Phase Behavior and Photoreactivity in Diacetylene-Containing Block Copolymers

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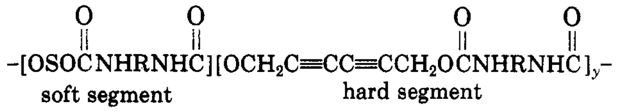
ABSTRACT: The photoreactivity of diacetylene-containing solid block copolymers is determined not only by the structure of the diacetylene repeat unit but also and to an even greater extent by the phase behavior of the segmented blocks. Photoreactivity, as measured by the quantum yield of polymerization in the solid matrix, depends in particular on the degree of phase separation, i.e., on the fraction of diacetylenes contained inside hard-segment domains, as distinct from isolated diacetylenes dispersed in the soft-segment phase. It depends also on the morphology of the hard-segment phase, the shape and size of the diacetylene stacks, and the degree of crystallinity in these domains. These factors in turn depend on the nature of the hard-segment and soft-segment components, on their interactions with each other and with the casting solvent, on the composition of the polymer, and on the molecular weight of the components. How far the potential of the thermodynamic driving forces is realized in the solid film depends on the thermal history of the sample, i.e., on the time and the temperature of annealing. All these interrelations are demonstrated on examples from a series of block copolymers synthesized in this laboratory.

Introduction

The photoinitiated polymerization of crystalline diacetylenes is known to occur with high quantum efficiency.[1,2] This makes the process attractive for potential imaging applications. The first use of diacetylenes as photographic materials was reported by Penzien in 1975.[3] He dispersed diacetylene crystals in a binder and recorded images in terms of the red coloration of the poly(diacetylenes) that were produced on exposure to UV. For more recent photographic applications of diacetylenes see ref 4 and 5.

The use of the photoinitiated polymerization of diacetylenes as a cross-linking mechanism seemed particularly promising since it would combine the amplification factor of a chain reaction with the amplification inherent in the cross-linking of macromolecules. We have realized this idea by preparing a series of block copolymers containing diacetylenes as chain extenders in their hard segments.[6-8] Similar block copolymers were recently described by Rubner et al.,[6b] but these were aimed at a different application. These block copolymers have the general structure shown below. R stands here for hexamethylene,



$$-[\mathrm{OSO\overset{\overset{O}{\|}}{C}NHRNH\overset{\overset{O}{\|}}{C}}][\mathrm{OCH_2C{\equiv}CC{\equiv}CCH_2O\overset{\overset{O}{\|}}{C}NHRNH\overset{\overset{O}{\|}}{C}}]_y-$$

$-(CH_2)_6-$, introduced via hexamethylene diisocyanate (HDI), or for cyclohexylene, introduced via *trans*-1,4-cyclohexanediyl diisocyanate (CHDI). S stands for one of the four soft-segment components used in this work: poly(butadiene)diol (PBD), poly(oxytetramethylene glycol) (PTMG), poly(caprolactone)diol (PCL), and poly(dimethylsiloxane–ethylene oxide)dicarbinol (SiEO, 50:50).

In other communications[7,8] we have described the synthesis, characterization, and the photographic behavior of the block copolymers. It was found that the photosensitivity of these materials depends not only on the structure of the diacetylene monomers but also to a large extent on the morphology of the system in the solid state. Here we are concerned with the relation between phase behavior and photosensitivity, with the compositional factors that determine both and with the kinetics of phase evolution in the solid films.

Experimental Section

All the block copolymers were prepared in THF solution by the prepolymer method, under dark conditions and in a nitrogen atmosphere. Detailed polymerization procedures and polymer characteristics are given in an earlier communication.[8]

Table I
Casting and Developing Solvent Systems

polymer	casting solvent[a]	developing solvent[b]
HDI[c]-PBD[d]-35[e]-1350[f]	DMF/xylene/THF (3/7/90)	A
CHDI-PBD-35-1350	toluene/THF (10/90)	B
HDI-PTMG-35-2000	DMF/cyclohexanone/THF (5/10/85)	C
HDI-PTMG-20-2000	cyclohexanone/THF (10/90)	C
HDI-PTMG-35-1000	dioxane/cyclohexanone/THF (4/8/88)	C
HDI-PTMG-20-1000	cyclohexanone/THF (10/90)	C
HDI-PTMG-35-650	dioxane/cyclohexanone/THF (4/8/88)	C
HDI-PCL-35-1250	dioxane/cyclohexanone/THF (4/8/88)	A
HDI-PCL-20-1250	cyclohexanone/THF (10/90)	A
HDI-PCL-35-2000	dioxane/cyclohexanone/THF (4/8/88)	A
HDI-SiEO-35-2400	dioxane/xylene/THF (7/7/86)	A

