REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. AGENCY USE ONLY *(Leave blank)*	2. REPORT DATE June 1994	3. REPORT TYPE AND DATES COVERED Preprint Book Chapter for EOY 06/93-06/94

4. TITLE AND SUBTITLE
NOVEL OPTICAL AND MECHANICAL PROPERTIES OF
DIACETYLENE CONTAINING SEGMENTED POLYURETHANES

5. FUNDING NUMBERS
N00014-91-J-1381

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8. PERFORMING ORGANIZATION REPORT NUMBER
Technical Report No. 17

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10. SPONSORING / MONITORING AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES
Manuscript Book Chapter accepted for publication in Thermoplastic Elastomers, Second Edition, G. Holden, N. Legge, R. Quirk, H. Schroeder, Eds., Hanser Publishers, 1994.

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13. ABSTRACT *(Maximum 200 Words)*

The extremely versatile class of thermoplastic elastomers known as segmented polyurethanes has expanded from its roots as processible rubbers to include materials for the high technology industry. Today, SPU's are found in biomaterials, optical adhesive and waveguide materials, and protective coatings for microelectronics packaging. Functionalization of a segmented polyurethane with linear or nonlinear optical moieties presents the opportunity to develop thermoplastic elastomers which play an active, rather than a passive, role in sensors, optical switches, and other devices. The ability to couple the optical and mechanical behavior of a TPE presents a world of opportunities, which include the ability to process highly oriented, optically anisotropic materials, and the possibility of an extensible mechano-optic sensor which may be coated onto a surface or molded into any number of desirable shapes. The development of a new series of diacetylene-containing elastomers has successfully combined the elastomeric properties of segmented polyurethanes with the optical properties of polydiacetylenes. This new class of materials has ushered thermoplastic elastomers into the arena of optical polymers and smart materials.

14. SUBJECT TERMS
Segmented Polyurethanes, Diacetylene-Containing Polyurethanes, Diacetylenes, Polydiacetylenes, Polyurethane-Diacetylenes, Opto-Mechanical Properties, Chromism, Elastomers, Smart Materials

15. NUMBER OF PAGES
40

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
UNCLASSIFIED	UNCLASSIFIED	UNCLASSIFIED	UL

19961016 262

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GRANT or CONTRACT N00014-91-J-1381

R&T Code 313M007
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Technical Report No. 17

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Published

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Thermoplastic Elastomers, Second Edition,
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Hanser Publishers (1994).

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June 1994

Novel Optical and Mechanical Properties of Diacetylene Containing Segmented Polyurethanes

Paula T. Hammond and Michael F. Rubner[a]

I. Introduction

Introductory Remarks

The extremely versatile class of thermoplastic elastomers known as segmented polyurethanes has expanded from its roots as processible rubbers to include materials for the high technology industry. Today, SPU's are found in biomaterials, optical adhesive and waveguide materials, and protective coatings for microelectronics packaging. Functionalization of a segmented polyurethane with linear or nonlinear optical moieties presents the opportunity to develop thermoplastic elastomers which play an active, rather than a passive, role in sensors, optical switches, and other devices. The ability to couple the optical and mechanical behavior of a TPE presents a world of opportunities, which include the ability to process highly oriented, optically anisotropic materials, and the possibility of an extensible mechano-optic sensor which may be coated onto a surface. or molded into any number of desirable shapes.

The development of a new series of diacetylene-containing elastomers has successfully combined the elastomeric properties of SPUs with the optical properties of polydiacetylenes[1-3]. This novel class of materials has ushered thermoplastic elastomers into the arena of optical polymers and smart materials. In the polyurethane-diacetylene (PU-DA) copolymers, a polydiacetylene network is produced in the hard domains upon irradiation in the solid state. The resulting cross-polymerized polyurethanes undergo color changes that are inherently coupled to elastomeric strain (mechanochromism), as well as to temperature changes (thermochromism). The mechanochromic behavior in the diacetylene SPU's has been observed up to 700% strain, and involves dramatic color changes from blue to red or yellow. The chromic responses are generally reversible within a given strain or temperature range. The chemical structure of PU-DAs may be altered to vary the mechanical and elastomeric properties from very stiff, small strain materials to highly viscoelastic, soft rubbers. Such alterations change the range of mechanochromic response as well as the potential applications of these materials.

As mentioned above, the PU-DA's are candidates for mechano-optic stress or pressure sensors, and the excellent coating properties of polyurethanes make sensory coatings an interesting application. Additonally, the polydiacetylene backbone of the polyurethanes provides a molecular scale probe of the level of stress within the hard (or soft) segments. The visible absorption spectra of the highly anisotropic PDA chain can be used with visible dichroism to gain information on the orientation of polymer segments upon deformation, processing, or heating. The PU-DAs discussed in this review also provide new opportunities in the area of post-processible thermoplastics; the solid state topochemical polymerization of the diacetylene groups produces a covalently bonded network of conjugated polydiacetylene chains. Following processing of the elastomer into a specific form, such as a film or fiber, ultraviolet light or other forms of irradiation can be used to convert the thermoplastic into a thermoset. The degree of effective crosslinking imposed on the polyurethane can be controlled to induce conversion of an initially low modulus elastomer to a strong, tough rubber, and ultimately to a high modulus, brittle material by simply adjusting the radiation dosage.

Since the initial synthesis of the polyurethane-elastomers, considerable effort has gone towards understanding their mechanical, thermal and optical behavior. This review will detail some of the most important findings of these studies. The importance of this new class of materials in the areas of sensor technology, optical spectroscopy of polymers, and materials post-processing has been noted; however, the diacetylene-containing elastomers also offer a prime example of the interplay between conventional polymer science and optically responsive organic materials.

Overview of Diacetylenes and Diacetylene Macromonomers

The polymerization of diacetylene groups is a solid-state, topochemical process which was first characterized by G. Wegner[4, 5]. Diacetylene monomer, arranged in a crystal lattice, undergoes a 1,4 addition with its nearest neighbor to yield a conjugated polymer. The diffusionless process involves rotation of the monomer units within the lattice. Generally, the substituents remain in approximately the same positions throughout the reaction as the diacetylene groups shift in position to attain contact with adjacent groups. For this reason, changes in crystallographic spacing and symmetry following topochemical polymerization are relatively small . For a large number of monomers, this process occurs in one solid phase, thus yielding perfect polymer crystals [6]. Methods such as optical spectroscopy and gel permeation chromatography have been used to observe high degrees of polymerization in single crystals[7]. The reactivity of diacetylene monomers is determined in large part by the packing of the monomer unit; the topochemical polymerization can only take place in an ordered lattice of monomer molecules stacked such that specific geometric constraints on parameters such as stacking distance (d) and angle between the polydiacetylene axis and the diacetylene monomer (γ) are satisfied , as shown in Figure 1a)[8]. Diacetylene reactivity is also affected by the mobility of the side group. Even with the appropriate lattice parameters d and γ, some diacetylenes may not be reactive due to the lack of flexibility of the substituent R group.

The linear optical properties of polydiacetylenes are highly dependent on the effective conjugation length of the main chain. The effective conjugation length is loosely defined as the distance in number of p orbitals along which electrons can travel; higher conjugation lengths result in lower energies required for electronic processes in the polymer. Changes in the effective conjugation length result in subsequent changes in the wavelength of absorption in the visible spectra. Other effects, such as direct tension or compression effects on the en-yne alternating backbone, and electronic interactions with the substituent sidechain groups, can also affect the energy at which a polydiacetylene chain absorbs in the visible region. These effects often give a color change with changes in temperature or application of stress, and are known as thermo- or mechano-chromism, respectively. Chromism may also be observed upon solvation or extraction of polydiacetylenes. In studies of thermochromic behavior in soluble polydiacetylenes, the changes in the visible absorption spectra have been correlated to changes in the polymer conjugation length[9] due to a loss of planarity along the polymer backbone during the solvation process. This information, followed by FTIR and NMR studies of substituted polydiacetylenes, led to the realization that chromism is driven primarily by conformational changes of the polydiacetylene chain, rather than changes in its electronic bonding state[10, 11-12].

The conjugated, one dimensional backbone of polydiacetylene chains and their highly ordered states are the source of many interesting optical and electrical properties in addition to chromism. Although polydiacetylenes cannot be doped to obtain metal-like conductivity, they have very large electronic carrier mobilities along the chain direction ($> 10^3$ cm^2 v^{-1} sec^{-1}), making these materials of interest for electronic devices [12]. It has been found that ion implantation of some polydiacetylene crystals using ion beam irradiation increases their conductivity by fifteen orders of magnitude[13]. The optical properties of polydiacetylene also include a large $X^{(3)}$ nonlinear optical susceptibility coefficient. This has sparked interest in the use of diacetylene-containing materials in electro-optical and optical devices. The polydiacetylene backbone vibrations are also Raman active; therefore, Raman spectroscopy has been used to characterize the vibrational modes in polydiacetylene crystals[14, 15]. Because polydiacetylene vibrations change frequency with the application of stress, large single crystal "fibers" have been used to determine strain distributions of fibers imbedded in a composite matrix [16-18]. The stress state of the polydiacetylene backbone can be measured accurately even in thick or opaque samples using Raman spectroscopy. The resolution of frequency vs. strain plots is extremely high for polydiacetylenes, and researchers have used polydiacetylene crystals as molecular "strain gauges" in composites.

Segmented Polyurethane-Diacetylene Macromonomers

Linear polymers containing diacetylene groups within the repeat unit also have been synthesized and characterized. Such polymers are often referred to as *macromonomers*; when exposed to heat or light radiation, the diacetylene units react with neighboring macromonomers to produce a conjugated backbone transverse to the chain direction of the macromonomer[4]. For the topochemical reaction to occur, the geometrical packing criteria discussed earlier must be met; therefore, well ordered semi-crystalline polymer systems are often more reactive. However, amorphous polymers have also been found to react, particularly if some type of paracrystalline or semi-ordered state exists. The macromonomer reaction process, termed cross-polymerization to distinguish it from the more typical random polymer crosslinking, is shown in Figure 1b.; in the schematic, a polymer with alternating rigid and flexible groups is shown to undergo cross-polymerization.

On the premise that an ideal material would have the tough elastomeric properties of a thermoplastic elastomer, and the chromic properties of polydiacetylene chains, the Rubner research group developed a series of segmented copolymers which contain diacetylene groups incorporated in the hard segments [1]. Upon exposure to suitable radiation or thermal annealing, the diacetylenes undergo solid state topochemical reaction to form a conjugated polydiacetylene network connecting the host polyurethane segments. This cross-polymerization process imparts large differences in the mechanical and optical properties of the polyurethanes, with only small morphological changes.

The structures of the polyurethanes designed and synthesized by Rubner and associates are shown in Figure 2. The polymers consist of urethane-diacetylene hard segments for which the average number of diisocyanate monomer units incorporated per segment is two. The hard segments alternate with polytetramethylene oxide (PTMO) soft segments with molecular weights of 1000, 2000 and 3000. The hard segment structures are varied to obtain a range of morphologies and mechanical characteristics. Hard segmentys based on 4-4' methylenebis(phenyl isocyanate) (MDI) based hard segments contain two aromatic rings between the polyurethane linkages to provide a semi-rigid hard segment structure. Hexamethylene diisocyanate (HDI) is used to obtain a highly regular, aliphatic hard segment. In all cases, the diol chain extender contains the diacetylene group. The length of the chain extender is either one methylene group (2,4 diacetylene diol) or four methylene groups (5,7 diacetylene diol). The nomenclature used for the series of PU-DAs investigated by the Rubner group is as follows: Hard Segment type-Chain extender- PTMO molecular weight (e.g. HDI-2,4-1000). This nomenclature will be used throughout this review to refer to this set of polyurethanes.

The polyurethanes are synthesized using a two step solution polycondensation method. First, dihydroxyl terminated PTMO is endcapped with diisocyanate using a 2:1 ratio of isocyanate to PTMO. Next, the diacetylene diol chain extender is added in a 1:1 ratio with the PTMO prepolymer. This second step results in the formation of polyurethane linkages as the molecular weight of the polymer increases. The weight average molecular weights of these materials range from 30,000 to 100,000 or greater. The use of the two-step solution polymerization differs from many industrial methods such as one shot bulk polymerizations or reaction injection molding, which generally result in a very large distribution of hard segment sizes. The size distribution of hard segments is expected to be much narrower for the PU-DAs. The well-defined chemical structure of these materials make them ideally suited for morphological and mechanical studies.

Segmented polyurethanes with diacetylene groups were also introduced by .Liang and Reiser at approximately the same time as Rubner's materials[19]. The intended application of the Reiser polyurethanes was for use as deep UV photoresist materials. The hard segments were based on hexamethylene diisocyanate or on cyclohexanediyl diisocyanate, using 2,4-hexadiyn-1,6-diol as a chain extender. The soft segments used included polytetramethylene oxide, polybutadiene, polycaprolactone, and poly(dimethylsiloxane-ethylene oxide)dicarbinol. In their investigations, the authors exposed select areas of polyurethane-diacetylene films to UV light using a photolithographic mask, and then used a variety of solvents to wash away the unexposed areas. The photoreactivity of each of the various polymers has been investigated, and a detailed study has been completed on the effects of segmented polyurethane morphology on UV reactivity[20].

More recently, other researchers have also begun to synthesize and examine the properties of the PU-DAs. These groups include the work of Young and associates[21-23], who have developed polyurethanes of similar structure to those of Rubner, but using a single step bulk polymerization method that results in different polydispersities and film morphologies. A primary focus of this work has been to examine the optomechanical properties of the polymers using Resonance Raman spectroscopy to measure stress in the polydiacetylene backbone during deformation. Huang and Edelman have recently produced polyetherurethaneureas that contain diacetylene groups in the hard segments[24]. These materials are synthesized from hexamethylene diisocyanate, 2,4-hexadiyn-1,6-diol, and an amine terminated oligoether. A range of morphologies were obtained by varying the amount of hard segment; the diacetylene reactivities were seen to vary with morphology as well.

It is evident that there are many aspects of the family of segmented PU-DAs that have been addressed, or are under current investigation. The research efforts mentioned above will help to expand the horizons for applications of these novel materials. This review will focus primarily on the investigations of the Rubner research group, introducing the more general aspects and properties of diacetylene-containing segmented block copolymers, as well as their unique crosslinking capabilities and optical properties.

II. Characterization of Polyurethane-Diacetylene Segmented Elastomers

WAXD and Thermal Characterization of PU-DA's

Segmented polyurethanes phase segregate to form thermodynamically favored "hard" and "soft" domains. For the PU-DAs the reactive diacetylene groups reside in the hard domains. It is within these domains that cross-polymerization takes place. The rate and extent of diacetylene polymerization is affected by the order and packing characteristics of segments in the hard domain. As with most segmented polyurethanes, the hard domain order is dependent on the history of the sample. The morphology of the segmented PU-DAs also affects their mechanical properties, deformation behavior of the films, and mechanochromic response. Given the importance of the phase morphology, the thermodynamic behavior, and the ordering of the PU-DA's, this section will address these basic characteristics of thesepolymers.

