymerization of enriched "all-trans" isomer of 1,2,3,4-tetramethyl-1,2,3,4-tetraphenylcyclotetrasilane provides polymers with new microstructure not accessible by reductive coupling.

Additional advantage of ring opening polymerization is its regioselectivity. 1,3-Dimethylhexaphenylcyclotetrasilane is attacked predominantly at the methylphenyl substituted Si atom to produce more stable diphenyl substituted silyl anion. This reaction provides alternated copolymer poly(methylphenylsilylene-alt-diphenylsilylene):

(Eq.2)

Polymerization of the enriched trans isomer leads to a polymer with two peaks in the methyl group region due to the absence of syndiotactic triads and presence of isotactic and atactic triads .

The ring-opening process, under the proper conditions, has a well-defined number of active chains and can be used in the preparation of functional polymers and block copolymers which may show supramolecular control by microphase separation.

2.3. MODIFICATION OF POLYSILANES.

Displacement of phenyl groups with triflic acid from silicon chains can be used not only in the preparation of monomers but also in the process of modification of high molecular weight polysilanes. Here again chemo- and regioselectivity play an important role.

Dearylation of poly(methylphenylsilylene) with triflic acid competes with the cleavage of Si-Si chains[13]. Selectivity of the former reaction exceeds 95% and at relatively low degree of modification, no significant chain scission is observed. At higher degrees of modification (above 30%) a decrease of molecular weight is found due to cleavage of Si-Si bonds corresponding to 94% chemoselectivity for the dearylation reaction. This may have origins in low regio- and stereoselectivity in this process. Using model compounds, it was determined that the presence of a triflate group on the silicon atom reduces the rate of the dearylation at neighboring Si atom by a factor of 23 times[14].

This effect decreases with the distance separating the "attacked" atoms and equals 13, 10, and 7 for the dearylation at β, γ, and δ Si atoms[15]:
(Eq. 3)
The strong retardation in the latter case gives evidence for strong electron communication even through five bonds in polysilanes which resemble polyenes rather than single bonded alkanes.

It may happen that, at higher degree of substitution, bulky triflate moieties (radius nearly 3 Å) have very strong repulsive interactions, especially in syndiotactic triads, so strong that they result in chain cleavage.

Silylated triflate backbone is very reactive and triflate groups can be easily displaced by a variety of nucleophiles such as alcohols, amines, organometallic reagents, etc. This chemistry resembles the modification of chlorinated polyphosphazenes[16]. A variety of functional groups lead to new materials which are lipophobic, hydrophilic, and some of them show additional phase ordering. For example, the attachment of a p-methoxybiphenyl mesogen via long flexible spacer with six methylene units to partially triflated poly(methylphenylsilylene) leads to modified polysilanes with liquid crystalline behavior. Shorter spacers and weaker mesogens form only isotropic materials. Probably inherent incompatibility of the main chain and side groups as well as the rod-like behavior of polysilanes prevent ordering of side chain mesogen groups in most systems.

Another area of modifications is the preparation of graft copolymers. We have successfully applied grafting polytetrahydrofuran from triflated polysilanes. Other systems are being investigated at present.

2.4. COPOLYSILANES

Polysilanes with long alkyl substituents form at ambient temperatures highly ordered crystalline phases which are transformed to columnar mesophase at higher temperatures. The morphology of the crystalline phase depends on the structure of substituents and, for two n-hexyl groups at each Si atom, the low temperature phase has the form of a planar zig-zag with a trans conformation in the backbone[17]. However, under similar conditions, di-n-butyl and di-n-pentyl derivatives form 7/3 helical structures in which the main chain is distorted by 26 ° from the trans conformation[18].

We prepared a series of copolymers of di-n-hexylsilylene with di-n-pentylsilylene, di-n-butylsilylene, and di-n-propylsilylene[19]. The 620 MHz ^{1}H

NMR spectra of these copolymers (it was possible to determine proportion of up to heptads) indicate that a nearly random distribution of units is present. Thus, no longer blocks are incorporated and copolymers with a small proportion of silylenes with shorter chains may be regarded as defects in poly(di-n-hexylsilylene) structure.

Indeed, the increased proportion of defects leads to controlled changes in transition from the trans structure to helical and to disordered state. These transitions can be followed by UV spectroscopy in thin polymer films as well as in solid state ^{29}Si NMR[20].

The transitions are strong enough to be detected by thermal methods. Initially, a decrease in the transition temperature is observed due to the higher proportion of defects when comparing pure poly(di-n-hexylsilylene) (315 K) with copolymers containing up to 30% defects (≅270 K). Subsequently, an increase of transition temperature is noted with the formation of a more regular helical structure (343 K). as shown in Fig. 5. Copolysilanes form isodimorphic structures and identical columnar mesophases. The ordered crystalline phase is still accompanied by typical chain folding since single crystals with a typical screw-dislocation are formed from poly(di-n-pentylsilylene). A micrograph of a larger amount of these crystals indicates (as expected) that an equal amount of crystals with left-handed and right-handed dislocation are present.

It was of interest to control supramolecular structure of these crystals and to prepare all crystals with one-handed dislocation. This was accomplished by incorporation of 5 to 20% of chiral 2-methylbutvl (isopentyl) groups into poly(di-n-pentylsilylene). Micrographs show a one-sense dislocation in a collection of single crystals formed from the copolymer with 5% to 20 % content of chiral units. This may be attributed to the preferential formation of one-directional helices which may lead to the formation of lamellae with one-sense screw dislocation.

These copolymers show relatively weak optical activities in solution and the optical rotation is approximately 50 times higher than predicted from the content of chiral substituents. The molar optical rotations increase with a decrease of temperature and become very large after addition of a non solvent (isopropanol). Polysilanes adopt a random coil structure in solution and there is only a small proportion of a helically oriented chromophores, especially at low proportion of chiral unit (every 10 or every 20 silicon atoms). However, at lower temperatures and at limited solubilities, a helical structure is formed which is accompanied by a dramatic increase in optical activity (100 times or 5,000 times based on optical activity of isolated chiral unit). This increase can be also partially ascribed to the intermolecular coupling of chromophores.

In agreement with this explanation, solid films of the copolymers with chiral groups exhibit strong optical activities and strong elipticities measured by circular dichroism. (Fig. 6)

2.5. SUMMARY OF STRUCTURAL CONTROL IN POLYSILANES

As discussed in previous sections, several methods can be used to manipulate the chemoselectivity in polysilane synthesis. We can prepare monomodal polymers, we can influence polydispersities, and control molecular weights to a certain degree. Sonochemical synthesis, ring opening polymerization and modification reactions can be used as instruments for tuning chemoselectivity.

Regioselectivity determines the sequence and position of substituents in the backbone. Both the ring opening process and modifications provide materials with controlled regioselectivity.