[a] Volume ratio. [b] A: DMF/95% ethanol (13-16/7-4) B: DMF/cyclohexanone (1)-11/9-11) C: DMF/water (19-18/1-2). [c] Indicates the diisocyanate used. [d] Indicates the soft segment used. [e] Indicates the weight percent of the hard segment. [f] Indicates the molecular weight of the soft segment used.

Film Casting. Solid films for photosensitivity and DSC studies were cast from prefiltered 1–2% solutions onto quartz plates in a laminar flow cabinet. Solvents for film casting were selected from the point of view of optimal film-forming properties, drying time, and photosensitivity. (See Table I.) After casting, the films were dried first in the open air and subsequently under vacuum at room temperature to remove any residual solvent; they were preconditioned for 20 min at 80 °C immediately before use. Samples for the thermal history studies were preconditioned at 80 °C under a nitrogen atmosphere for a predetermined period of time.

Irradiation. A low-pressure mercury lamp (8 W) was used for irradiation. The intensity of the incident light was determined with a modified ferrioxalate actinometer.[9] After exposure, the films were postbaked at 80 °C for 10 min to release any stresses developed during photo-cross-linking.

Development. Cross-linking insolubilizes the irradiated areas of the film. The process can therefore be used to prepare polymer images by exposing the film to a radiation pattern and later washing away the unexposed areas with a suitable solvent or "developer". Different solvent systems have been employed to develop images for different types of block copolymers (Table

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I). The choice of solvent is critical for the quality of the images. The following rule of thumb was found helpful: the developer should be a good solvent for the hard segment of the block copolymers and only a diluent or a nonsolvent for the soft segment. Solvent mixtures were more often successful than single solvents. Work in process on the relation between developing solvent, image quality, and wet adhesion will be reported in a future communication.

After development, the image was dried and further hardened for 20 min at 80 °C. Surface profiles and image thicknesses were measured on a Sloan Dektak II instrument. Gel doses (E_G) and quantum yields (Φ) were obtained by the method of ref 10.

Differential Scanning Calorimetry. All DSC thermograms were run at a heating rate of 15 °C per minute, on a Du Pont Model 910 microcalorimeter connected to a 1090 thermal analyzer. Before exposure, the samples (5 + 0.5 mg) were lifted off the quartz plates on which they had been coated. Great care was taken to avoid contamination by moisture. The assignments of the melting transitions appearing on the thermograms were confirmed by parallel measurements on the corresponding monomeric model compounds.

UV Absorption Spectra. Changes in the UV absorption of the films as a function of exposure time were recorded on a Cary 210 UV spectrometer. The optical density at exposure time t of the poly(diacetylenes) at 580 nm $(OD_{580})_t$ was normalized with the optical density of the diacetylenes at 257 nm before exposure $(OD_{257})_0$.

Results and Discussion

The photoreactivity of the diacetylene-containing polymers is determined by the mutual arrangement in space of the diacetylene groups that act as each other's reaction partners. In systems where cross-linking occurs by a chain reaction, the quantum yield (ϕ) of the chemical process is defined as the number of monomer units reacted to the number of quanta absorbed. It is given by the product[1,11]

$$\phi = qn$$

Here q is the probability of initiation per quantum absorbed and n is the kinetic chain length of the polymerization reaction. In crystalline diacetylenes, the kinetic chain length is determined by the height of the defect-free portions of the diacetylene stacks, while q depends, in addition to other photochemical considerations, on the degree of phase separation. This is defined here as the fraction of diacetylene units located in stacks, as opposed to isolated units dispersed in the soft phase. There is here a clear connection between the phase behavior of the system and its photoreactivity.