The thermal transitions of some of the PU-DAs, as determined by differential scanning calorimetry, are shown in Table 1[25]. The samples used were cast from a toluene/tetrahydrofuran solvent combination that has been shown to best promote phase separation and more ordered hard domains. Endothermic melt transitions at approximately 100°-120°C have been observed for each of the elastomers, with the exception of MDI-2,4-1000. These transitions are due to melting of the crystalline portions of the polyurethane hard domains, as indicated by DSC, TMA and visual observations of melt behavior[3]. The most pronounced melt endotherms, with the largest enthalpies are those of HDI-5,7-1000 and -2000, indicating that the HDI polyurethanes are considerably more crystalline. On the other hand, MDI-2,4-1000, which contains 32% hard segment by weight, is non-crystalline; no high temperature peaks appear for this material (see Table 1). WAXD results verify these findings, indicating sharp, distinct Bragg reflections for the HDI polymers, but no crystalline refections for the MDI polymers. Reasons for the low crystallinity of MDI-2,4-1000 include the lack of flexibility needed for the somewhat bulky MDI unit to achieve crystallinity with an average hard segment size of only two MDI units. Increasing the length of the chain extender apparently allows the additional flexibility needed for a small amount of crystalline ordering to occur, and a small melt endotherm is observed for MDI-5,7-1000.

Glass transition temperatures of each of the polyurethanes are also listed in Table 1. The HDI materials indicate lower glass transitions than the MDI systems of the same PTMO molecular weight, an indication that the degree of phase separation is greater in the aliphatic HDI polyurethanes. The aliphatic, crystalline nature of the HDI hard segments appears to make the HDI systems the most highly phase separated of this series. The effect of doubling the PTMO molecular weight is to increase the degree of phase separation, as seen by the change in the glass transition temperature of -20°C. Soft segment crystallization is also observed in the PTMO 2000 polymers, as shown by the low termperature melt endotherms present in those elastomers. Infrared spectral analysis of the PU-DAs was used to attain a better sense of the phase segregation in these copolymers. A convenient measure of phase separation that has been used in other polyurethane studies is a measurement of the fraction of inter-urethane bonded carbonyl[26]. The ratio of hydrogen bonded carbonyl absorbance versus total carbonyl absorbance is determined and used as a comparative measure. It was found that cast films of the PU-DAs exhibited a wide range of inter-urethane bonding. HDI-5,7-1000 had the highest percentage of inter-urethane bonding both before and after annealing, indicating the largest degree of phase segregation. HDI-2,4-1000 has the next highest fraction, followed by the MDI elastomers, both of which exhibit the lowest degrees of phase segregation.

All of the PU-DAs exhibit exotherms at 200°C-300°C or greater. This exotherm has been attributed to a combination of thermally induced liquid state cross-polymerization, and thermal degradation. Thermal studies have shown that the size of these exotherms generally decrease with irradiation, indicating that some of the enthalpy is probably due to polymerization of the diacetylene groups in the liquid state; thermal gravimetric analysis indicates that degradative weight loss is also observed at these temperatures. This phenomenon has been observed with a large number of diacetylene monomers and macromonomers.

Studies of Domain Morphology

Small angle X-ray scattering has also been used to study the morphology of the segmented polyurethanes[27]. The average d spacing obtained from these studies gave a general idea of the characteristic domain size for each polymer. HDI-5,7-1000 and -2000 exhibit interdomain spacings of 130 and 140 Å respectively; these values are roughly twice the length of the HDI hard segment (70 Å), and are close to the expected average length obtained from the two step polymerization process. MDI-2,4-1000 and MDI-5,7-1000 films have long spacings of 82 and 91 Å; the length of the MDI 2,4 hard segment is 30 Å. A SAXS Porod analysis confirmed that the phase interface is more diffuse for MDI elastomers than for HDI based copolymers. The relative degree of phase separation, as determined by the electron density variance and Porod's invariant, was also lower for the MDI as compared to the HDI elastomers. Finally, it was found that cross-polymerization had little or no effect on any of these parameters, confirming the idea that morphology is not disrupted by cross-polymerization.

To further develop models of this unique series of PU-DAs and their mode of deformation, an electron microscopy study of their morphology and microstructure also has been performed[28, 29]. This study has provided important information on both the superstructure and microstructure of the MDI and HDI polyurethanes, as well as some verification of preliminary models derived from thermal analysis and X-ray scattering. Transmission electron microscopy (TEM) was used to examine the thick (0.125 mm) solution cast, electron beam irradiated films used for mechanical and mechano-optical testing, as well as extremely thin films of polymer cast from solution directly onto TEM copper grids, and then irradiated with UV light.. The thin films that were examined were quite illustrative of the representative morphologies of each of the polyurethane types. Figure 3a contains a TEM micrograph of HDI-5,7-1000; the darker regions contain the osmium stained hard domains, and the light regions are soft segment rich domains. A pre-spherulitic (hederitic) superstructure is evident throughout this film, with electron dense centers of approximately 0.8 to 1.0 microns in size. The branches split into many fine hair-like fibrils which are approximately 100 to 200 Å wide. In general, the hard and soft domains form phases which are well-defined, with sharp phase boundaries and an organized interconnected superstructure. In contrast, MDI-2,4-1000 exhibits an ill-defined superstructure, as shown in Figure 3b). The macrostructure consists of hard segment rich globules dispersed in a continuous soft segment phase. Both the sizes and shapes of these structures are irregular; the diameters of the dark domains range from 0.1 to 6 microns in diameter. The phase boundaries between hard and soft domains appear to be more diffuse than that of HDI-5,7-1000, which suggests a lower degree of phase separation in this polymer. Unlike the HDI-5,7-1000 films, the hard and soft domains do not appear to be highly interdispersed, and there is no apparent connectivity between the isolated hard domain superstructures.

The mechanical and mechanochromic measurements of these materials were actually done on much thicker films cast during a slow, 2 or 3 day solvent evaporation period under a steady nitrogen flow. TEM revealed that the superstructures observed in the slow evaporated thin films had coalesced into larger two dimensional structures in the film. Spherulites became flattened disks in the plane of the film, and cross-sections perpendicular to the film plane revealed lamellar domains with much greater thicknesses of 300 to 400 Å, thought to be the result of coalescence of two or more hard domains during the solvent evaporation process. Figure 3c) shows a cross-section of an HDI-5,7-2000 slow-evaporated film. It is clear that the major aspects of the polyurethanes's morphology - well phase-separated and highly interconnected domains - are visible in these samples, as well as in the thin films.

III. Mechanical Properties of Polyurethane-Diacetylenes

The tough elastomeric properties of segmented polyurethanes have been attributed to the dissipation of stress through the deformation and reorganization of the hard domains. Therefore, it is important to understand specifically the effect of hard domain cohesiveness and rigidity on polyurethane mechanical behavior. The polydiacetylene backbone can be formed in both highly organized, interconnected crystalline PU-DA hard domains and in poorly ordered, non-continuous paracrystalline domains. The reactivity, extent of polymerization, and therefore the effective increase in rigidity of the hard domains and change in tensile properties differs for each of these cases. The examination of the mechanical properties of these two types of polyurethane materials presents the opportunity to gain a deeper understanding of deformation for two morphological extremes.

Effects of Molecular Weight and Annealing on Uncross-polymerized Elastomers

The mechanical properties of a select number of PU-DAs of varying molecular weight were determined by Nallicheri and Rubner,[25] and are shown in Table III. Each of the elastomers exhibits a relatively low initial modulus at very low strains of 2 to 5%, followed by strain softening as the polymer is extended to strains of 200% and higher; in some cases, the modulus increases at higher strains due to strain-induced crystallization of the soft segments. The moduli, ultimate tensile strengths, and ultimate strains observed for these polyurethanes are close to those of other SPUs with similar composition and molecular weights [30]. In comparing the mechanical properties of these polymers to common industrial polyurethanes, it should be kept in mind that the percentage of hard segment in the PUDAs is relatively low, ranging from 22 to 35%, and that a two step synthesis was used, rather than a single step reaction injection molding process which results in a broader distribution of hard segment lengths.

Increased molecular weights result in higher ultimate tensile strengths, but little or no change in the ultimate strain or the initial modulus. The increases in UTS observed here are similar to those observed in bulk polymerized polyurethanes with increasing molecular weights by Schollenberger[31] . As the molecular weight is increased, the number of hard domains that a single polymer chain passes through increases, as well as the number of chain entanglements present in the network. The overall effect is a more interconnected, well established network. Annealing was also found to greatly increase UTS, through the formation of larger, more stable domains and improved crystalline or paracrystalline ordering.

Effects of Diacetylene Cross-Polymerization on Thermal and Mechanical Properties

Each of the PU-DAs undergoes cross-polymerization of the reactive diacetylene groups when exposed to gamma or electron beam irradiation; some are also reactive to ultraviolet light or high temperature annealing. The cross-polymerization process manifests itself as a dramatic color change from translucent, colorless films or powders to deep blue, purple or red materials (the color depends on the material and the sample history). The colors are the result of the presence of conjugated polydiacetylene chains, which absorb strongly in the visible light region; linear optical effects will be discussed in detail in Section IV.

The cross-polymerization process has a large effect on the thermal properties of the PU-DAs. Figures 5a and b show the thermal mechanical scans of the elastomers before and after exposure to large dosages of gamma radiation. The softening points of the original polymers, which were all found to be at or near the melting point, disappear almost completely in the highly cross-polymerized materials. This indicates the formation of an infusible polymer network. Interestingly, the glass transitions of the soft segments from TMA do not change very much upon cross-polymerization, illustrating that the polyurethanes are only crosslinked within the hard domains. If there are diacetylenes present in the form of phase-mixed hard segments in the soft domains, they are either completely isolated from each other, or are not present in a form that is ordered enough to support topochemical diacetylene polymerization. To demonstrate that the improved thermal stability was due solely to the polymerization of reactive diacetylene groups, Rubner also exposed a conventional polyurethane prepared from MDI, butanediol, and PTMO to the same amount of gamma radiation, and found no significant increase in the temperature of the softening point for this non-diacetylenic counterpart.

Figure 6 displays the stress-strain curves of MDI-5,7-1000 of different molecular weights, as a function of electron beam radiation dosage. Greater levels of radiation dosage result in higher degrees of cross-polymerization; therefore, these two parameters are used interchangeably. It is apparent that the mechanical behavior of this MDI based polyurethane is strongly influenced by the cross-polymerization process. The molecular weight is also clearly a factor in the degree of change obtained from the formation of a cross-polymerized network, as seen in Figure 6. The ultimate tensile strength of the lowest molecular weight sample of MDI-5,7-1000 is increased by a factor of more than two as the sample is exposed to up to 10 Mrad of electron beam irradiation. Beyond this point, the UTS decreases again. The ultimate tensile strain decreases with increasing radiation dosage. These observations can be explained by examining a model of deformation for MDI elastomers. The phase morphology of the MDI polyurethanes is less interconnected, and therefore the hard domains act as reinforcing crosslink points, virtual crosslinks that connect soft segments to form a network. Deformation involves the extension and alignment of the soft segment at low and moderate strains, and finally the plastic deformation of the hard domains at high strains. The increased rigidity of the hard domains achieved by diacetylene cross-polymerization causes a strain amplification effect in the soft segments, as the local strain within the soft domains exceeds the macroscopic strain level. This causes orientation and crystallization of the soft segment, which in turn reinforces the polymer. The increased cohesion of the hard domains also enhances the overall rigidity of the sample, and results in some increase in modulus as well. At very high irradiation levels, the hard domains become crosslinked to the point that plastic deformation can no longer take place at high stress. The result of this embrittlement is that the ultimate tensile stress decreases as the hard domains become less efficient at warding off the propagation of cracks. Thus, there exists an optimal level of irradiation at which the UTS reaches its maximum value.

When the molecular weight is increased, the effects of cross-polymerization become less significant. The higher molecular weight samples have more fully established virtual crosslinks due to the larger number of hard segments per polymer chain. The effects of chain pullout and slippage are reduced for the high molecular weight polymers. It is for this reason that the effects of cross-polymerization are not as strongly felt in these cases. This appears to be true in general for any form of improved hard domain reinforcement. For example, well annealed samples also show less sensitivity to the effects of cross-polymerization. Generally, molecular weight or annealing effects that improve the ultimate tensile strength increasing the cohesion of the hard domain structure render further improvements obtained from cross-linking less noticeable.

The stress-strain curves of HDI-5,7 -1000 and HDI-2,4-1000 elastomers as a function of radiation dosage are shown in Figure 7. The phase morphology of these elastomers is highly interconnected and well phase-separated; the hard domains are known to be highly crystalline as well. The application of strain to the HDI polyurethanes results in simultaneous deformation of the hard and the soft domains. Cross-polymerization increases the rigidity of the hard domains, rendering them less deformable. The tensile strength is increased as the hard domains are reinforced, and the loss of plasticity of the hard segments results in lower ultimate strains, as well. There is no strain amplification effect because the soft segments are not able to become fully extended in the HDI morphology. However, the interconnected nature of the domains means that modifications to hard domain rigidity greatly affect modulus. The 100% strain modulus, in fact, increases by a factor of 2 when exposed to 0.56 Mrad.

The mechanical behavior of the HDI-based PU-DAs is generally less responsive to radiation-induced changes. This is consistent with the fact that the hard domains are well phase-segregated and highly crystalline. The well-ordered domains do not experience as dramatic an improvement in ultimate tensile strength. The sensitivity of the cross-polymerization effects to molecular weight and annealing has not been measured at this time. Preliminary experiments suggest that molecular weight is not as dominant a variable as it is with the MDI based equivalents.

Measurements of the percent hysteresis exhibited in the polyurethanes with increased degrees of cross-polymerization support the models of mechanical deformation described above[32]. Cross-polymerization of MDI-5,7-1000 resulted in a decrease in hysteresis; this is due to the reinforcement of hard domain cohesion. The hard domains were less likely to break-up prematurely when crosslinked, thus reducing energy losses and permanent set. Alternately, cross-polymerization of HDI-5,7-1000 resulted in an increase in hysteresis. In this case, deformation involves the simultaneous disruption of highly interconnected hard and soft domains. Crosslinking the hard domains only serves to increase the energy losses experienced with strain, as more irreversible plastic deformation is required to extend the polyurethane.

Cross-polymerization also affects the thermal and swelling characteristics of PU-DA elastomers. The melt/disordering endotherms of the moderately crosslinked elastomers used for the mechanical studies exhibit broadening, decreased enthalpies, and higher temperatures than the non-irradiated equivalents. The fact that the melt endotherm is still present indicates incomplete conversion, and therefore, some mobility of the polymer chains. Highly cross-polymerized samples exhibit no endotherms, and have very poor mechanical strength. Lightly cross-polymerized PU-DAs swell in solvents such as toluene and THF. In fact, the degree of swelling can be controlled by varying the degree of cross-polymerization.

IV. Linear Optical Properties of Segmented Polyurethane-Diacetylenes

Each of the MDI and HDI series of PU-DAs can be cross-polymerized using ultraviolet light or electron beam irradiation to give highly colored elastomeric films.

The color obtained, generally blue, purple or red, reflects the degree of planarity and the static strain effects of the resulting network of conjugated backbones. The optical absorption spectra of polydiacetylene chains are expressions of the relative amounts of order, packing, and degree of strain experienced by the conjugated backbone in its host environment. It is therefore possible to use the polydiacetylene chain as a visual monitor of changes that take place within the host monomer or polymer matrix. Thus it indicates whether that matrix is an amorphous or highly ordered crystalline environment, and whether it is in the solid, liquid, or solvated states. The rich morphologies of the polyurethanes provide an opportunity to examine the relationships between the absorption spectra or color and the status of the host system.

Thermochromism

A comprehensive examination of the thermochromic behavior of cross-polymerized PU-DAs illustrates the different types of chromism that can be observed in these polymers[2]. Specifically, the optical changes observed for HDI-5,7-1000 were found to be quite different in nature from those of HDI-2,4-1000 and the MDI systems. In every case, the spectral shifts and variations in linewidth could be correlated to molecular processes taking place within the hard domains of the polyurethanes as the temperature was increased. For the visible absorption studies discussed below, the hard domains of all polyurethane films were lightly cross-polymerized (< 5% crosslinked) by exposing cast films to UV or electron beam irradiation. At such low levels of cross-polymerization, the films remained transparent, although deeply colored, allowing the visible spectroscopy to be done in transmission mode. Under these circumstances, the predominant host environment of the polydiacetylene chains is that of the original polyurethane host hard segments to which the conjugated backbone is covalently bonded.