Control of stereoselectivity, manifested by the manipulation of chain microstructure and optical activity, has been attempted in a ring-opening process with some initial success. We hope to increase stereoselectivity by the proper choice of reaction conditions, using pure isomers and special additives.

Supramolecular control can be accomplished in copolysilanes by varying the composition of random copolymers and also in block and graft copolymers with a tendency for microphase separation. Some special substituents such as mesogens or chiral units provide materials with supramolecular control up to a level of single crystals (dimensions in the range of 1 μm).

The cited examples illustrate the beginning of the structural control in polysilanes and compete with other synthetic methods such as reductive coupling of oligosilanes and polymerization of masked disilenes which also lead to well-defined polysilanes with properties different from ill-defined polymers prepared by a classic reductive coupling process.

3. POLYPHOSPHAZENES

There are a few synthetic routes to polyphosphazenes which are shown schematically in Scheme 4.

Thermal[21] (or activated by electrophiles[22]) ring opening polymerization of hexachlorocyclotriphospazene is the most important and the commercial method for the formation of chlorinated polymer. The latter is not stable in the presence of moisture and has to be stabilized by the substitution of chlorine atoms by various nucleophiles such as alkoxy, aryloxy, or amino groups[16]. There are hundreds of polyphosphazenes with various substituents prepared this way. Some of them contain very special functional groups with potential uses in medicine, biology or catalysis. Polyphosphazenes can be used as low temperature elastomers, as solid electrolytes for batteries, bioinert materials, etc. The thermal ring-opening process requires a few days at temperatures above 200 °C and has to be stopped at limited conversions due to the crosslinking reactions which occur at higher conversions. Polymers with very high molecular weights ($M \cong 1{,}000{,}000$ g/mol) and usually very broad polydispersities ($M_w/M_n \cong 10$) are formed. The structure of the end groups remains unknown. Substitution reactions are usually random in spite of the tremendous effort and progress in controlling these reactions.

Direct synthesis of polyphosphazenes from disubstituted chlorophosphines and sodium azide leads to a mixture of three- and four membered rings instead of high polymer[23].

Thermal polymerization of phosphoranimines (a few days at 200 °C) apparently occurs as a chain process since high polymer is formed at a low conversion[24]. Surprisingly, condensation of halogenated phosphoranimines again provides cyclics whereas the trifluoroethoxy derivative leads to linear polymers. This method is also the only one for the synthesis of entirely dialkyl and arylalkyl substituted polymers with direct P-C bonding. On the other hand, the monomer synthesis is quite difficult and requires four steps with limited yields.

Trialkoxy substituted phosphoranimines can be formed in high yield in the direct reaction between tris(trifluoroethyl)phosphite and trimethylsilyl azide (Staudinger reaction)[25]. The monomer was again reported to polymerize thermally in the range of 200 °C and to provide polymer with $M_n \cong 10{,}000$ at partial conversion.

3.1. CATALYZED POLYMERIZATION OF PHOSPHORANIMINES

Thermal polymerization of phosphoranimines has a chain reaction character with high polymer formed at low conversion and with noticeable induction periods. We decided to follow up this chain reaction and to explore possibility of the catalysis in this process. The induction periods indicate that in the initial stage, some kind of active species might be slowly formed which later become responsible for the chain growth nature of the process. It is known that the silyl group in phosphoranimines has a high mobility and that cations of a type $R_2P\text{-}N^+\text{-}PR_2$ are quite stable due to strong delocalization of the positive charge. Thus, we first assumed that polymerization may have an anionic character and that we should provide initiators which will carry bulky cations and anions with a high affinity towards the trimethylsilyl group. The obvious choice was tetrabutylammonium fluoride which tremendously accelerated the reaction and provided high polymer within one hour at 100 °C (compare with a few days at 200 °C for a noncatalyzed process). Polymers with molecular weights ranging from 20,000 to 100,000 g/mol were prepared using tetrabutylammonium fluoride and other anionic initiators which include various salts with crowned and cryptated cations as well as some nonionic initiators[26]. Yields are quantitative and NMR indicate a linear polymer structure (>95%). Molecular weight distribution are in the range of $M_w/M_n \cong 1.2$ to 1.5.

A simplified plausible reaction mechanism is presented in Eq. 5 :

Eq. 5

More detailed kinetic analysis of this polymerization as well as change of the molecular weight with conversion indicate that some other reactions also play an important role. Reactions between end groups, not important at the beginning of the reaction (large excess of monomer), lead to increase of molecular weight by interchain condensation :

(Eq. 6)

Initiation is slow and high polymers are formed at the beginning of the reaction. Low external orders in initiator suggest that macromolecular phosphoranimines terminated with silyl groups may be reactive enough to react directly with monomer or via some activation by various catalysts. Thus, the catalyzed polymerization of phosphoranimines is a potential route to the formation of well defined polyphosphazenes with controlled molecular weight and controlled structure of end groups, but has to be thoroughly investigated.

3.2. POLYPHOSPHAZENES BY DIRECT REACTION BETWEEN PHOSPHONITES AND PHOSPHINITES WITH TRIMETHYLSILYL AZIDE

The approach via phosphoranimines has a number of possibilities for the introduction of various substituents on the phosphorous atom in the monomer. We are trying to explore direct synthesis using Staudinger reaction between various phosphites, phosphonites, and phosphinites with trimethylsilyl azide. It seems that the structures of the substituents at phosphorous play an extremely important role in the pathway of this reaction as well as on the reactivity of the final phosphoranimines.

Alkoxy and aryloxy substituted compounds lead in a relatively clean way to phosphoranimines. The triphenoxy derivative is so reactive that it decomposes thermally during synthesis and can not be isolated. Replacement of two phenoxy groups by two trifluoroethoxy groups provides phosphoranimine in up to 20% yield in addition to *in situ* formed polymer. A comparison of leaving group ability between phenoxide and trifluoroethoxide in mixed phosphoranimines indicate that the former is only 6 times better leaving group, much less than expected from the 5 orders of magnitude difference[27] in pK_a:

(Eq.7)

Reactions of phosphonites and phosphinites with silyl azide have to be carried out with extreme care. In addition to the Staudinger reaction, the formation of phosphine azides is observed. These compounds explosively decompose in a chain reaction to polyphosphazenes and nitrogen :

(Eq. 8)

The relative proportion of path **A** (phosphine azide) and **B** (phosphoranimine) depends on substituents at phosphorous and the reaction conditions. Thus, phosphites do not form phosphine azides, phosphonites yield a mixture of products, and phosphinites give nearly exclusively phosphine azides and no phosphoranimines.