The photographic efficiency of the resist is characterized by the quantum yield Φ of effective cross-link formation, defined as the number of effective cross-links produced per photon absorbed. As in all cross-linking photopolymers Φ is inversely proportional to the gel dose E_G. The two quantities are related by the equation[10]

$$\Phi = d/(2.303 m \epsilon M_w E_G) \tag{1}$$

where d is the density (specific gravity) of the material, ϵ is the molar extinction coefficient of the chromophores at the wavelength of irradiation, m is their molarity in the solid film, M_w is the weight-average molecular weight of the polymer, and E_G is the radiation dose leading to just incipient gel formation.

It must be emphasized at this point that not all cross-links are effective in the sense of contributing to the interconnectedness of the gel network. For example, if in a diacetylene crystal containing y adjacent single diacetylene stacks all diacetylenes polymerize, only one column of cross-links will be effective; the other adjacent columns will connect the same block copolymer chains and will not further contribute to gel formation. From the point of view of resist insolubilization they will be redundant. The quantum yield of cross-linking, Φ, is therefore in general smaller than the chemical quantum yield ϕ.

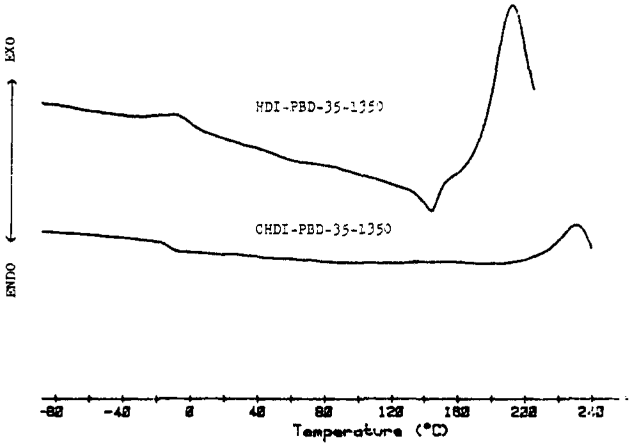

Figure 1. DSC thermogram for two TPUs containing different hard-segment components.

The average stack width, y, expressed as the number of diacetylene-containing units per block, is determined by the composition of the block copolymer via the equation

$$y = 1/(1 - z) \tag{2}$$

where z is the mole fraction of diacetylene-containing units that build up the hard segments.

Experimentally, the cross-linking quantum yield is accessible through gel point determination[10] and the chemical quantum yield through spectral measurements that monitor either the disappearance of the reactant or the appearance of the product, poly(diacetylene).

It has been shown previously[7] that both the relative degree of crystallinity and the cross-link redundancy increase with increasing hard-segment content in the polymer. These two opposing factors balance at a hard-segment content of approximately 35% and at that composition a maximum in the quantum yield of cross-linking is observed. In this paper we discuss the effect of compositional variables other than hard-segment content on the morphology and on the photosensitivity of diacetylene-containing block copolymers.

Effect of Type of Hard Segment. It has been shown[8] that diacetylene-containing polyurethanes derived from aromatic diisocyanates, such as *m*- and *p*-phenylene diisocyanate, 4,4′-diisocyanodiphenylmethane etc., are much less photosensitive than those derived from aliphatic diisocyanates. This has been attributed to the optical filter effect of the aromatic rings. In this study we have used two aliphatic diisocyanates: hexamethylene diisocyanate (HDI) and *trans*-1,4-cyclohexandiyl diisocyanate (CHDI) in order to avoid interference from the filter effect.

The effect of hard-segment structure on crystal packing and on photosensitivity is illustrated by a comparison of HDI-PBD-35-1350 (Φ = 380) and CHDI-PBD-35-1350 (Φ = 38), which differ only in the diisocyanate used in synthesis. Their thermograms taken under identical conditions are shown in Figure 1. A sharp melting peak of the hard-segment phase is observed for the HDI polymer and none for the other. It is not unexpected that a thermoplastic polyurethane (TPU) prepared from the linear diisocyanate HDI should pack more closely and have higher crystallinity than a TPU derived from the less stereoregular cyclic CHDI, and the difference in photosensitivity is qualitatively in keeping with the results of thermal analysis. However, the most important observation is the

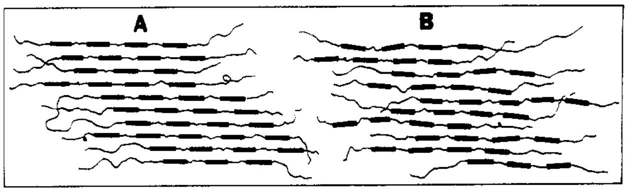

Figure 2. Schematic of crystalline and paracrystalline arrangement of diacetylene segments in block copolymers.

high absolute photosensitivity ($\Phi = 38$) of CHDI-PBD-35-1350 in a state where there is evidently no crystallinity at all. In this system the reaction must have occurred in a paracrystalline phase.