Figure 8 shows the visible absorption spectra of cross-polymerized HDI-2,4-1000 taken at increasing temperatures. At room temperature, an excitonic peak at 570 nm is visible, along with a broad second band representative of a large distribution of conjugation lengths present in the polydiacetylene. The vibronic sidebands of the conjugated bonds in the hard domain are convoluted with this second peak. Upon heating, the excitonic peak gradually decreases in intensity as the absorption band shifts to higher energies; these effects occur as the polymer undergoes thermal expansion, and finally begins to melt at higher temperatures. The peaks become broader with temperature, indicating a wide range of poorly organized polydiacetylene conformations present. The gradual shift to lower wavelengths and the loss of order observed in the spectra illustrate a clear example of an order-disorder transition. This transition is reversible up to 100°C, which is close to the melting temperature of the un-cross-polymerized polyurethane hard segments. Beyond this point, the disordering of the hard domains that is characteristic of the melting process induces irreversible changes in the conjugation length of the polydiacetylene backbone. As the melting range is spanned, the excitonic transition peak decreases in intensity until it is completely lost in a featureless band. The thermochromism is affected by the melting of the unreacted macromonomer lattice; in fact, fully cross-polymerized HDI-2,4-1000 does not undergo any melting behavior or thermochromic transition at all. The presence of residual diacetylene macromonomer in the lattice influences the conformation of the conjugated backbone.

At room temperature, the elastomeric film is deep red in color. As it is heated, the color changes from red to yellow. It has also been found that when cooling the film to liquid nitrogen temperatures, the film becomes blue. This color change is due to thermal contraction of the polymer lattice, which causes a gradual shift of the excitonic transition toward higher wavelengths, and is a direct result of the high coefficient of thermal expansion of this lightly cross-polymerized polyurethane-diacetylene. In summary, the HDI-2,4-1000 polymer undergoes chromic transitions that directly correspond to the thermodynamic changes in the host polymer lattice.

The nature of the thermochromic transition of HDI-5,7-1000 is quite different from that of the HDI-2,4 elastomer. Instead of a gradual order-disorder transition in which the features of the absorption curves become broadened and poorly defined, the spectra undergo dramatic changes while retaining a high degree of order. The visible absorption spectra taken during a series of heat/cool thermal cycles of cross-polymerized HDI-5,7-1000 are shown in Figures 9 a and b. The first excitonic transition slowly moves to lower wavelengths due to thermal expansion of the polyurethane matrix. An entirely new peak appears at 90°C and continues to increase in size with increasing temperature, at the expense of the original 650 nm peak. At 160°C, the original peak is completely replaced by the new one. The population of polydiacetylene chains then exists completely in this second, well-ordered phase at 511 nm.

The color changes observed during this thermochromic transition extend from a blue film corresponding to the original excitonic peak at 650 nm, to a yellow color characteristic of the new absorption curve. The thermochromism is completely reversible up to approximately 130°C. Above this temperature, the yellow phase remains highly visible in the spectrum upon cooling to room temperature, but the size of the blue phase is diminished. The blue phase does remain present when the temperature is returned to 25°C, however, even after cooling from 160°C. The coexistence of the two primary peaks suggest that they represent two thermodynamic phases in which the hard domains may exist, each with its own characteristic average polydiacetylene conjugation length. The yellow phase is at least as highly ordered as the blue phase, judging from the clear excitonic peak, and the well-defined vibronic sidebands that are visible in the room temperature spectra of Figure 9b. These sidebands, which appear at 475 and 462 nm, correspond to the double and triple bond vibrations of the conjugated polydiacetylene backbone; the definition of these peaks at higher temperatures was compromised by thermally induced line broadening. The presence of such a highly ordered visible absorption spectrum at such low wavelengths is quite rare for polydiacetylene containing materials. The implication is that a well ordered, regular arrangement of polydiacetylene chains exists that has a low effective conjugation length.

FTIR studies of the inter-urethane hydrogen bonding of the cross-polymerized polyurethanes indicate that cross-polymerization results in the retention of hydrogen bonding well above the original polymer melting points. However, a change in the slope of the percent inter-urethane bonding versus temperature curve is found for HDI-5,7-1000, as opposed to the constant slope derived for HDI-2,4-1000[3]. This slope change indicates a change in the thermal expansion coefficient of HDI-5,7-1000 at 90°C, and corresponds directly to the onset of the thermochromic transition observed optically. These findings imply that a crystallographic or conformational transition occurs at this temperature which involves a volume change of the original polymer lattice. In fact, to further understand what is taking place on a molecular level, Rubner performed the FTIR study of poly-ETCD mentioned earlier[10]; ETCD is a urethane substituted diacetylene monomer with a structure similar to that of the HDI 5,7 hard segments. It was found that the thermochromic transition of poly-ETCD involves a localized conformational rearrangement of the methylene spacer groups at the thermochromic temperature, which results in the relaxation of the conjugated polydiacetylene chain to a conformation less conducive to electron delocalization. NMR studies on poly-ETCD and on diacetylene-polyamides suggest that these conformational changes are trans-gauche transitions of the alkyl side groups. It is believed that HDI-5,7-1000 undergoes a similar conformational rearrangement to form the yellow phase. In both cases, it is the retention of hydrogen bonding which prevents complete relaxation and disordering of the polydiacetylene backbone. HDI-2,4-1000 undergoes thermal expansion and melting, and hydrogen bonding is ultimately lost in this system, as seen in an order-disorder thermochromic transition.

The visible absorption spectra of cross-polymerized MDI-2,4-1000 was taken at room temperature, and after heating to 120°C and cooling back to 25°C. A primary absorption peak at 630 nm was observed for this PU-DA. The lack of definition of the absorption band is due in part to the low degree of ordering and phase segregation in the polyurethane film. After heating MDI-2,4 -1000, permanent changes are seen in the absorption curve. The absorption band has shifted to higher energies, and an expansive, completely featureless curve at 500 nm remains. The gradual decrease in wavelength and broadening of the original bands that occurs upon increasing temperature is characteristic of an order-disorder transition, the result of the gradual disordering of the hard domains as the material is heated. Interestingly, the absorption spectral changes are analogous to those observed during the dissolution of soluble hydrogen bonded polydiacetylenes. The paracrystalline hard domains of the segmented polyurethane undergo a gradual breakup and disordering as the polymer is heated; these changes are irreversible, and the color change from purple to red becomes permanent upon heating.

Mechanochromism

Just as the visible absorption spectra of the conjugated polydiacetylene backbone is sensitive to changes in temperature, it is also responsive to mechanical stress and deformation. In fact, the polydiacetylene chain is a highly sensitive molecular probe that can be used to gain insight into the state of stress of its host lattice. The mechanochromic properties of the segmented polyurethanes can be used to observe the relative amount of stress experienced by the hard domains.

An additional aspect of the polydiacetylene backbone that can be exploited in mechanochromic studies is the anisotropy of the conjugated polymer chain. The optical absorption coefficients of polydiacetylene chains are highly directional, with the predominant component existing along the conjugated backbone. Dichroism measurements using polarized light can be used to assess the degree and direction of orientation of the polydiacetylene backbone within the hard domains. This technique, combined with the change in the shape of the absorption spectra with mechanical stress, provides the opportunity to closely examine the deformation process of the segmented polyurethanes with varying chemical structure, morphology, and hard domain rigidity. Several studies have been completed on the mechanochromism of the PU-DA segmented block copolymers[2, 33-35].

A simple mechano-optical measuring technique has been used to examine the chromic transitions and strain induced orientation in the hard domains of the polyurethanes. Thin films cast from a THF/toluene solvent mixture are irradiated to achieve low levels of cross-polymerization. The visible absorption spectra are measured during tensile deformation of the films. The sample is subjected to loading and unloading cycles at increasing levels of strain. For each strain level, horizontally and vertically polarized visible spectra are recorded while the sample is held in the strained state; the sample is then relaxed to zero load, and polarized spectra are measured in the relaxed state. The cycle is repeated to higher strain levels until the sample fails mechanically. Results for MDI-2,4-1000 are shown in Figures 10 and 11 for the stretched and relaxed state, respectively.

The visible spectra recorded at 0% strain represents the initial state of the polydiacetylene backbone; the lowest energy peak appearing at 625 nm is the excitonic peak typically seen in polydiacetylenes and is gives rise to the blue color seen prior to straining the MDI-2,4-1000 film. Figure 10(a) presents data obtained from the sample in the vertically polarized stretched state; as the level of strain increases, the peaks gradually broaden and shift to higher energies (i.e. lower wavelengths). This is seen as a blue to red color change in the film. As stress is applied to the elastomer, some of it is transferred to the stiff hard segments, which contain conjugated polydiacetylene backbones. As these backbones become distorted due to the stress, planarity of the pi orbitals is lost and the conjugation length decreases. The broadening of the peaks is indicative of the widening distribution of conjugation lengths present in the sample. At high strains, only a broad, featureless peak remains, and at 500% strain and higher (not shown), strain induced crystallization is observed as a change from a transparent to a translucent film.

The absorption spectra in horizontally polarized light (Figure 10(b)) indicates that there is very little shift in energy for conjugated backbones oriented lateral to the strain direction, thus the level of stress is relatively low in this direction. Also note that the area under the curves decreases rapidly with increasing strain, indicating orientation of the polydiacetylene chains along the direction of stress during tensile elongation. Because the polydiacetylene backbone is approximately perpendicular to the host polyurethane hard segments, we can conclude that the hard segments connected by polydiacetylene chains orient perpendicular to the stress direction during the deformation process.

It is apparent from vertically polarized spectra of the polymer in its relaxed state, shown in Figure 11, that the mechanochromic effect is highly reversible up to 350% strain. At higher strains, some permanent changes are noted; the relative intensity of the excitonic transition at 615 nm decreases with respect to the broad peaks at lower wavelengths, and a high energy tail is formed at very high strain levels. These changes are evidence of the gradual permanent disruption of hard domain ordering that occurs at high strains. Similar observations are made for the visible spectra taken with horizontal polarization. As in the thermochromic behavior of MDI-2,4-1000, this transition appears to be to an order-disorder transformation. However, unlike the case of thermochromism, the transition is quite reversible to fairly high levels of strain.

The visible absorption spectra of HDI-5,7-1000 in the stretched state is shown in Figure 12. The excitonic transition appears at 615 nm, and the secondary, broad absorption band at lower wavelengths is due to disordered polydiacetylene chains with a wide distribution of effective conjugation lengths that probably exist in less ordered areas of the hard domains. Figure 12a presents data from the vertically polarized stretched state. At low levels of strain, a new peak appears at 495 nm; this peak is representative of a new phase with a lower average conjugation length. Just as was observed in the thermochromic behavior of HDI 5,7 elastomers, the hard domains undergo a pronounced phase transition that results in the appearance of a second, well ordered phase. This is the first reversible mechanically induced chromic transition reported, and it illustrates the concept of a well ordered, controlled mechanochromic response. Two different, ordered molecular environments exist for the polydiacetylene backbone in this case; upon stretching, the yellow phase at 495 nm increases in proportion, as the blue phase at 615 nm is decreased. The appearance of this transition at strains as low as 15% is thought to be the result of a highly interconnected phase morphology, in which stress is transferred to the hard domains early in the deformation process. Both peaks gradually broaden and shift to higher energies. At high strains, only a broad, featureless peak at 450 nm remains. Upon relaxation , the absorption spectra (not shown) illustrate reversibility up to 300% strain. After stretching to higher strain levels, the yellow phase remains present in the spectra, although the blue phase continues to dominate the relaxed state absorption spectra even when stretched to 700% strain. This phase transition is very similar to the thermochromic transition observed for HDI-5,7-1000. It is probable that the same sort of gauche-trans conformational rearrangement of the methylene spacer groups occurs upon stretching the elastomer as upon heating it.

The absorption spectra in horizontally polarized light (Figure 13b) indicates that there is very little shift in energy among conjugated backbones oriented lateral to the strain direction, thus the level of stress is relatively low in this direction. Also note that the area under the curves decreases rapidly with increasing strain, indicating orientation of the polydiacetylene chains along the direction of stress.

Dichroic ratios from visible absorption studies of MDI-2,4-1000, HDI-5,7-1000 and HDI-5,7-2000 were calculated by taking the ratio of vertical and horizontal polarized spectra at each strain level. These results are shown in Figure 13[35]. It is apparent that in the stretched state a great deal of orientation takes place in the polyurethanes. This suggests that initially, the hard segments are stacked with their molecular axes perpendicular to the long axis of the hard domains. The domains orient parallel to the stress direction during the deformation process, thus causing the conjugated backbone connecting the hard segments to also line up along the stress direction. There is a maximum in the dichroic ratio of each of the polyurethanes shown. For the film samples shown, the maximum occurs at approximately 300% strain; as will be discussed shortly, the point at which the maximum appears, and even the appearance of a maximum at all, depends on the degree of cross-polymerization and the thermal history of the polymer samples. The observed decrease or leveling of the vertical orientation with increased strain may be due to the physical break up of the original hard domains, and subsequent re-ordering of the hard segments along the direction of stress. This type of hard segment orientation has been suggested by Bonart [36], Seymour et. al. [26] and Kimura et al.[37]. It is important to note that because the visible spectra data only include information on hard segments linked by polydiacetylene chains, and the levels of cross-polymerization are low in these materials, it is not clear from this technique alone whether the average, non crosslinked hard segment orients transverse or parallel to the stress direction. Infrared dichroism would provide this information.

The dichroic ratios of the HDI elastomers indicate greater degrees of orientation in the hard domains than in the MDI polyurethane. This is consistent with the fact that the HDI hard domains are highly crystalline, and are more likely to exhibit higher order parameters in the stretched state than the paracrystalline MDI polymer. On the other hand, the dichroic ratios calculated for the relaxed states of the polyurethanes indicate that HDI-5,7-1000 experienced the greatest levels of residual orientation, an indication of permanent set and deformation of the hard domains due to the fact that the hard and soft domains tend to deform simultaneously in the interconnected HDI phase morphology, and that the hard domains experience a great deal of permanent deformation. The domains of HDI-5,7-2000 are thought to be highly interconnected, as well; however the longer soft segment molecular weight allows for a greater amount of overall extensibility, and therefore, less permanent set. Finally, MDI-2,4-1000 does not have an interconnected morphology. This segmented copolymer consists of more isolated hard domains in a continuous soft segment matrix, thus allowing the soft segments to deform initially, followed by hard segment deformation and break-up at higher strains.

Investigations on the effect of increased cross-polymerization on the polyurethanes have recently been completed, and indicate that at low conversion levels, the deformation orientation behavior of the hard domains is a function of the degree of conversion[28]. For example, the visible absorption dichroic ratios of HDI-5,7-2000 films irradiated at three different levels are shown in Figure 14. The levels of cross-polymerization were too low to note any change in the stress-strain behavior of the polyurethane samples. Despite this fact, even slight changes in the degree of cross-polymerization can make large differences in the degree of orientation and the permanent deformation experienced by the hard domains. At 0.02 Mrad, the dichroic ratio does not get much higher than 5, whereas a dichroic ratio of 9 is achieved in the 0.08 Mrad sample. The amount of permanent set is also considerably higher in the 0.08 than in the 0.02 Mrad sample, particularly at strains below 500-600%, as indicated by the much lower dichroic ratios in the relaxed state of the lower irradiation sample. Finally, at very low conversions, a maximum is not present in the plot of dichroic ratio versus strain level; instead, the vertical orientation of the hard domains increases monotonically up to 650% strain. On the contrary, the 0.08 Mrad sample clearly undergoes a maximum at 350% strain, followed by a decrease in vertical orientation. As discussed above, the presence of a maximum indicates the breakup and re-alignment of the original hard domains.