The most interesting case is bis(trifluoroethyl) phenylphosphonite which starts to react with silyl azide at 70 °C. The polymerization occurs spontaneously and without catalyst poly(phenyltrifluoroethoxyphosphazene) in up to 80% yield is formed. The remaining 20 % of the phosphoranimine could not be polymerized thermally up to 200 °C. Therefore, polymer can not be formed from phosphoranimine but rather in a parallel pathway **A**. Indeed, the reaction run at 120 °C provides phosphoranimine in 41% preparative yield, and much lower amount of polymer. Apparently pathway B has a higher activation energy and is preferred at higher temperatures. This polyphosphazene is an amorphous polymer due to a stereo random microstructure deduced from NMR studies. This polymer has a glass transition temperature at -31 °C, and is thermally stable up to 300 °C.

Reaction of trifluoroethyl diphenylphosphinite occurs explosively in bulk but can be mediated in solution. Reaction in diglyme starts at temperatures about 60 °C with the intense formation of a yellow color, and after the first few bubbles of nitrogen are formed, the reaction accelerates dramatically in spite of rapid external cooling. A few seconds after the nitrogen stops evolving, poly(diphenylphosphazene) precipitates as a white powder. This reaction again has strong chain process character, which once initiated, continues at even lower temperatures. Polymerization is quite sensitive to solvent effects and in alcohols and chlorinated solvents provides mostly oligomers.

The examples presented of the polymerization of phosporanimines and phosphine azides which were formed *in situ* demonstrate the possibility for the preparation of polyphosphazenes in previously inaccessible range of molecular weights, polymers with increased control of macromolecular structure (modalities, polydispersities) and new polymers with e.g. diphenyl and phenyl/trifluoroethoxy substituents. It is believed that more thorough studies on new synthetic routes towards polyphosphazenes will enable additional control of microstructure, macromolecular structure and supramolecular structure in these important materials.

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Captions for Figures:

Figure 1
Three dimensional GPC of oligo(methylphenylsilylenes) showing increase of the maximum of absorption with polymerization degree.

Figure 2
GPC traces of poly(methylphenylsilylene) obtained in the reductive coupling with sodium in toluene at various temperatures using ultrasound.

Figure 3
^{29}Si NMR spectrum of three isomers of 1,2,3,4-tetramethyl-1,2,3,4-tetraphenyl-cyclotetrasilane.

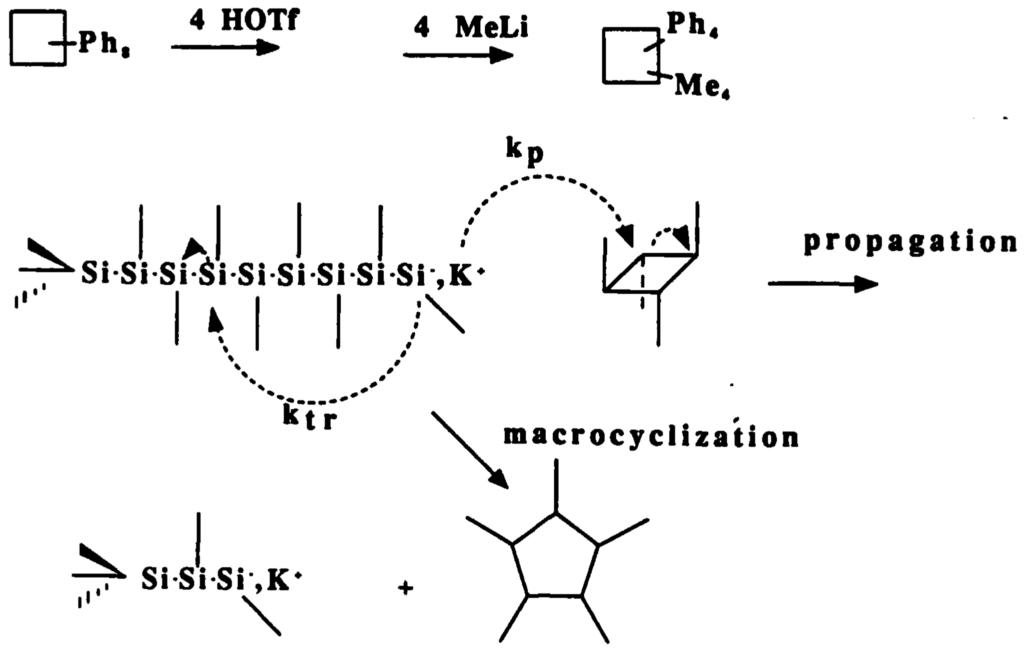
Figure 4
Dependence of the molecular weight of poly(methylphenylsilylene) on the ratio of concentartions of monomer to initiator in the ring-opening polymerization initiated by n-BuLi/Cryptand [2.1.1] in benzene at 25 °C.

Figure 5
Entropies and transition temperatures measured by DSC for various copolymers of PDHS and PDPS.

Figure 6.
Circular dichroism of thin films (ª200 nm) of poly(di-n-pentylsilylene-co-di-isopentyl*silylene) (90:10)

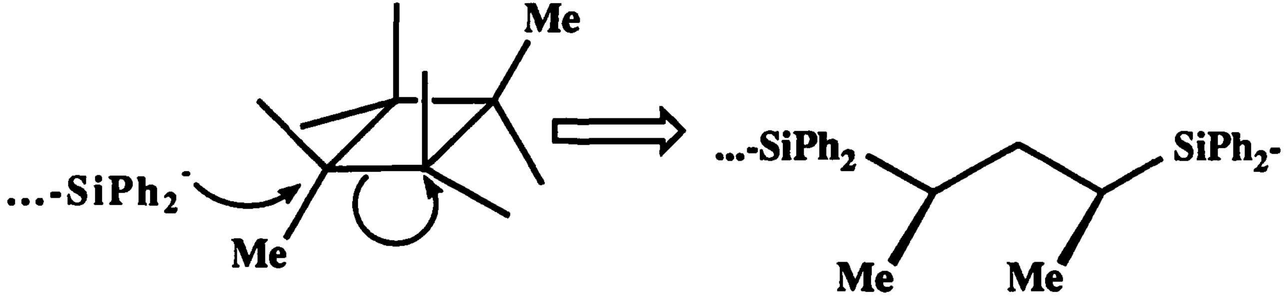
Figure 7
620 MHz and 300 MHz ^{1}H NMR spectra of stereorandom poly(phenyltrifluoroethoxyphosphazene)

Scheme 1:



(" —— " indicates phenyl group, methyl groups are not shown)

(Eq. 2)