This view is supported by the observation that most of the HDI-based polymers containing less than 20% hard segments (see the following sections) and no melting peak in the 120–160 °C region have nevertheless high values of Φ. At the same time, these materials show clear order–disorder transitions in the region between 80 and 100 °C that are characteristic for a paracrystalline phase. It appears that diacetylenes are highly reactive not only in the crystalline but also in the paracrystalline state.

The behavior of the block copolymers in solution leads to a similar conclusion. For example, a solution of CHDI-PBD-35-1350 in THF is totally photoinert, but when butyl acetate is added to this solution (butyl acetate is a poorer solvent for the hard segments but still a good solvent for the soft-segment component) the solution becomes photosensitive and on irradiation rapidly develops the characteristic red color of poly(diacetylene). Now it is known that in solutions of block copolymers with segments of different solubility characteristics, the less soluble blocks tend to aggregate and form macromolecular micelles while the more soluble segments remain on the outside of the micelles and act as protective colloids.[14–16] Because diacetylenes can react only in ordered arrays and since films of CHDI-PBD-35-1350, even after prolonged annealing, do not show any crystallinity, the spatial arrangement of the diacetylenes in the hard-segment micelles must correspond to an imperfectly ordered state, halfway between a crystalline and an amorphous phase that has been termed the paracrystalline state. This state has been termed the paracrystalline state. A more extensive investigation is now under way.

For the purpose of this discussion the paracrystalline state[17,18] may be described as follows: in an ensemble of rodlike elements, and that is the nature of the diacetylene hard segments, a parallel arrangement of the units develops almost of necessity. It is assumed that the paracrystalline state in the micelles as well as in the hard-segment domains of solid block copolymers is ordered with respect to the principal axis of the segments and represents a state of two-dimensional order reminiscent of the state of a nematic liquid crystal. To arrive at an estimate of the difference in sensitivity between a crystalline and a paracrystalline phase, we recall that in the polymers of this study the average stack width, y, varies between 2 and 5, which means that the width of the individual stacks may vary in the range 1–8. Under these conditions, even with a lower degree of order, there will be many instances where single stacks are formed by members of adjoining chains, and these stacks will have the same geometry (and reactivity) as similar stacks in the crystal. However, not every unit in the paracrystal will form part of a stack, and, in general, the stacks will be shorter than in the true crystal, hence the lower quantum yield of cross-linking.

The situation is schematically indicated in Figure 2, where A refers to a crystalline and B to a paracrystalline domain. If the effect of the inclusion of soft segment and the high degree of imperfection in the two-dimensional arrangement are considered, sensitivity differences observed between the crystalline HDI-PBD-35-1350 and the paracrystalline CHDI-PBD-35-1350 can be qualitatively understood.

Table II
Effect of Type of Soft Segment

polymer[a]	T_m,[b] °C	$\bar{M}_{GPC}$[c]	y	E_G, mJ/cm^2	Φ
HDI-PBD-35-1350	144	5150	3.9	0.5	380
HDI-PTMG-35-1000	140	9830	3.3	2.8	36
HDI-PCL-35-1250	124	6330	3.8	4.3	36
HDI-PTMG-35-2000	152	20500	5.2	2.9	16
HDI-PCL-35-2000	140	25050	5.2	4.3	9.1
HDI-SiEO-35-2400	137	8500	5.7	4.3	27

[a] Notations are the same as in Table I. [b] Hard-segment melting peak temperature measured by DSC. [c] Estimated from GPC and intrinsic viscosity.

Effect of Type of Soft Segment. The soft segment influences morphology and photoreactivity by its thermodynamic interaction with the hard segments. In the four components used as soft segments in this work, the degree of thermodynamic incompatibility with the hard segments, as measured by the position and intensity (integrated area) of the hard segment melting peak, T_m, (see Table II) decreases in the order PBD > PTMG > PCL > SiEO.