These differences can be understood if one considers the fact that cross-polymerization effectively increases the rigidity and cohesiveness of the hard domains, and that the HDI morphology consists of considerably interconnected domains. As the hard domains become more cohesive, they will become more oriented in a stress field, as they begin to bear more load relative to the highly extensible soft segments. The extensibility of the hard domains is effectively decreased, however, resulting in the early rupture and re-ordering of the hard segments. Increased rigidity is also evidenced in the actual absorption spectra obtained from the samples. The onset of the mechanochromic transition actually takes place at slightly higher strains. Apparently, greater strain levels are needed to induce the conformational transition in the more highly cross-polymerized samples. The fact that these differences were detectable even at very small degrees of cross-polymerization indicates the large effect of cross-polymerization on the hard domain rigidity. The insignificant differences found in the mechanical stress-strain curves of the samples, on the other hand, suggest that these changes in rigidity must be occurring only in very localized areas. Similar observations have been made for MDI-2,4-1000. Visible absorption and dichroic observations made in a separate study on samples that were more highly crosslinked revealed that the hard domains remain intact to larger strains; for example, the dichroic ratio does not reach a maximum within the strain limits of the elastomer. These observations are in keeping with the proposed mode of deformation for the MDI series, in which isolated hard domains are reinforced by cross-polymerization, and are therefore less likely to be permanently deformed at low or moderate strains. In short, just as the effects of cross-polymerization on hysteresis are reversed for the MDI versus the HDI polyurethanes, so the effects of irradiation on the visible dichroism results differ, and for similar reasons. Remarkably, the polydiacetylene cross-polymerization process appears to be capable of micro-manipulating deformation behavior on a very localized level at low dosages, and of making significant changes in the overall mechanical properties at high radiation levels.

Morphological Model of Deformation

A model describing the deformation of the cross-polymerized PU-DAs can be constructed from the information obtained from mechanical stress-strain data, mechanochromic and visible dichroism measurements, and the TEM and SAXS results. Figure 15 is a schematic of the proposed deformation process for an HDI based polyurethane-diacetylene. Randomly oriented lamellar or cylindrical domains are shown, based on the lamellar regions seen in HDI-5,7 elastomers. In the model shown, it is assumed that these regions consist of single stacks of hard segments oriented perpendicular to the long axis of the domains. The variation in lamellar thickness variation is due to the range of hard segment lengths present in the polyurethane. For these polyurethanes, the average hard segment length should be two repeat units, but some variation in size about a standard distribution is to be expected . It has been mentioned that the lamellar regions in the micrographs may be superstructure composites of two or more stacks of hard segment; this is not illustrated in the model shown here, but the hard segment orientation and deformation behavior for this case should be quite similar. Soft segments exist as randomly coiled, entangled chains connecting the hard domains. Branching, as seen in the TEM micrographs, is shown here as the result of smaller hard segments separating to accommodate soft segments, as suggested by Fridman and Thomas in their spherulitic model.

At low levels of strain, the hard domains are shown orienting along the strain direction. The polydiacetylene backbone is shown connecting cross-polymerized hard segments within the domains. The vertical orientation seen in visible dichroism is explained by the transverse orientation of the hard segments. The soft segments begin to orient parallel to the direction of stress, as hard domains are sheared past each other. At strains greater than 300%, the hard segments are pulled out of their original domains, and begin to re-orient along the stress direction. This causes the dichroic ratio to reach a maximum value and then decrease as the average direction of the polydiacetylene backbones is altered. The high levels of stress and distortion are also seen in the decrease of average conjugation length.

The data obtained from visible dichroism yields information only on the hard segments connected by the polydiacetylene backbone. At low levels of cross-polymerization, a small minority of hard segments will have reacted to form the polydiacetylene chain. The non-crosspolymerized hard segments may undergo very different deformation behavior; without the added cohesiveness of the cross-polymerized network, the hard domains may break up at much lower strain levels, or orient so that the hard segments are parallel, rather than perpendicular, to the direction of tensile stress. Many studies, including those of Seymour, Allegreza and Cooper[26], and Bonart[36], have revealed parallel orientation of hard segments upon deformation, sometimes from the point at which stress is applied. As mentioned earlier, IR dichroism studies would clarify this issue. Despite this fact, the visible light dichroism studies give an accurate picture of the effects of increased rigidity in the hard domains, and the state of mechanical stress of this unique class of segmented copolymers.

V. More Recent and Future Developments

The next frontier for the segmented elastomer diacetylenes lies in the use of molecular scale design of this unique class of materials to achieve new levels of versatility and control in their thermo- and mechanochromic behavior. This may be accomplished by further functionalization of the polyurethanes, and systematic variation of the chemical structure of both hard and soft segments to achieve the desired range or ranges of chromic response. The development of more highly functionalized elastomers is currently being accomplished by the incorporation of the diacetylene group into the soft segments, as well as the hard segments, of the polyurethanes[38]. The thermochromic response of the polydiacetylene macromonomer systems is often tied to the melting transitions of the host polymer. Because the melting range of the soft segment is generally 30°C to 100°C below that of the hard segment, it is actually possible to observe thermochromic transitions from each of the two phases. The lower melting temperatures of the soft segments result in chromic changes from 30 to 70°C, while the more rigid hard segments undergo thermochromic transitions from 90 to 120°C. Variation of the chemical structure of the hard and soft segments allows the temperature or strain level at which chromism is observed to be varied, thus resulting in new multifunctional elastomeric materials whose response is controlled by design. Potential applications and uses for such materials include the use of polydiacetylene as a molecular probe in mechanical studies. Lightly cross-polymerized samples would allow the separate observation of deformation and orientation behavior in the hard and soft segments using visible absorption experiments. The ability to crosslink the soft as well as the hard segments also provides the opportunity to further enhance and vary the mechanical properties in the solid state.

The structures and maximum melt transitions of the polyester-diacetylene soft segments that have been synthesized so far are shown in Figure 16. Their molecular weights range from 600 to 3000 g/mol, and they contain hydroxyl end groups to allow their incorporation into polyurethanes via conventional methods. These materials exhibit melting behavior at or near room temperature or body temperature, making them interesting for temperature sensors in the packaging industry, medical industry, and for use as novelty or display items. The structures were varied to achieve desired melt ranges, and to obtain the desired level of crystallinity in the soft domains. Soft segments which are highly crystalline result in non-elastomeric mechanical properties; however, some degree of crystalline ordering is desirable to provide the ordered environment required for solid state topochemical polymerization of the diacetylenes. The ability to easily vary the melt temperature, and therefore the temperature and/or strain level of the chromic response, by straightforward chemical modifications is a key concept in the issue of molecular design of these polyurethane systems.

The polyesters undergo a large shift in their absorption band when heated beyond the melt temperature. For example, the original excitonic transition of poly-10,12-docosadiyne-1,22 malonate is at 650 nm at room temperature. When heated beyond 30°C, a sharp decrease in the original peak is observed, and a new broad, featureless peak appears at 475 nm. This particular polyester is interesting in that the thermochromic transition is triggered at body temperature. Polyurethanes have been synthesized using the soft segments shown in Figure 16 by the two step method using hexamethylene diisocyanate and 5,7 dodecadiyne-1,12 diol as the chain extender. Preliminary results indicate that the resulting polymers exhibit two separate thermochromic transitions; detailed studies of these multifunctional materials will be addressed in later work. Once characterized, this new family of PU-DAs may be tailored by chemical modifications or processing conditions to achieve polymeric materials sensitive to a number of temperature ranges or mechanical strain levels.

These new materials may also undergo selective cross-polymerization, in which only the hard domains undergo solid state cross-polymerization, or in which both hard and soft segments are crosslinked. This is done by controlling the thermal conditions under which ultraviolet irradiation induces cross-polymerization. When the polymer film is heated to a temperature above the melt point of the soft segments, but below the melt temperature of the hard domains, the polyester soft segments in the melt state are too disorganized to undergo topochemical cross-polymerization. In this case, only the hard domains may be cross-polymerized. If irradiation takes place at room temperature, on the other hand, both the hard and soft segments are in their semi-crystalline states, and are ordered enough to undergo diacetylene crosslinking.

The first set of curves shown in Figure 17 are the visible absorption spectra of an HDI based polyurethane with diacetylene groups present solely in the hard domains. It is clear that the absorption spectra is the same whether diacetylene polymerization occurs at room temperature, or between the soft and hard segment melt temperatures.

Polyurethanes containing diacetylenes solely in the soft segment only exhibit visible absorption spectra if cross-polymerized below the soft segment melt temperature, as shown by the second set of curves. Above $T_{m,s}$, no cross-polymerization takes place, as evidenced by the flat absorption curve shown in Figure 17. When a polyurethane containing diacetylenic hard and soft segments is irradiated at room temperature, as shown in the third set of curves, the absorption spectra of hard and soft domains are superimposed. Irradiation between the two melt temperatures results in only the absorption spectrum characteristic of the hard domains. The ability to selectively crosslink the hard versus the soft segments means that the effects of crosslinking separate environments may be studied using optical studies, and the organization and mechanical responses of the two domains may be examined independently.

A different approach to multifunctional thermochromic materials has recently been described using the mesogenic transitions of liquid crystalline polymers or host monomers as a means of inducing two or more first order thermochromic transitions[39-41]. Aromatic liquid crystalline diacid and diol diacetylene monomers, and aromatic semi-rigid main chain liquid crystalline polyesters containing the diacetylene group in the repeat unit have been designed, once polymerized or cross-polymerized to exhibit chromic transitions at the melting and clearing points of the corresponding host environment. The concept of controlled chromic behavior via the engineering of liquid crystalline diacetylenes may be extended to the hard or soft segments of a segmented polyurethane. The future development of segmented PU-DAs may well include liquid crystalline polyurethanes, using liquid crystalline polyester-diacetylenes, or diacid or diol mesogenic monomers as a basis for new polymers. The range of thermo- and mechanochromic behavior could then be expanded to include the multiphasic behavior of mesogenic polymers, and the high level of orientation possible in such systems might yield highly anisotropic optical properties that could prove interesting in the number of linear optical applications, including the possibility of new mechano-optical effects.

VI. Conclusions

With the development of diacetylene containing segmented polyurethanes, the behavior of thermoplastic elastomers has been expanded to include the mechano-optic and chromic properties characteristic of polydiacetylenes. The presence of the diacetylene group in this new class of polymers also provides a means to topochemically cross-link thermoplastic elastomers in the solid state using irradiation techniques, and thus obtain large variations in the polymer's mechanical properties without altering its original morphology. The possibilities for applications of PU-DAs are numerous. The diacetylene cross-polymerization could be used to form highly cross-linked, rigid fibers or films with enhanced mechanical properties. The thermochromic and mechanochromic properties could be used to design optical sensors for stress or temperature, or could be further developed as molecular probes to better the understanding of the deformation process in more conventional polyurethanes. The future of these materials will be directed by the further development and evaluation of these materials in practical applications. As further functionalization and molecular design of PU-DAs is achieved, and as the ability to control and manipulate the optical and mechanical properties of these systems on higher levels is mastered, these polymers will reach their potential, and new applications will evolve.

Acknowledgements

The authors gratefully acknowledge the Office of Naval Research for their continued support of this research.

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List of Figures and Figure Captions

Figure 1. a)Topochemical polymerization of diacetylenes[8]. b)Cross-polymerization of macromonomer chains illustrated for a semi-rigid main chain polymer. (Rectangular areas indicate structurally rigid portions of the polymer chain.)

Figure 2. Chemical structures of hard segments for PU-DAs.

Figure 3. Transmission electron micrographs of various PU-DAs: a) thin film of HDI-5,7-1000 cast from solution onto copper grid; b) thin film of MDI-2,4-1000 cast from solution onto grid; c) ultra-cryomicrotomed cross-section of a slowly evaporated solvent cast film of HDI-5,7-2000. In all cases, dark regions represent hard domains.

Figure 4. Stress-strain curves of MDI-5,7-1000 and HDI-5,7-1000 as a function of annealing time and temperature.

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Figure 8. Visible absorption spectra of cross-polymerized HDI-2,4-1000 as a function of temperature (spectra have been arbitrarily offset for clarity).

Figure 9. Visible absorption spectra of cross-polymerized HDI-5,7-1000 as a function of temperature: a) heated state; b) cooled to room temperature after heating to the indicated temperatures (spectra have been arbitrarily offset for clarity).

Figure 10. Visible absorption spectra of MDI-2,4-1000 recorded in the stretched state as a function of increasing strain: a) vertically polarized light; b) horizontally polarized light. Numbers indicate strain levels (spectra have been arbitrarily offset for clarity).

Figure 11. Visible absorption spectra of MDI-2,4-1000 recorded after relaxation from the indicated strain levels as a function of increasing strain: a) vertically polarized light; b) horizontally polarized light. Numbers indicate strain levels. (spectra have been arbitrarily offset for clarity)

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Figure 13. Dichroic ratios of a) MDI-2,4-1000, b) HDI-5,7-1000 and c) HDI-5,7-2000 in the stretched and relaxed states as a function of increasing strain level. For the HDI-based elastomers, the closed data points represent hysteresis runs, whereas the open points represent continual stretching runs.

Figure 14. Dichroic ratios of HDI-5,7-2000 as a function of increasing electron beam irradiation levels.

Figure 15. Schematic illustrating proposed mechanisms of deformation in HDI-based PU-DAs.

Figure 16. Diacetylene containing polyester soft segment structures

Figure 17. Selective cross-polymerization of the hard and soft segments of polyurethane-diacetylene.

List of Keywords

Segmented Polyurethanes
Diacetylene-containing Polyurethanes
Diacetylenes
Polydiacetylenes
Polyurethane-diacetylenes
Opto-mechanical Properties
Chromism
Thermochromic
Thermochromism
Mechanochromic
Mechanochromism
Elastomer
Thermoplastic
Mechano-optic
Polydiacetylene Block Copolymer
Topochemical Polymerization
Solid State Polymerization
UV-curable Polymers
Crosslinkable Thermoplastic
Post-Processible Thermoplastic
Smart Elastomers
Smart Materials
Conjugated Polymers
Cross-polymerization

Table 1

Thermal Transitions of the Polyurethane–Diacetylene Elastomers

material	annealing treatment	low-temp DSC (T_g, T_{exo}, T_{endo}), °C	endotherms, °C	exotherms, °C
MDI-5,7-1000-(D)	90 °C, 45 min	−54, none, none	none, 103 (122)[a]	321
MDI-5,7-2000	90 °C, 45 min	−72, −28, 11	64, 107	315
HDI-5,7-1000	90 °C, 45 min	−73, none, none	46, 107	319
HDI-5,7-2000-(C)	90 °C, 45 min	−76, none, 13	none, 103	331
HDI-2,4-1000	90 °C, 45 min	−73, none, none	45, 94	219

[a] Represents weak high-temperature shoulder.

Table 2

Fraction of Interurethane Hydrogen Bonding of the Copolymers Based on the Carbonyl Region

	fraction of interurethane bonded carbonyl[a]	
sample	solvent-cast films	maximum fraction[b]
MDI-2,4-1000	0.551	0.560
MDI-5,7-1000	0.491	0.571
HDI-2,4-1000	0.570	0.682
HDI-5,7-1000	0.712	0.862

[a] $ABS_{bonded}/[ABS_{bonded} + ABS_{free}]$. [b] Annealed at 90 °C for 2 h.