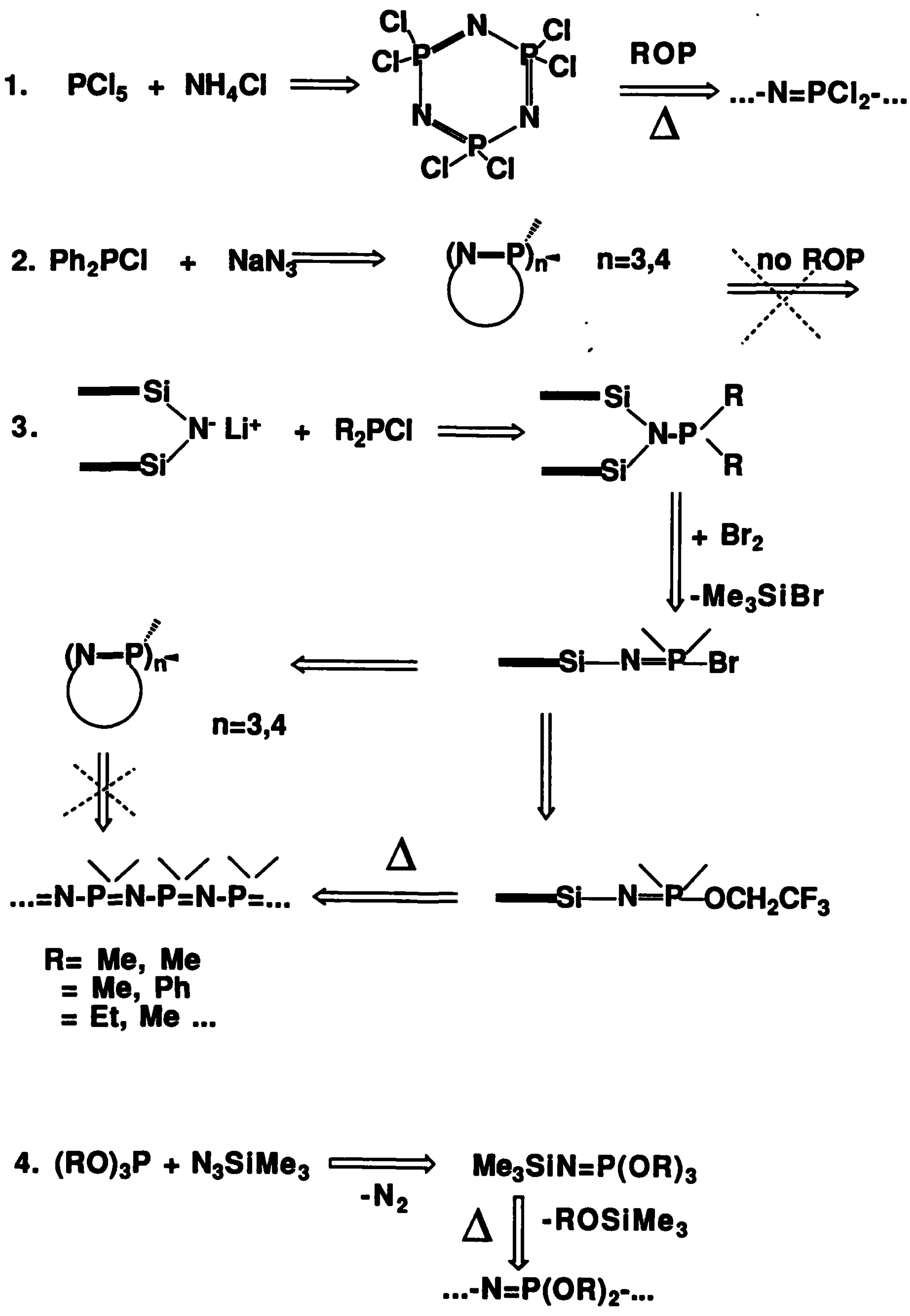


(Eq. 3)

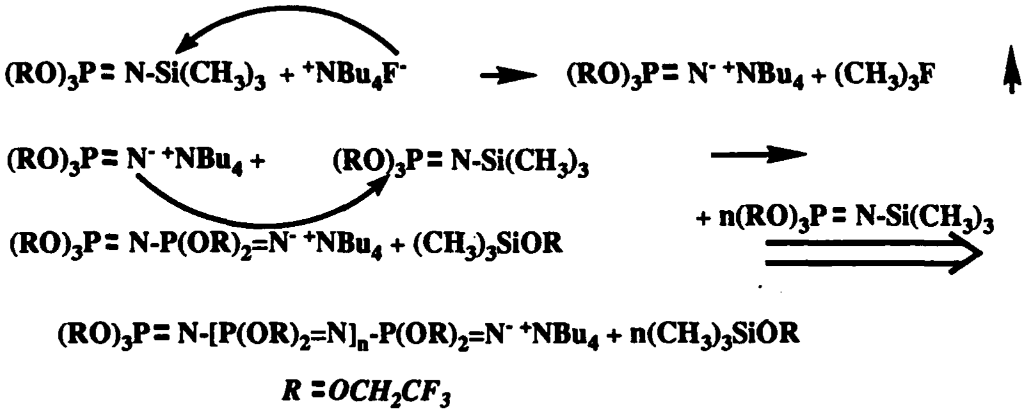
$$\mathrm{Ph\text{-}(SiMe_2)_n\text{-}Ph} \xrightarrow[k]{+\mathrm{HOTf}} \mathrm{Ph\text{-}(SiMe_2)_n\text{-}OTf} \xrightarrow[k']{+\mathrm{HOTf}} \mathrm{TfO\text{-}(SiMe_2)_n\text{-}OTf}$$

$k/k'=23,\ 13,\ 10,\ 7$ for $n=2,\ 3,\ 4,\ 5$

(scheme 4)


1. PCl5 + NH4Cl
Cl
Cl-P
N
Cl
P
Cl
N
N
P
Cl
Cl
ROP
Δ
...-N=PCl2-...
2. Ph2PCl + NaN3
(N—P)n
n=3,4
no ROP
3.
Si
N- Li+
Si
+ R2PCl
Si
N-P
R
R
Si
+ Br2
-Me3SiBr
Si—N=P—Br
(N—P)n
n=3,4
Si—N=P—OCH2CF3
Δ
...=N-P=N-P=N-P=...
R= Me, Me
= Me, Ph
= Et, Me ...
4. (RO)3P + N3SiMe3
-N2
Me3SiN=P(OR)3
Δ
-ROSiMe3
...-N=P(OR)2-...