The order of photosensitivity is PBD ≫ SiEO > PTMG > PCL. It parallels the order of phase separation, except in the case of SiEO. The soft segment SiEO is itself a block copolymer consisting of 50% ethylene oxide and 50% dimethylsiloxane. The presence of the ethylene oxide blocks, which are relatively compatible with the urethane hard segments,[19,20] explains the low tendency toward crystallization in the TPU's derived from SiEO. The presence of dimethylsiloxane blocks on the other hand provides a highly nonpolar environment in which the hard segments aggregate into small but photoreactive paracrystalline domains, and it is this that leads to a higher than expected photosensitivity.

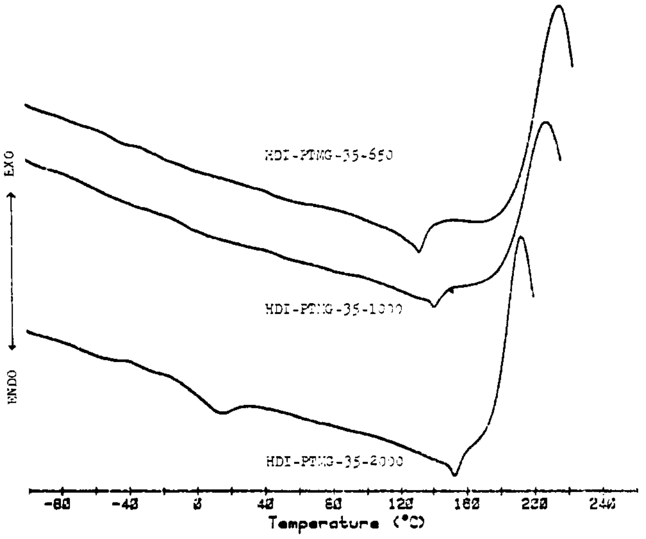

Figure 3. DSC thermograms of TPUs with soft-segment components of different molecular weight.

Effect of Molecular Weight of the Soft Segments. The effect of soft-segment molecular weight on morphology is illustrated by the DSC traces in Figure 3. These refer to polymers in which soft segments of identical type but different molecular weight have been used. As is usually

Table III
Effect of Molecular Weight of Soft Segment[a]

polymer	T_m, °C	M_{GPC}	y	E_G, mJ/cm^2	Φ
HDI-PTMG-35-2000	152	20 500	5.2	2.9	16
HDI-PTMG-35-1000	140	9 830	3.3	2.8	36
HDI-PTMG-35-650	128	15 900	2.6	2.1	29
HDI-PCL-35-2000	140	25 050	5.2	4.3	9.1
HDI-PCL-35-1250	124	6 330	3.8	4.3	36
HDI-PTMG-20-2000	120	19 100	3.0	10	7.1
HDI-PTMG-20-1000	none	34 060	2.1	13	3.9

[a] Notations are the same as in Table II.

observed in thermoplastic polyurethane elastomers,[19,20] the degree of phase separation increases with increasing molecular weight of the soft segment. This is revealed in the thermograms by the position and the intensity of the melting peak of the hard segments, which both increase with increasing molecular weight of the soft segments (see also Table III).

The effect of soft-segment molecular weight on photosensitivity is not as clear-cut. Even allowing for variations in stack width (y) the behavior of the block copolymers is ambiguous. In most polymers based on the soft-segment PTMG Φ increases with increasing soft-segment molecular weight, as one would expect, but there is an exception to this rule in compound HDI-PTMG-35-1000. Furthermore, the two polymers based on the soft-segment PCL show the opposite behavior. We have no explanation for this at the present time.

Effect of Thermal History. In many of our systems significant improvements in photosensitivity are observed after short periods of annealing. All annealing experiments were carried out by placing the sample in a thermostat at 80 °C and keeping it there for the indicated period of time. The annealing effect is more pronounced in polymers with a lower hard-segment content; the examples described in this section all refer to block copolymers with a hard-segment content of 20%. Figure 4 shows a typical result. Here the gel dose E_G is plotted as a function of annealing time. It can be seen that the sensitivity, i.e., the reciprocal gel dose, increases rapidly at first and levels off after some 25 min at twice the sensitivity of the sample before annealing. It is also seen that the introduction of 10% (by volume) toluene into the casting solvent for HDI-PBD-20-1350 brings about a significant increase in photosensitivity. A more detailed study of the effect of casting solvent on the photosensitivity of solid films is under way.