Table 3

Molecular Weight and Ultimate Tensile Properties of the Polyurethane–Diacetylene Elastomers

material	M_w	annealing treatment	UTS, psi	% strain at failure
MDI-5,7-1000-(A)	107 000	95 °C, 1 h	5800	710
MDI-5,7-1000-(B)	100 000	90 °C, 45 min	6500	760
MDI-5,7-1000-(C)	82 000	90 °C, 45 min	5300	850
MDI-5,7-1000-(D)	56 000	90 °C, 45 min	2400	700
HDI-5,7-2000-(A)	209 000	90 °C, 45 min	7700	820
HDI-5,7-2000-(B)	93 000	90 °C, 45 min	5000	840
HDI-5,7-2000-(C)	79 000	90 °C, 45 min	3500	840
HDI-2,4-1000-(A)	88 000	90 °C, 4 h	6100	820
HDI-2,4-1000-(B)	61 000	90 °C, 4 h	2900	920
HDI-5,7-1000	91 000	90 °C, 45 min	3700	790

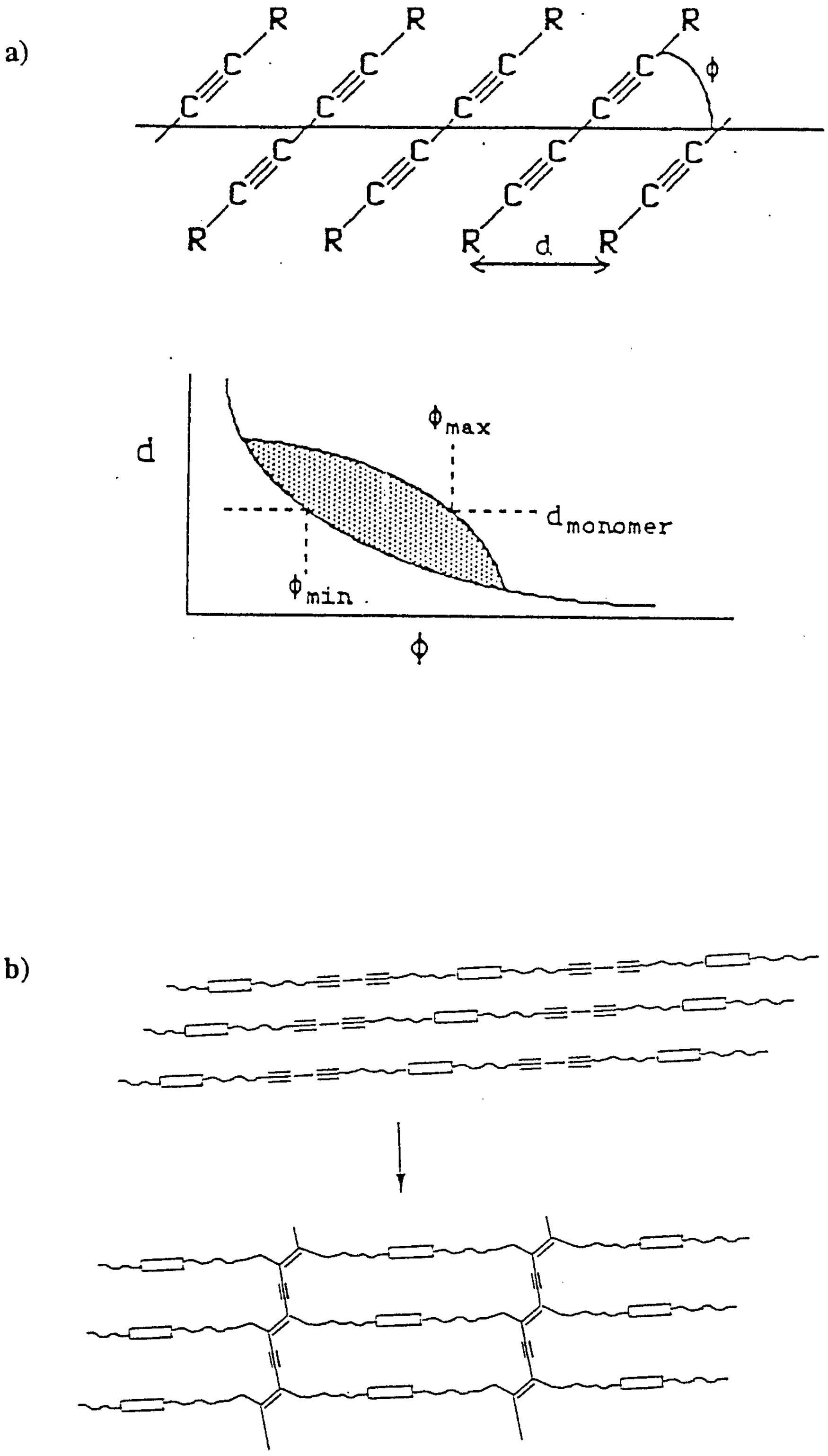
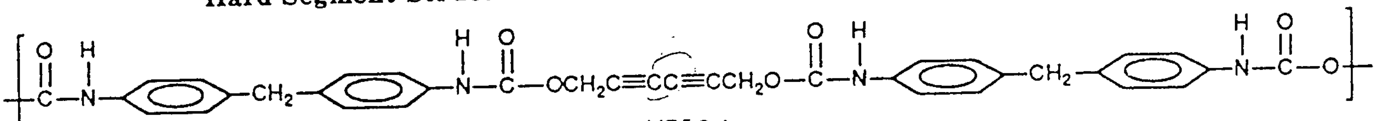
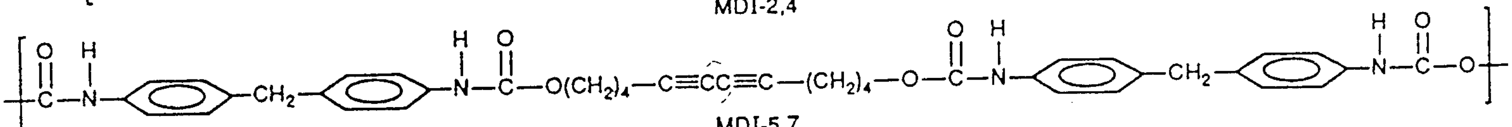


Figure 1.

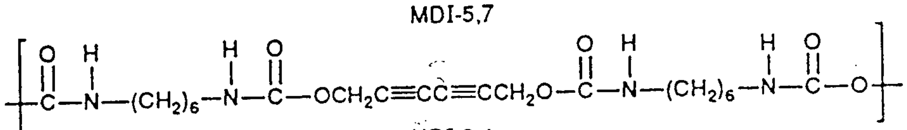
Hard Segment Structures of the Polyurethane–Diacetylene Elastomers



MDI-2,4

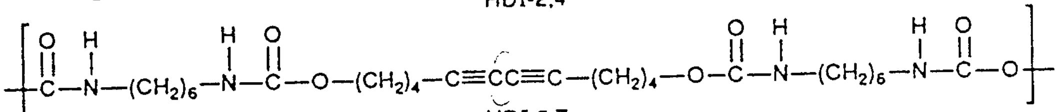


MDI-5,7



$$\left[\overset{\overset{O}{\|}}{C}-\overset{\overset{H}{|}}{N}-(CH_2)_6-\overset{\overset{H}{|}}{N}-\overset{\overset{O}{\|}}{C}-OCH_2C{\equiv}CC{\equiv}CCH_2O-\overset{\overset{O}{\|}}{C}-\overset{\overset{H}{|}}{N}-(CH_2)_6-\overset{\overset{H}{|}}{N}-\overset{\overset{O}{\|}}{C}-O\right]$$

HDI-2,4



$$\left[\overset{\overset{O}{\|}}{C}-\overset{\overset{H}{|}}{N}-(CH_2)_6-\overset{\overset{H}{|}}{N}-\overset{\overset{O}{\|}}{C}-O-(CH_2)_4-C{\equiv}CC{\equiv}C-(CH_2)_4-O-\overset{\overset{O}{\|}}{C}-\overset{\overset{H}{|}}{N}-(CH_2)_6-\overset{\overset{H}{|}}{N}-\overset{\overset{O}{\|}}{C}-O\right]$$

HDI-5,7

Figure 2

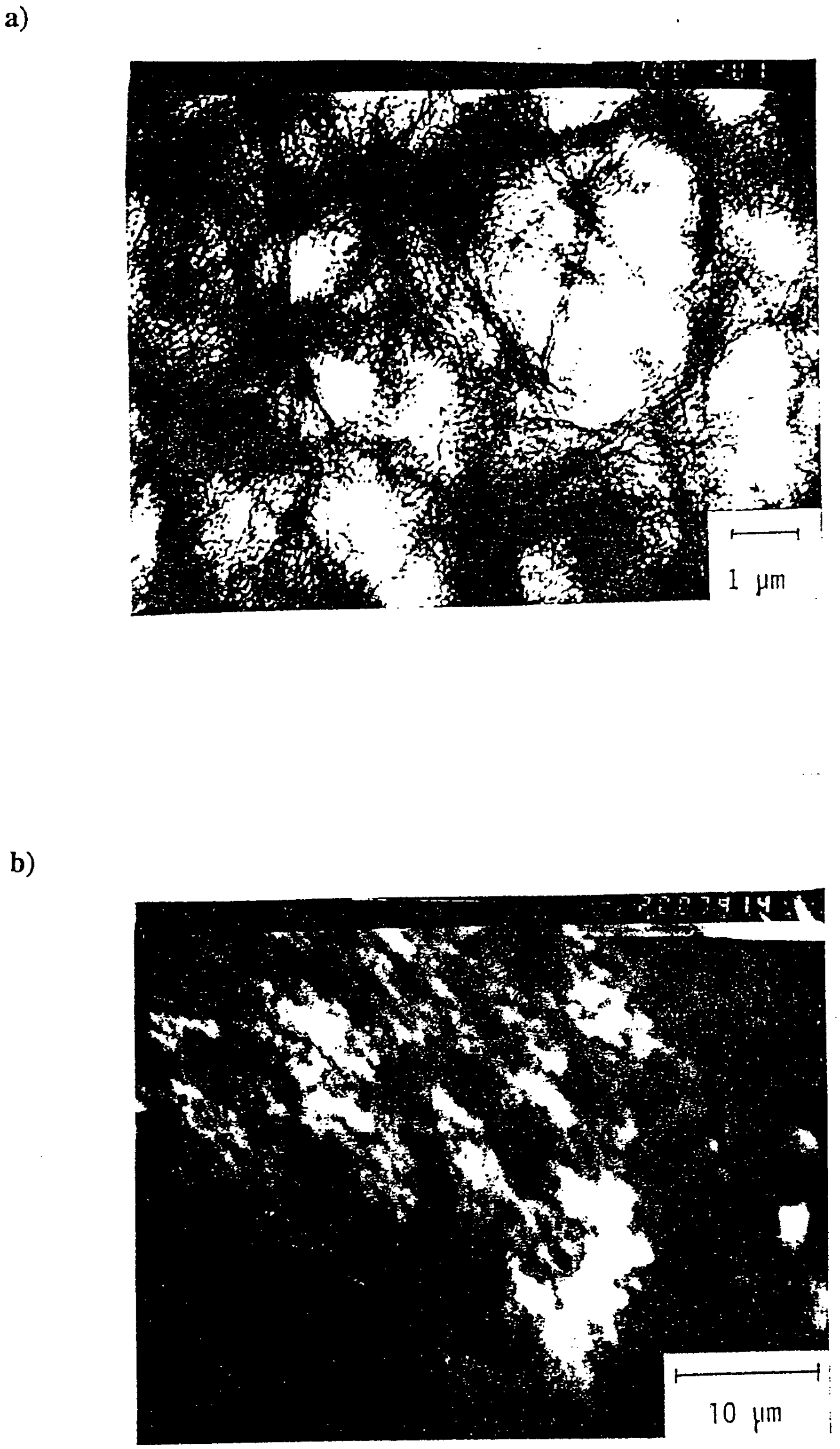


Figure 3

Figure 3

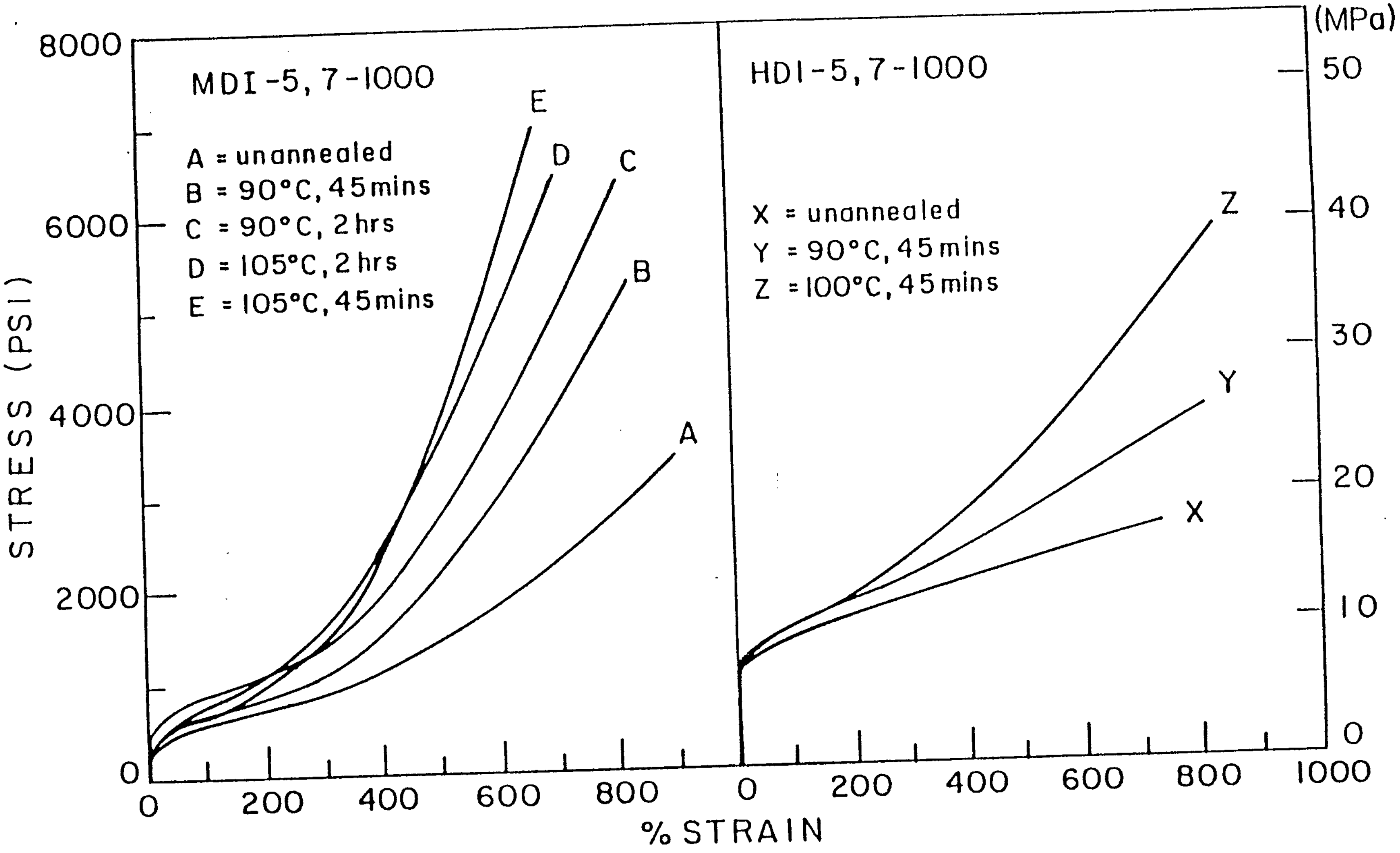
MDI-5, 7-1000
A = unannealed
B = 90°C, 45mins
C = 90°C, 2hrs
D = 105°C, 2hrs
E = 105°C, 45mins
A
B
C
D
E
HDI-5, 7-1000
X = unannealed
Y = 90°C, 45mins
Z = 100°C, 45mins
X
Y
Z
STRESS (PSI)
8000
6000
4000
2000
0
(MPa)
50
40
30
20
10
0
% STRAIN
0
200
400
600
800
0
200
400
600
800
1000