(Eq. 5)



$$(RO)_3P{=}N\text{-}Si(CH_3)_3 + {}^{+}NBu_4F^- \rightarrow (RO)_3P{=}N^-\,{}^{+}NBu_4 + (CH_3)_3F\uparrow$$

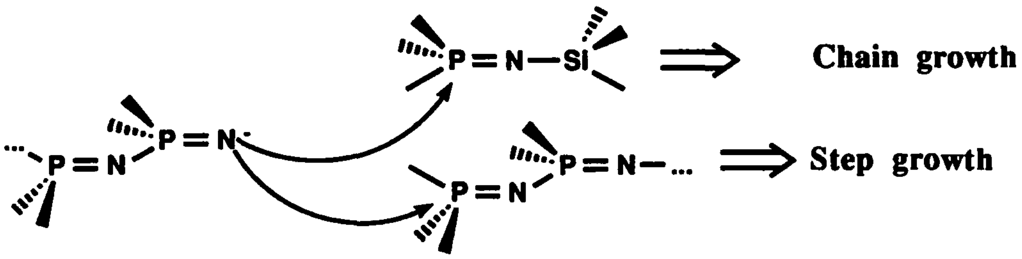
$$(RO)_3P{=}N^-\,{}^{+}NBu_4 + (RO)_3P{=}N\text{-}Si(CH_3)_3 \rightarrow$$

$$(RO)_3P{=}N\text{-}P(OR)_2{=}N^-\,{}^{+}NBu_4 + (CH_3)_3SiOR \xRightarrow{+\,n(RO)_3P=N\text{-}Si(CH_3)_3}$$

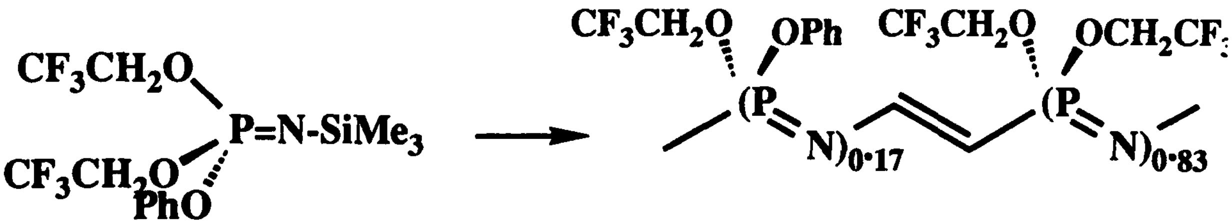
$$(RO)_3P{=}N\text{-}[P(OR)_2{=}N]_n\text{-}P(OR)_2{=}N^-\,{}^{+}NBu_4 + n(CH_3)_3SiOR$$

$R = OCH_2CF_3$

(Eq. 6)



(Eq.7)



(Eq. 8)

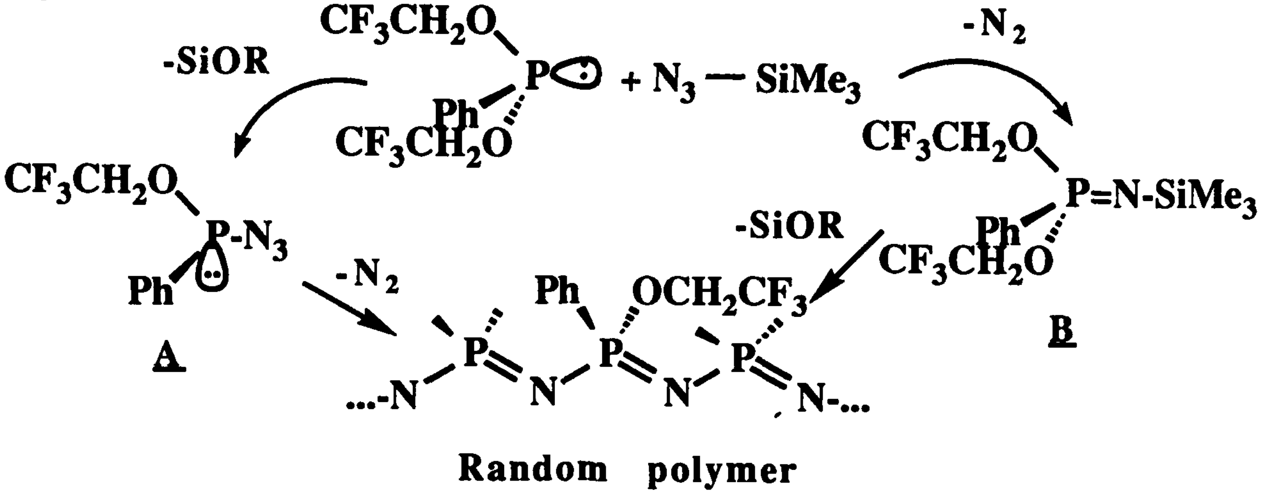
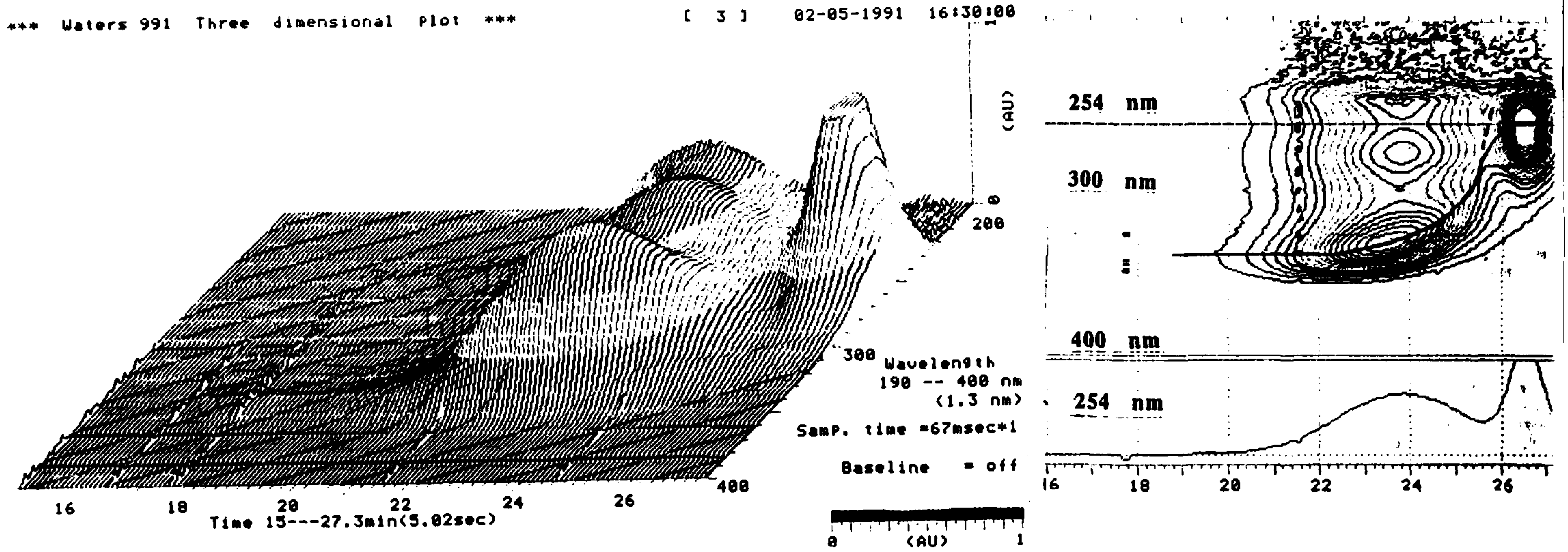
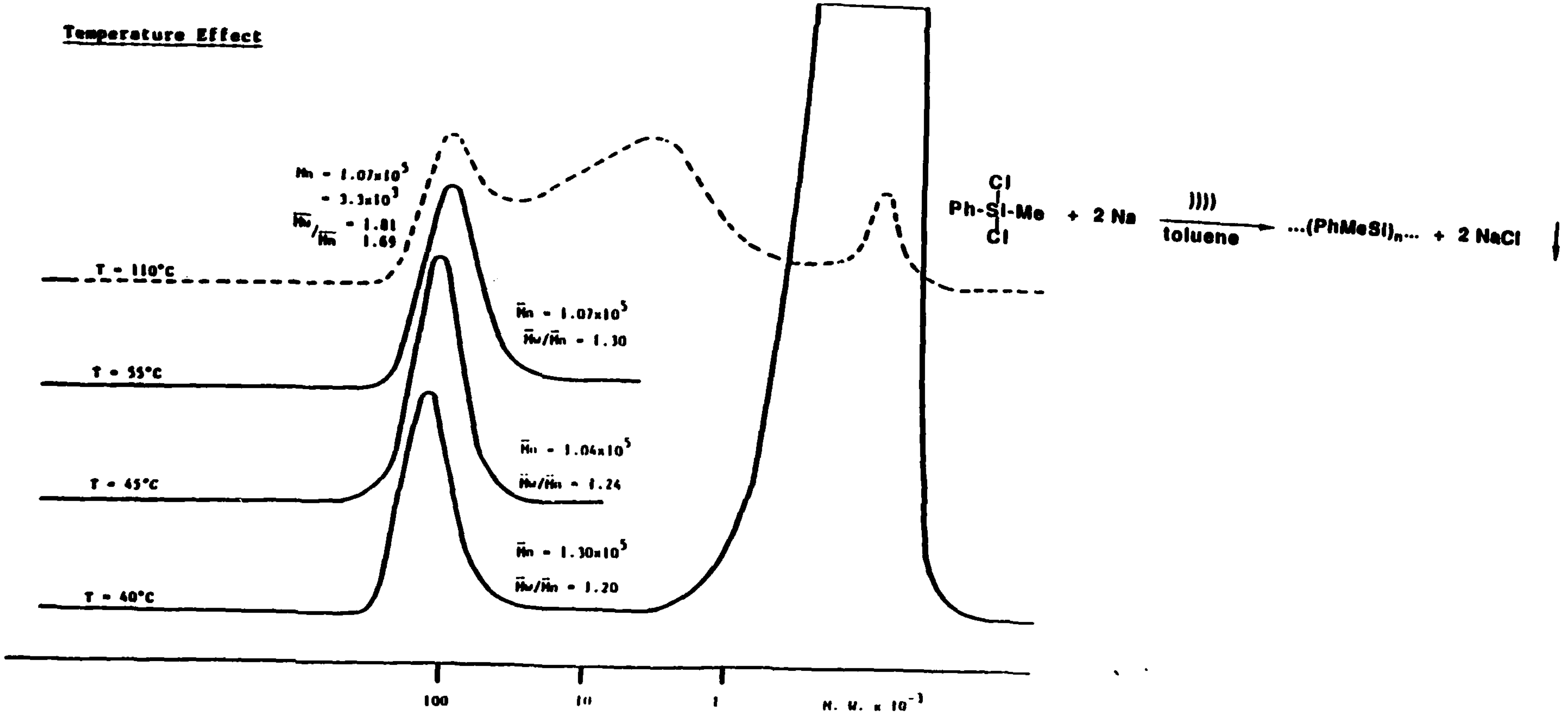