To gain some insight into the annealing process we have monitored it by microcalorimetry (DSC). Figure 5A shows the thermograms for the polymer HDI-PBD-20-1350 in the temperature range of the order–disorder transition. In Figure 5B the temperature of the order–disorder transition, T_{od}, and the normalized area of the peaks are plotted as a function of annealing time. A comparison of Figure 4 and Figure 5B, both plotted against the logarithm of annealing time, shows a leveling off in photosensitivity and in peak intensity but a steady progression in T_{od}.

The photoreactivity of the solid system, originally monitored by gel dose, can also be followed by monitoring the development of the red (absorption maximum at 580 nm) characteristic of poly(diacetylenes). In Figure 6 we have plotted the normalized optical density $(OD_{580})_t/(OD_{257})_0$ as a function of irradiation time for samples that had been annealed for different time intervals. The normalized optical density measures the relative conversion of diacetylenes, while the initial rate of conversion measures the photochemical quantum yield ϕ. In analogy to the quantum yield of cross-linking, derived from the gel dose, the photochemical quantum yield of diacetylene polymerization levels off after the first half-hour of annealing at 80 °C.

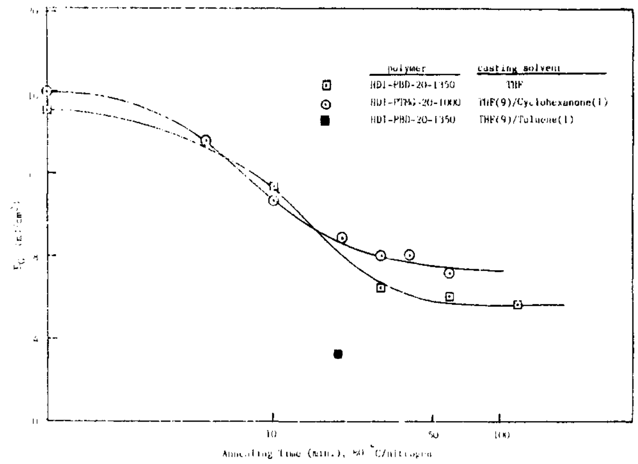

Figure 4. Effect of annealing time on photosensitivity as measured by gel dose E_G.

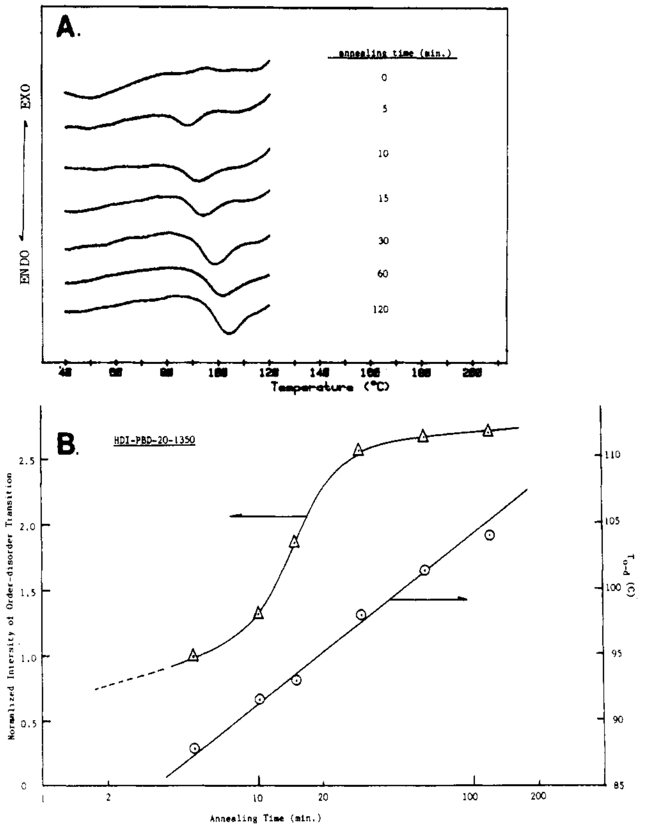

Figure 5. Effect of annealing time on the order-disorder transition at 85–105 °C: (A) thermograms; (B) plot of transition temperature and normalized peak intensity as a function of log annealing time.