Figure 4

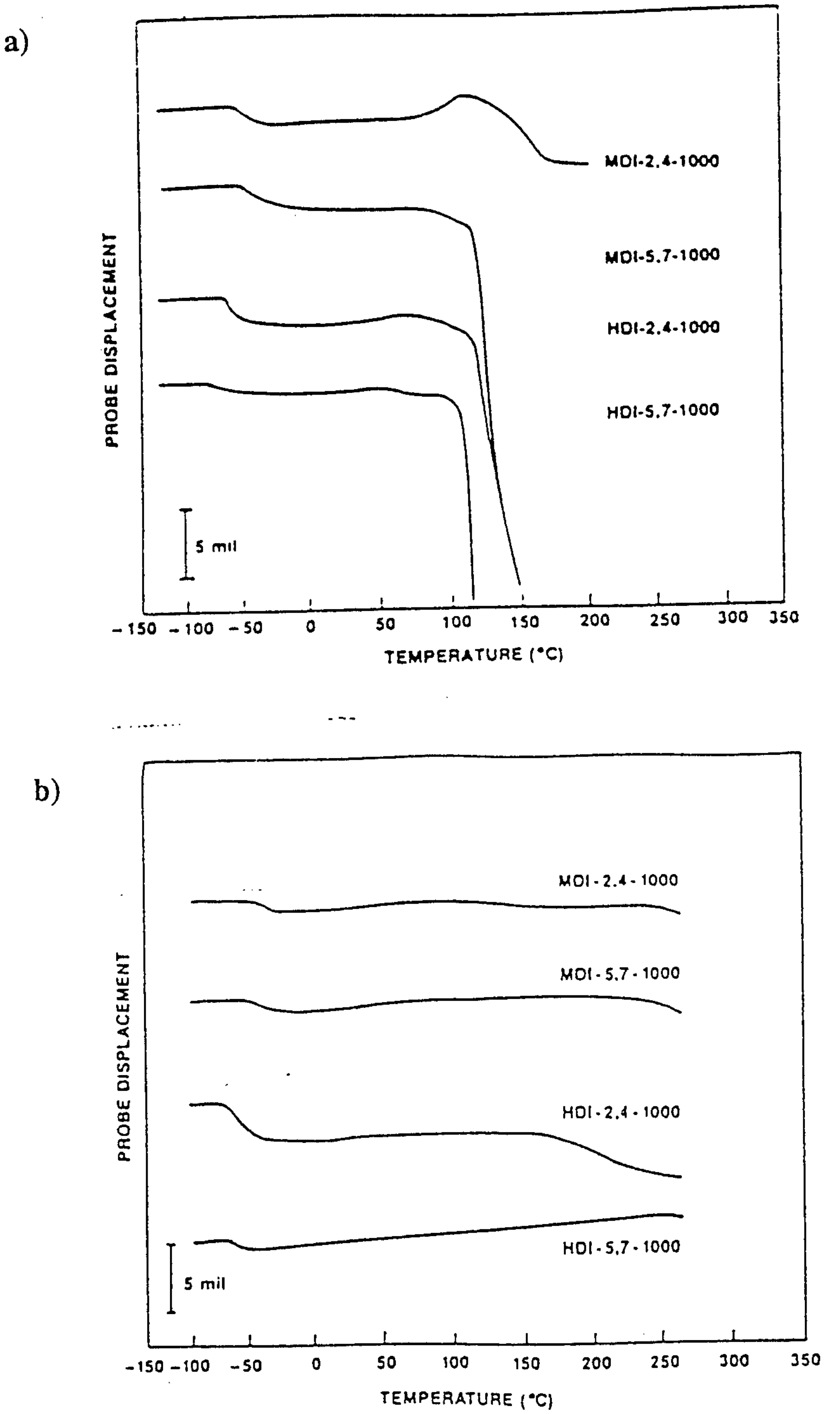

a)
MDI-2.4-1000
MDI-5.7-1000
HDI-2.4-1000
HDI-5.7-1000
PROBE DISPLACEMENT
5 mil
−150 −100 −50 0 50 100 150 200 250 300 350
TEMPERATURE (°C)
b)
MDI-2.4-1000
MDI-5.7-1000
HDI-2.4-1000
HDI-5.7-1000
PROBE DISPLACEMENT
5 mil
−150 −100 −50 0 50 100 150 200 250 300 350
TEMPERATURE (°C)

Figure 5

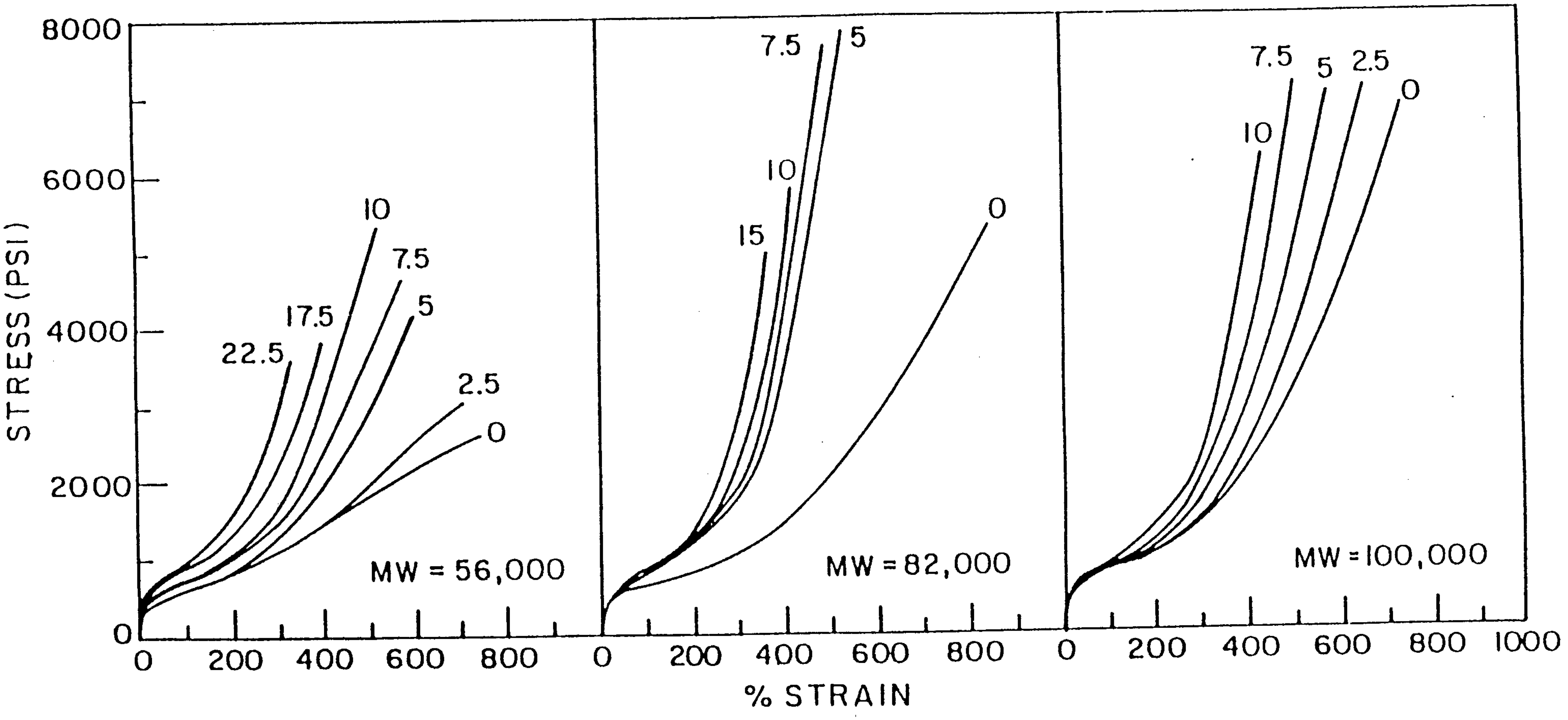
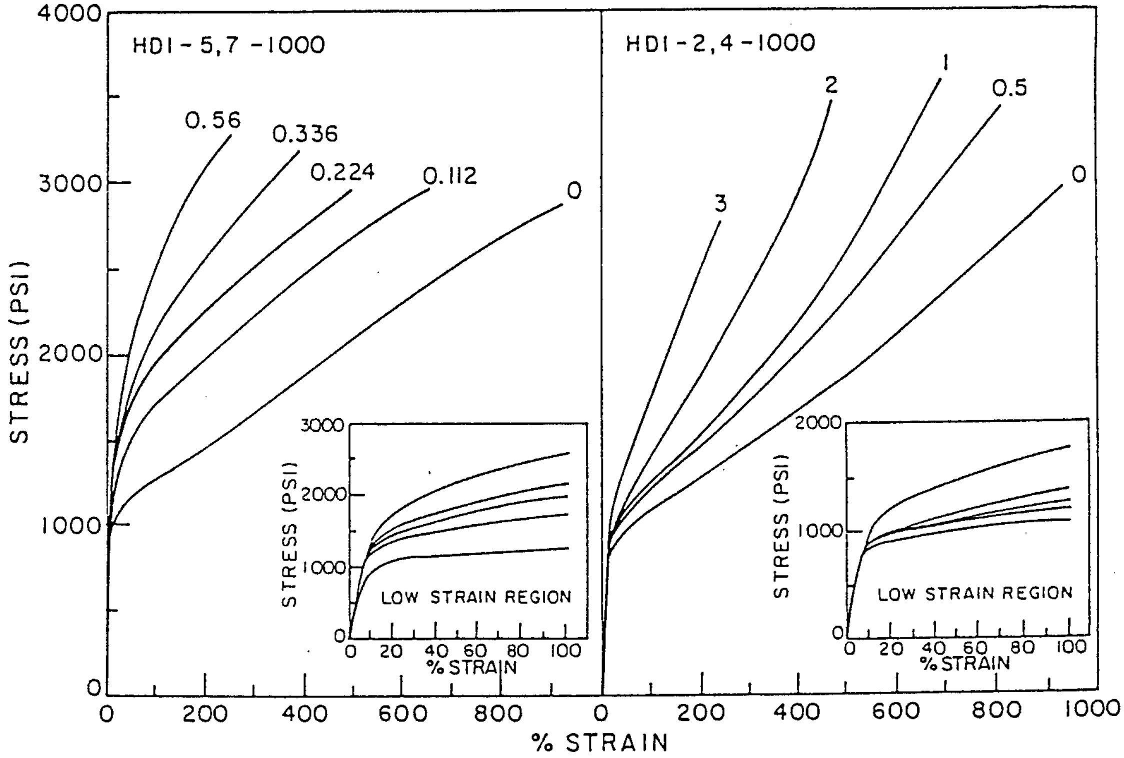

STRESS (PSI)
8000
6000
4000
2000
0
% STRAIN
0
200
400
600
800
1000
MW = 56,000
22.5
17.5
10
7.5
5
2.5
0
MW = 82,000
15
10
7.5
5
0
MW = 100,000
10
7.5
5
2.5
0

Figure 6



HDI-5,7-1000
HDI-2,4-1000
STRESS (PSI)
% STRAIN
0
1000
2000
3000
4000
200
400
600
800
1000
0.56
0.336
0.224
0.112
0
3
2
1
0.5
0
LOW STRAIN REGION
20
40
60
80
100

Figure 7

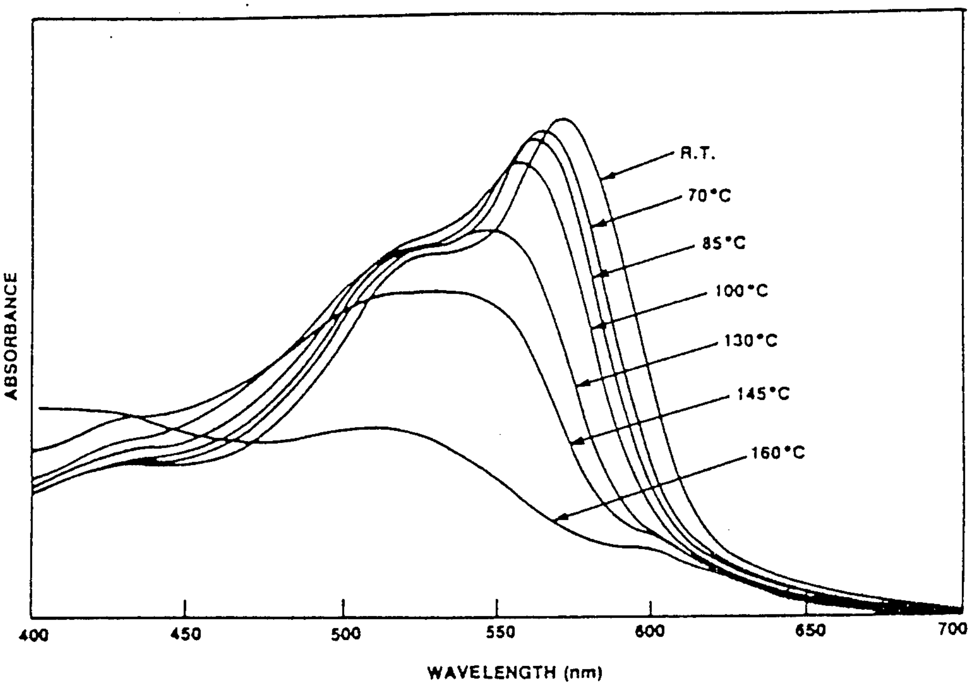

R.T.
70°C
85°C
100°C
130°C
145°C
160°C
ABSORBANCE
400
450
500
550
600
650
700
WAVELENGTH (nm)