CF3CH2O
P
Ph
CF3CH2O
+ N3 — SiMe3
-SiOR
-N2
CF3CH2O
P-N3
Ph
A
-N2
CF3CH2O
P=N-SiMe3
Ph
CF3CH2O
B
-SiOR
Ph
OCH2CF3
...-N
P
N
P
N
P
N-...
Random polymer

FIG. 1

DELOCALIZATION (λ_{max}) AS A FUNCTION OF DP OF $(SiMePh)_n$



SONOCHEMICAL SYNTHESIS OF POLYSILANES AT AMBIENT TEMPERATURES

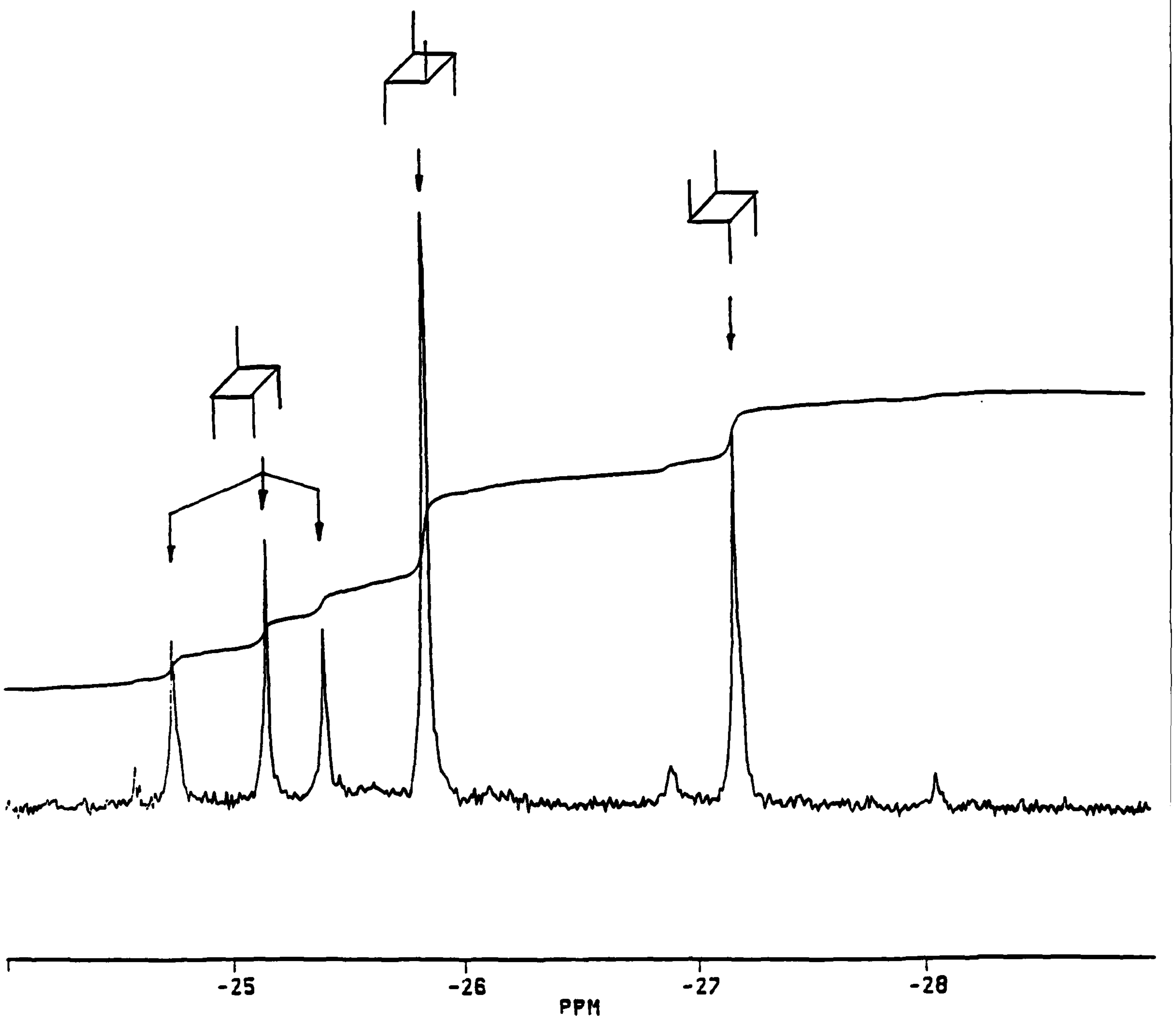


$$\text{Ph-}\overset{\text{Cl}}{\underset{\text{Cl}}{\text{Si}}}\text{-Me} + 