In agreement with the well-known phase behavior of thermoplastic polyurethanes, our observations suggest the following order of events. When the film is cast from a given casting solvent, a number of crystalline and paracrystalline centers or nuclei are formed. At this stage the interaction of the hard and the soft segments with the casting solvent determines the state of the system. in all the materials under discussion, the hard segments are the minority components and hard-segment domains are dispersed in a soft-segment continuum. Two processes occur during annealing:[20-22] isolated hard segments, which are dispersed in the soft phase, gradually join the crystalline or the paracrystalline domains. Evidence for the

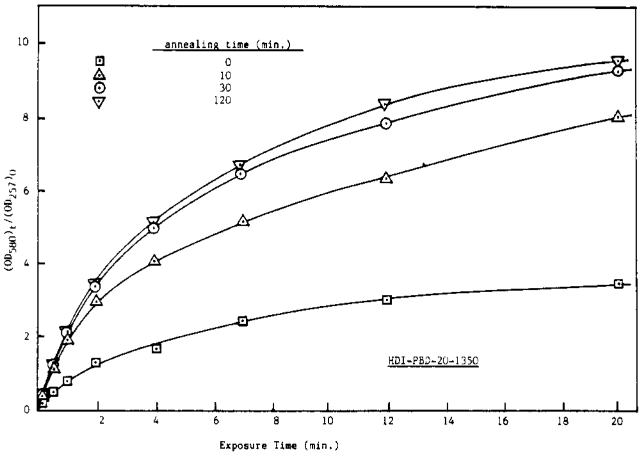

Figure 6. Effect of annealing on the rate of formation of poly(diacetylenes) in two TPUs with different soft segments. $(OD_{580})_t/(OD_{257})_0$ is the optical density of the polymer at 580 nm normalized to the initial optical density of the reactants at 257 nm at time zero.

growth of these two hard-segment phases is seen in the increase of the integrated areas of the order–disorder transition, (see Figure 5B). This process of phase separation is quite fast; in the samples referred to in Figure 5 it is over in less than 30 min. It collects unreactive, isolated diacetylene units into the reactive crystalline or paracrystalline hard-segment domains and has a profound effect on photosensitivity.

In parallel with phase separation, there occurs a process of phase reorganization. This process is known to be slow,[21] essentially because it requires the relative movement of hard segments in a phase that is below its glass transition temperature. Progress is monitored by the change in the temperature of the order–disorder transition, T_{od}. In a first approximation, the rise in T_{od} indicates a decrease in the level of contamination of the hard-segment phase with an impurity, the impurity in this case being the soft segment. Thus, the change of T_{od} monitors directly the exclusion of soft segments from the hard-segment domains. This is a diffusion process that is not driven by a concentration gradient but by a gradient of chemical potential: as the paracrystalline phase acquires a higher degree of order, the activity coefficient of the soft segments in that phase increases and the consequent gradient of activity leads to a mass transfer at the boundary of the domain.

Summary and Conclusions

The results of this investigation may be summarized as follows:

The photoinitiated polymerization of diacetylenes is a topochemical process that occurs only in molecular stacks of a certain favorable geometry. It is found that in diacetylene-containing block copolymers the topochemical conditions of the reaction are satisfied not only in the crystalline hard-segment domains but also in so-called paracrystalline domains of a lower degree of order. The photoreactivity observed in systems where only paracrystalline domains are present is lower than in their crystalline counterparts.

The overall photoreactivity of the solid copolymers depends on the degree of phase separation and on the morphology of the hard-segment domains. These factors in turn depend on the nature of the hard- and soft-segment components, on their thermodynamic compatibility with each other, on their interaction with the casting solvent, on the overall composition of the polymer, and on the molecular weight of the segments. All these variables determine the thermodynamic driving forces toward the formation of the various phases and toward their reorganization into a higher degree of order. How far this potential is realized in the actual growth of the phases and their final organization depends on the thermal history of the sample, i.e., on the time and the temperature of annealing. We have demonstrated these processes with examples from a series of diacetylene-containing copolymers synthesized in this laboratory.

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