Figure 8

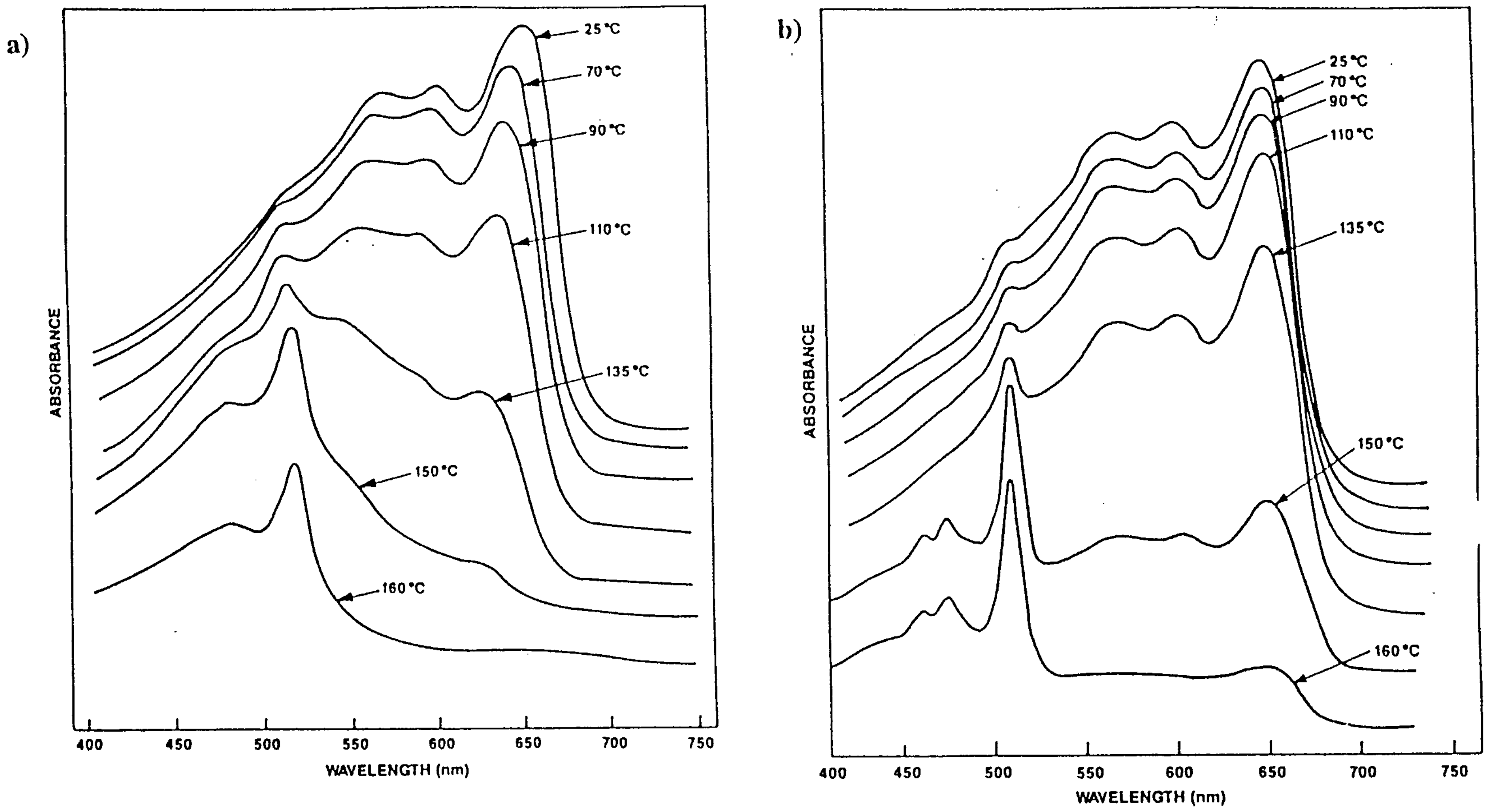

a)
ABSORBANCE
WAVELENGTH (nm)
400
450
500
550
600
650
700
750
25 °C
70 °C
90 °C
110 °C
135 °C
150 °C
160 °C
b)
ABSORBANCE
WAVELENGTH (nm)
400
450
500
550
600
650
700
750
25 °C
70 °C
90 °C
110 °C
135 °C
150 °C
160 °C

Figure 9

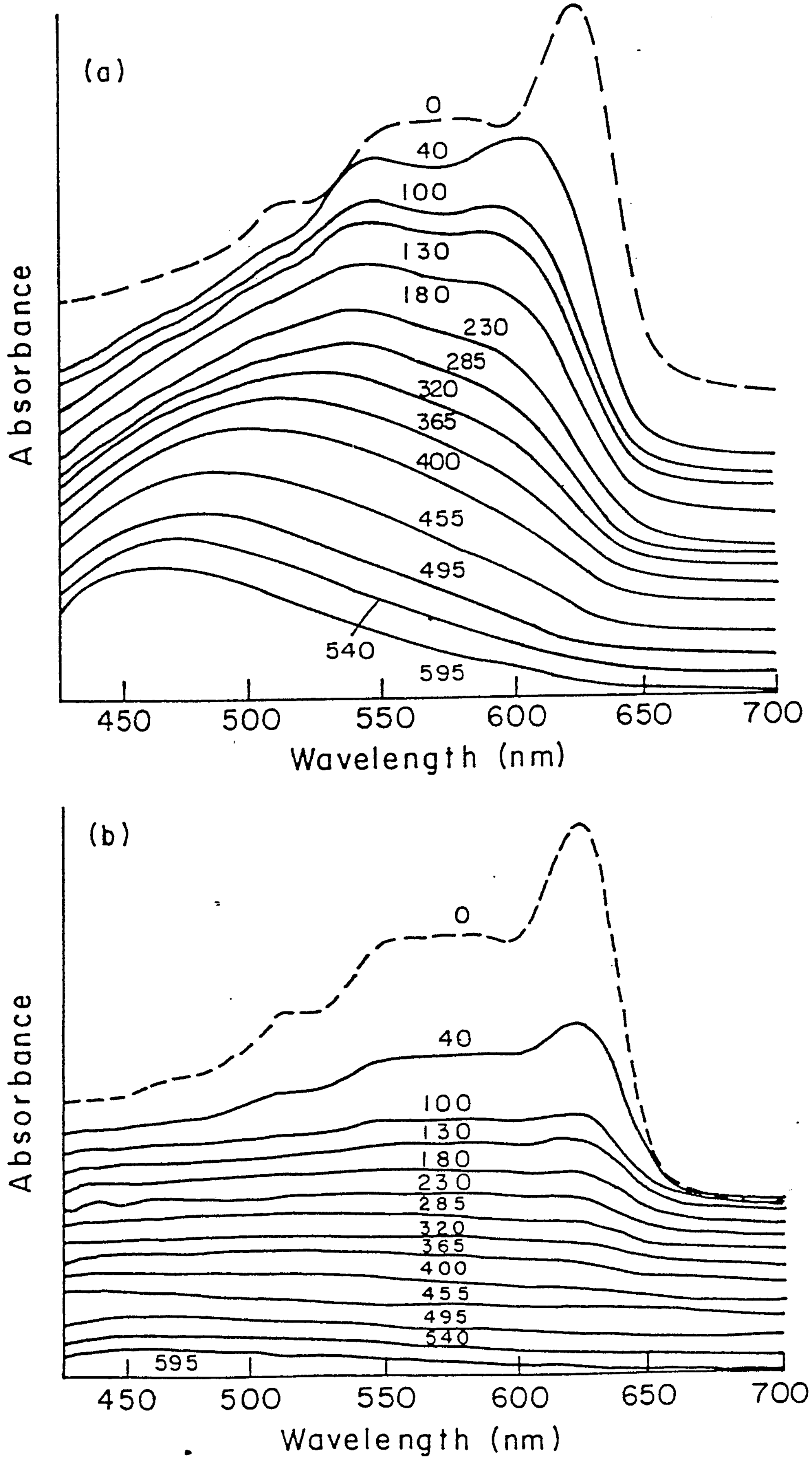

(a)
0
40
100
130
180
230
285
320
365
400
455
495
540
595
Absorbance
450
500
550
600
650
700
Wavelength (nm)
(b)
0
40
100
130
180
230
285
320
365
400
455
495
540
595
Absorbance
450
500
550
600
650
700
Wavelength (nm)

Figure 10

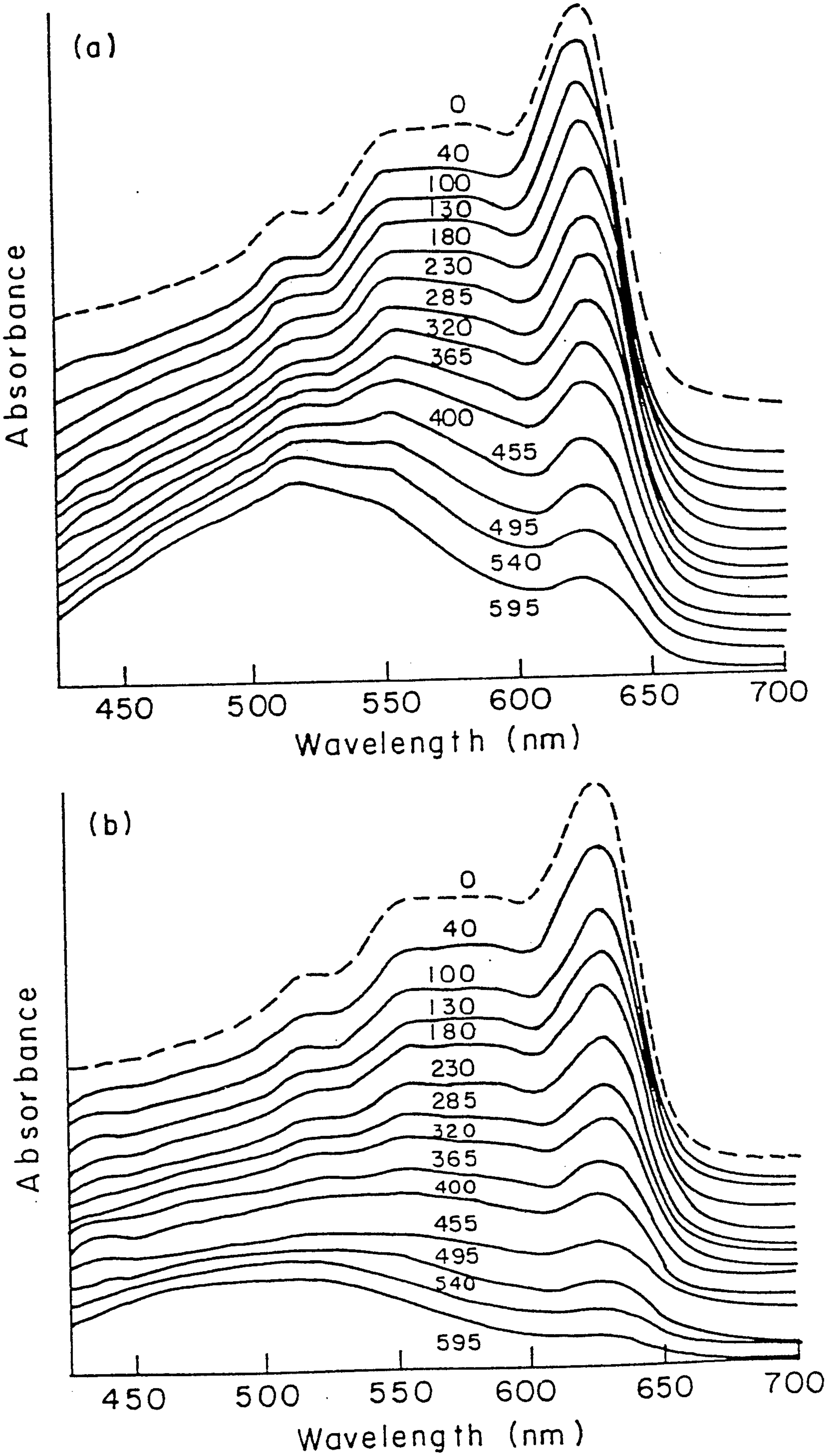

(a)
0
40
100
130
180
230
285
320
365
400
455
495
540
595
Absorbance
450
500
550
600
650
700
Wavelength (nm)
(b)
0
40
100
130
180
230
285
320
365
400
455
495
540
595
Absorbance
450
500
550
600
650
700
Wavelength (nm)

Figure 11

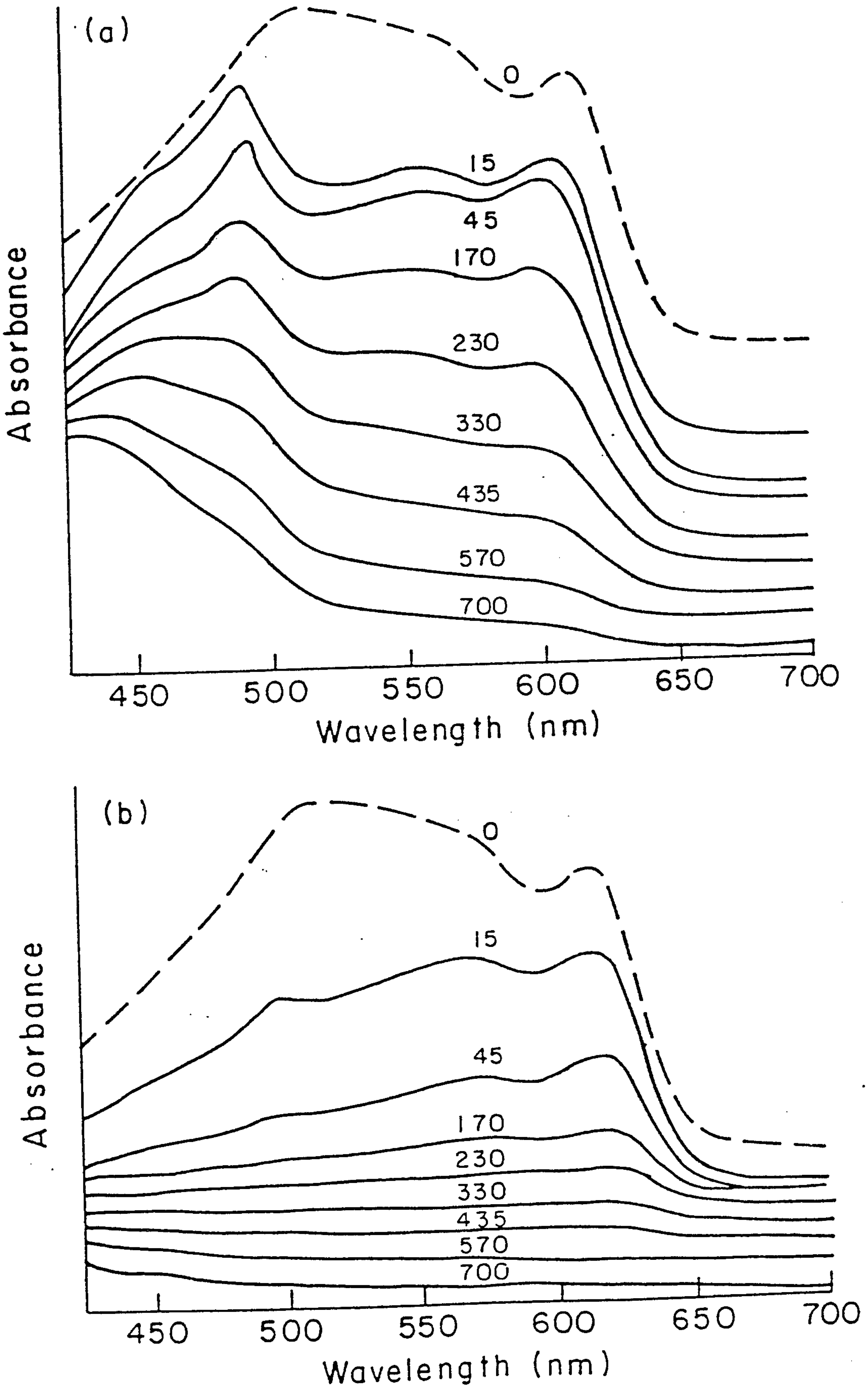

(a)
Absorbance
0
15
45
170
230
330
435
570
700
450
500
550
600
650
700
Wavelength (nm)
(b)
Absorbance
0
15
45
170
230
330
435
570
700
450
500
550
600
650
700
Wavelength (nm)