2\,\text{Na} \xrightarrow[\text{toluene}]{))))} \ldots(\text{PhMeSi})_n\ldots + 2\,\text{NaCl}\downarrow$$

1. No low molecular weight polymers (<10k)
-suppression of side reactions at lower T

2. Low polydispersities ($M_w/M_n < 1.2$)
-selective degradation of HMW fraction by shear forces
(homolytic cleavage)

Fig. 3



M_n OF POLY(METHYLPHENYLSILYLENE) AS A FUNCTION OF INITIATOR CONCENTRATION

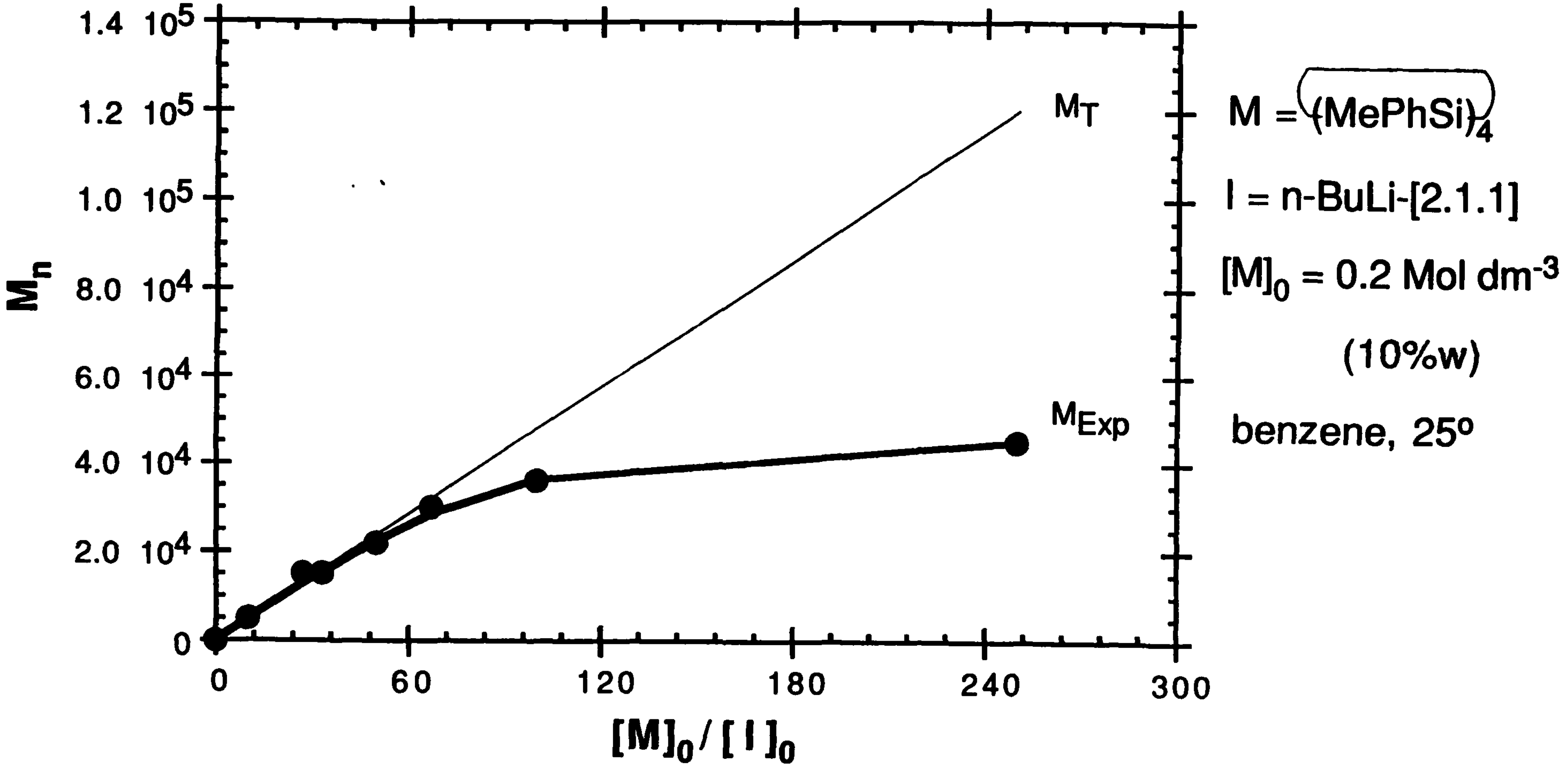
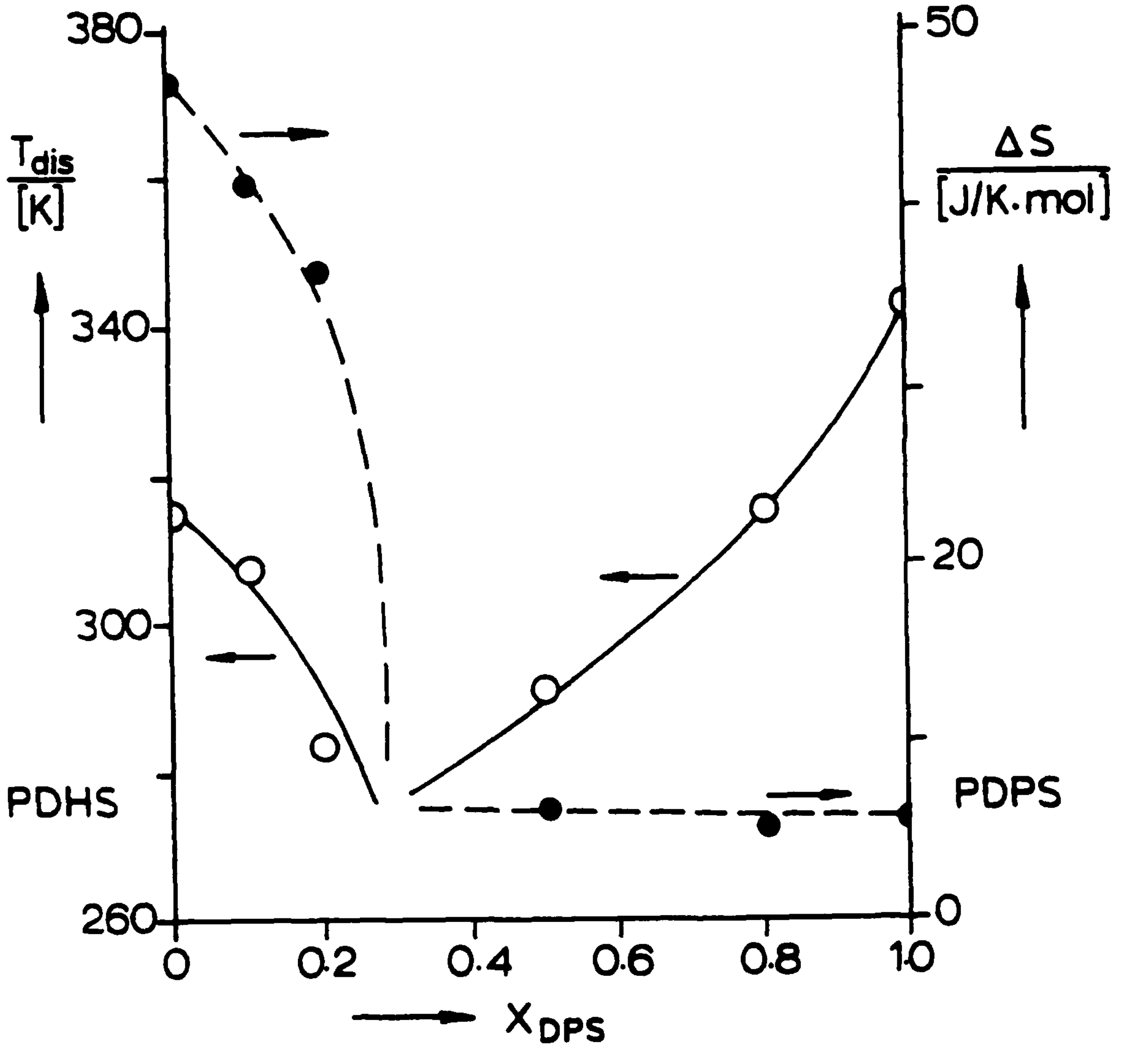