Figure 12

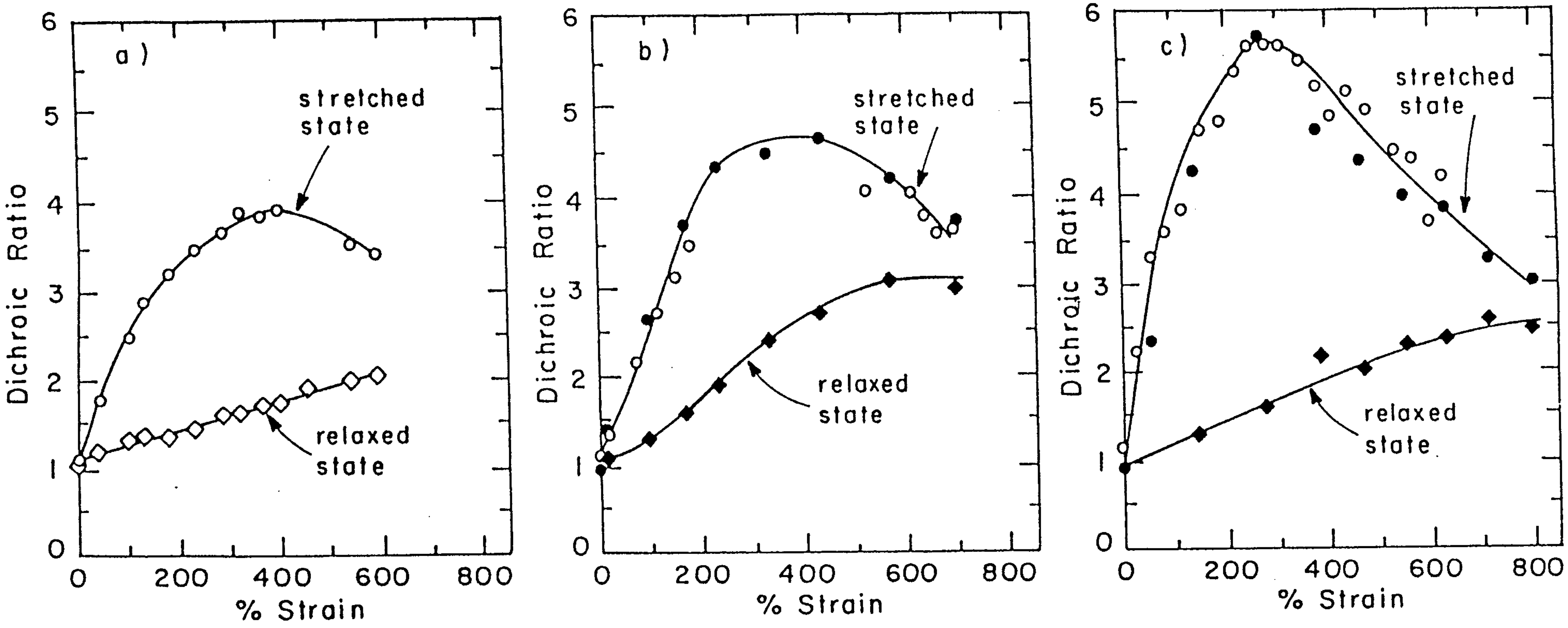

a)
b)
c)
Dichroic Ratio
% Strain
stretched state
relaxed state
0
1
2
3
4
5
6
0
200
400
600
800

Figure 13

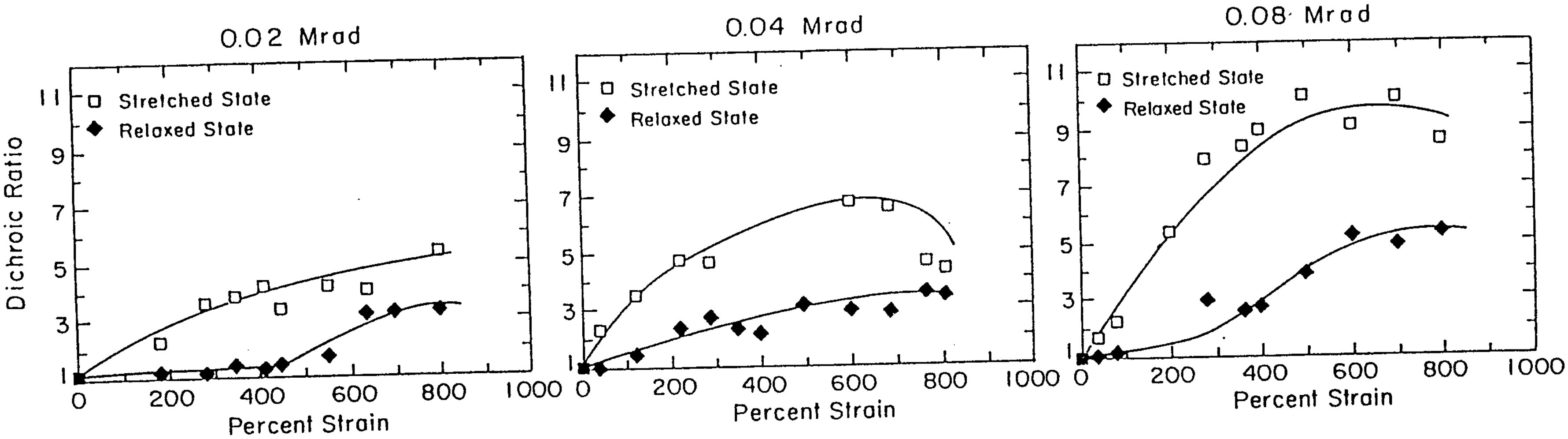

0.02 Mrad
0.04 Mrad
0.08 Mrad
□ Stretched State
◆ Relaxed State
Dichroic Ratio
1
3
5
7
9
11
Percent Strain
0
200
400
600
800
1000

Figure 14

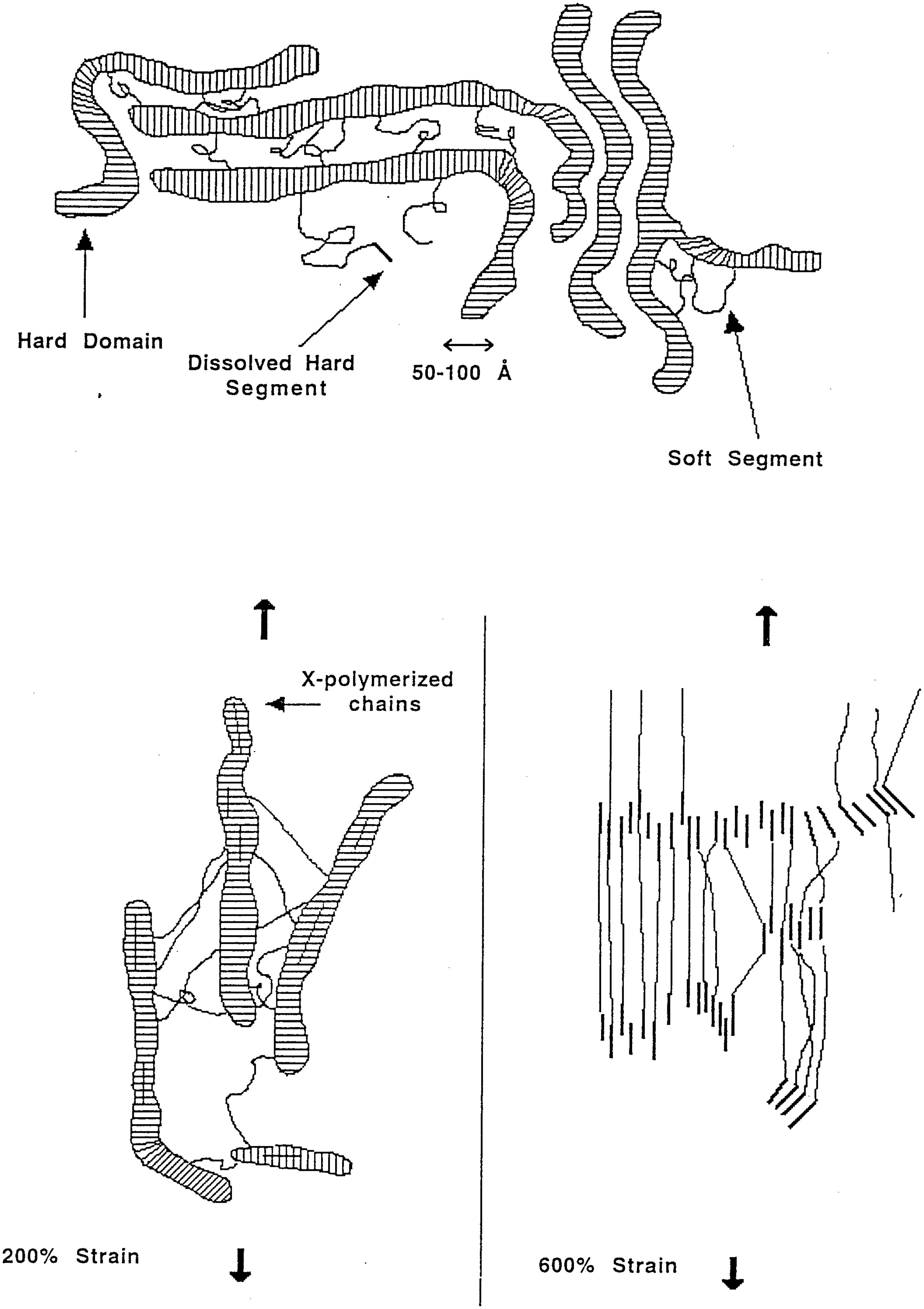

Hard Domain
Dissolved Hard Segment
50-100 Å
Soft Segment
X-polymerized chains
200% Strain
600% Strain

Figure 15

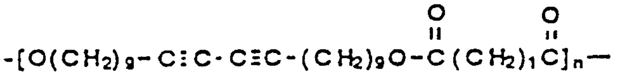
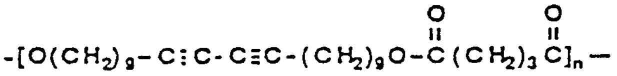
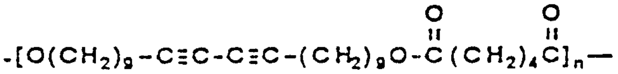
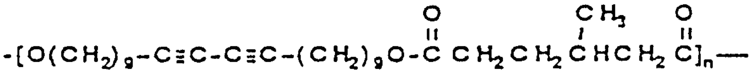
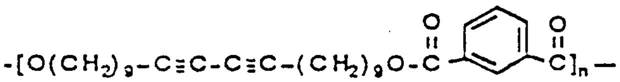
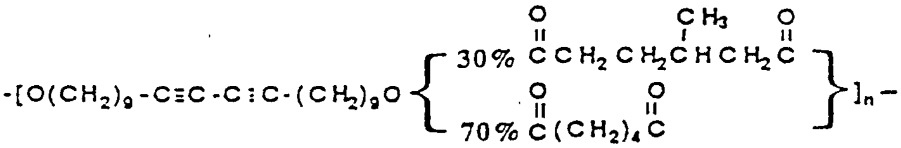
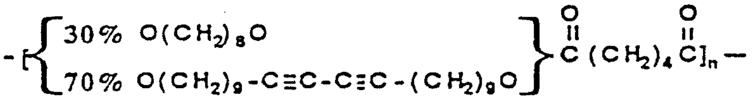
Series		T_m (°C)
1	 $-[O(CH_2)_9-C{\equiv}C-C{\equiv}C-(CH_2)_9O-\overset{\overset{O}{\|}}{C}(CH_2)_1\overset{\overset{O}{\|}}{C}]_n-$	35
	 $-[O(CH_2)_9-C{\equiv}C-C{\equiv}C-(CH_2)_9O-\overset{\overset{O}{\|}}{C}(CH_2)_3\overset{\overset{O}{\|}}{C}]_n-$	50
	 $-[O(CH_2)_9-C{\equiv}C-C{\equiv}C-(CH_2)_9O-\overset{\overset{O}{\|}}{C}(CH_2)_4\overset{\overset{O}{\|}}{C}]_n-$	59
2	 $-[O(CH_2)_9-C{\equiv}C-C{\equiv}C-(CH_2)_9O-\overset{\overset{O}{\|}}{C}CH_2CH_2\overset{\overset{CH_3}{\mid}}{C}HCH_2\overset{\overset{O}{\|}}{C}]_n-$	22
		34
3	 $-[O(CH_2)_9-C{\equiv}C-C{\equiv}C-(CH_2)_9O\left\{\begin{array}{l}30\%\ \overset{\overset{O}{\|}}{C}CH_2CH_2\overset{\overset{CH_3}{\mid}}{C}HCH_2\overset{\overset{O}{\|}}{C}\\ 70\%\ \overset{\overset{O}{\|}}{C}(CH_2)_4\overset{\overset{O}{\|}}{C}\end{array}\right\}]_n-$	48
	 $-[\left\{\begin{array}{l}30\%\ O(CH_2)_8O\\ 70\%\ O(CH_2)_9-C{\equiv}C-C{\equiv}C-(CH_2)_9O\end{array}\right\}\overset{\overset{O}{\|}}{C}(CH_2)_4\overset{\overset{O}{\|}}{C}]_n-$	46

Figure 16

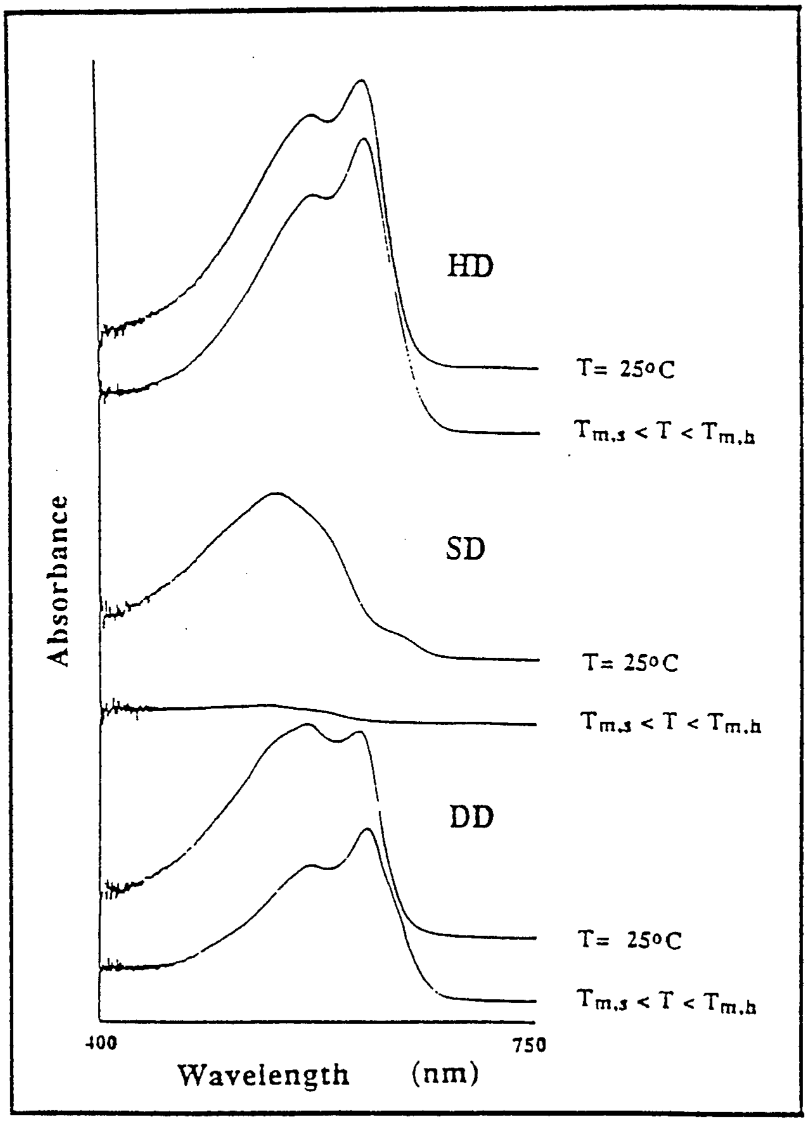

Absorbance
HD
T= 25°C
Tm,s < T < Tm,h
SD
T= 25°C
Tm,s < T < Tm,h
DD
T= 25°C
Tm,s < T < Tm,h
400
750
Wavelength (nm)

Figure 17