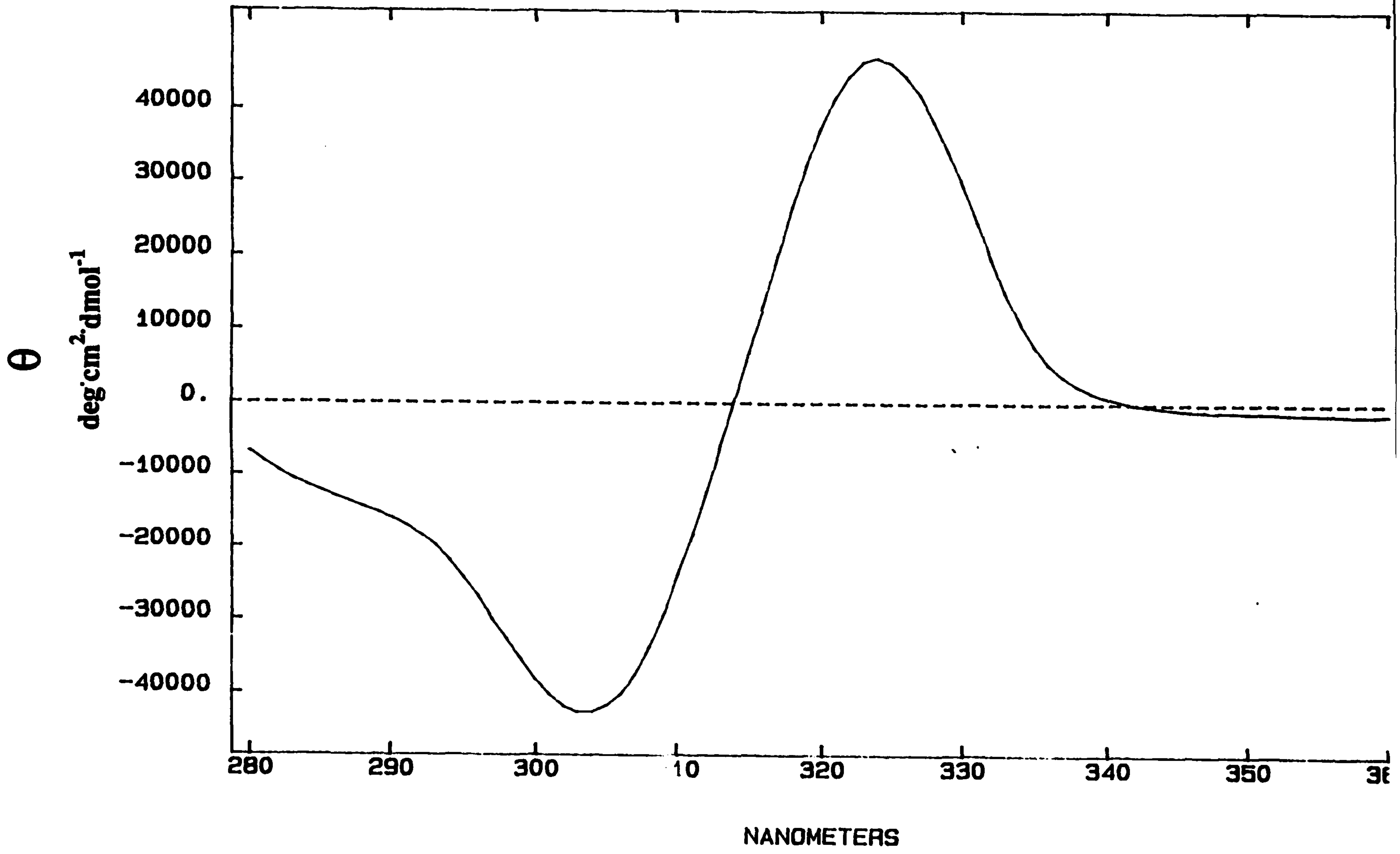
Figure 5

Transition Entropies and Temperatures of P(DHS/DPS) versus Composition



CD SPECTRUM OF THIN FILM (≅200 nm) OF POLY[$(DPS)_{0.90}$-co-$(DiP^*S)_{0.10}$]

annealed at 100 °C



300 & 620 MHz ^{1}H NMR SPECTRA OF POLY(PHENYLTRIFLUOROETHOXYPHOSPHAZENE)