

Photosensitive Poly(urethane acylsemicarbazide)s with Azobenzene Chromophores in the Main Chain

Aruna Palanisamy, Saimani Sundar, Ganga Radhakrishnan

Advanced Centre in Polymers, Central Leather Research Institute, Adyar, Chennai 600 020, India

Received 14 May 2003; accepted 29 December 2003

DOI 10.1002/app.20433

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Poly(urethane acylsemicarbazide)s were synthesized with a two-step process: (1) the *in situ* generation of diisocyanate through the thermal decomposition of an azobenzene-containing precursor diazide and a reaction with ester/ether polyols to form an isocyanate-terminated prepolymer and (2) chain extension in *N,N*-dimethylacetamide with aliphatic or aromatic dihydrazides. Films cast from *N,N*-dimethylacetamide solutions were characterized with attenuated total reflection/Fourier transform infrared spectroscopy, and the thermal properties were studied with thermogravimetric analysis and differential scanning calorimetry. The effects of the hard-segment content and chain extenders on the static and dynamic mechanical properties

were investigated. The photoresponsive behavior of the polymers and the effects of variations in the chromophore concentration and chemical composition on the kinetics of photoisomerization were investigated with ultraviolet-visible spectroscopy, which revealed that the rates were independent of the chromophore concentration. The photochemical behavior, assessed with creep-recovery measurements, proved that the systems underwent photochemical isomerization upon irradiation with ultraviolet light. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 93: 444–454, 2004

Key words: azo polymers; block copolymers; creep; FT-IR; UV-vis spectroscopy

INTRODUCTION

Poly(urethane acylsemicarbazide)s (PUSs) are highly elastic linear segmented polymers with a decreased degree of interactions between the rigid and flexible segments and, therefore, a high degree of phase segregation due to redistribution of the hydrogen bonds.^{1,2} Most of these polymers exhibit photoelastic³ and photodegradation resistance properties.⁴ Thermal and thermomechanical analyses of thermoelastic poly(urethane semicarbazide)s have revealed that structural transformations, which depend on the polymer composition, are reflected in the physicochemical and physicomechanical properties. Small changes in the structure of a chain-extender unit containing hard segments significantly affect the degree of segregation of hard and soft domains and the low- and high-temperature properties of polymers.^{5,6}

Several types of PUS ionomers,^{7,8} metal-containing polymers,⁹ and sulfur- and phosphorous-containing systems^{10,11} have been developed so far. These polymers have innumerable applications in various fields because of their ability to form tough, transparent, and

glossy films. In addition, ionic PUSs, when dispersed in water, are used as coating materials, especially for charged substrates such as leather, wool and keratin, adhesives, and printing inks. PUSs can also be used as vascular prosthetic materials, whereas polyurethane-poly(urea acylsemicarbazide)s are used for blood circulation systems.¹²

A variety of polymers and copolymers containing photochromic azobenzene molecules have been prepared and investigated as solutions, films, and membranes. The chromophores can be placed randomly in the polymer matrix, along the main chain or side chain. The ability of an azobenzene group to reverse trans-cis isomerization induced by light has been described in many articles.^{13–16} Under illumination with visible or ultraviolet (UV) light, the more stable trans form undergoes transformation to the less stable cis form. Reverse cis-trans relaxation takes place as thermal relaxation, and it is relatively slow. The photoisomerization of an azobenzene group is interesting because its result is a change in the physicochemical properties, such as the dipole moment, refractive index, and dielectric permittivity, of materials suited for practical applications in linear and nonlinear optics.

Bai and Zhao¹⁷ studied azobenzene thermoplastic elastomers. The films of these elastomers can be easily prepared and stretched to combine mechanical and optical effects, and this results in interesting properties and forms the basis of mechanically tunable optic and photonic devices. There has been much research fo-

Correspondence to: G. Radhakrishnan (clrieco@md3.vsnl.net.in).

Contract grant sponsor: Council of Scientific and Industrial Research.

cused on azoaromatic polyurethanes,^{18–20} ionic PUs, and their copolymers.

So far, there are no reports on the incorporation of azobenzene moieties into the backbone of PUSs to induce a photochromic nature. Mormann et al.²¹ reported the mesomorphic properties of 4,4'-diisocyanato azobenzene prepared through the phosgenation of an amine and showed that the PUS prepared with the mesogen did not show liquid-crystalline behavior. We have attempted in this study to synthesize copolymers with an even distribution of chromophores along the backbone of the polymer chain by incorporating them during the prepolymerization stage via the thermal decomposition of the precursor azide. The hard-segment content (HSC) and the nature of the chain extender have been varied to study the effect of the chromophore concentration on the photochemical isomerization rates and other thermal and mechanical properties of the solution-cast films.

EXPERIMENTAL

Materials

N,N-Dimethylacetamide (DMAc; S.D. Fine Chemicals, Ltd., Mumbai, India) was dried over BaO and distilled under reduced pressure. Dimethyl sulfoxide (DMSO; Ranbaxy, Ltd., SAS Nagar, India) was dried with calcium hydride and distilled under reduced pressure. Poly(tetramethylene oxide)glycols with number-average molecular weights (M_n 's) of 650 and 2000 and poly(ϵ -caprolactone) diols with M_n 's of 530 and 2000 (Aldrich, Milwaukee, WI) were dried under reduced pressure at 100°C before they were used. Dibutyl tin dilaurate (Aldrich) was used as received. *p*-Nitrobenzoic acid, thionyl chloride, and sodium azide (S.D. Fine Chemicals) were used as received. Oxalic acid (Ranbaxy), adipic acid (S.D. Fine Chemicals), sebacic acid (Aldrich), and terephthalic acid (S.D. Fine Chemicals) were used without further purification.

Characterization

Infrared (IR) analysis was performed with a Nicolet Avatar 360 Fourier transform infrared (FTIR) spectrometer (Thermo Electron Corp., Madison, WI) with the attenuated total reflection (ATR) accessory in the range of 500–4000 cm^{-1} . The viscosity measurements of the polymer solutions were carried out in a well-lit room (illuminated with visible light) at room temperature with different concentrations of the polymer in DMAc with an Ostwald viscometer. The intrinsic viscosities were determined from solutions of polymers of various concentrations in DMAc. The absorption spectra were measured with a PerkinElmer Lambda 14 ultraviolet–visible (UV–vis) spectrometer (Boston, MA), and irradiation was carried out with a Heber

HML Compact LP-MP-812 multilamp photoreactor (8-W, medium-pressure UV lamp) (Chennai, India) at 366 nm, and visible light was provided by a high-pressure mercury lamp. Thermogravimetric analysis (TGA) was carried out in a nitrogen atmosphere (flow rate = 50 mL/min) with a DuPont 951 thermogravimetric analyzer (Wilmington, DE) at a heating rate of 20°C/min. The differential scanning results were obtained with a DuPont 910 differential scanning calorimeter in a nitrogen atmosphere at a heating rate of 10°C/min. Strips (20 mm \times 10 mm \times 0.2 mm) of each film were analyzed with dynamic mechanical analysis (DMA; DMA 2980, TA Instruments, New Castle, DE) in the tension film mode in the temperature range of –100 to +100°C at a heating rate of 5°C/min, a strain amplitude of 20 μm , and a frequency of 1 Hz. The creep measurements were performed with the DMA 2980 in the creep mode with a tension film clamp with 20 mm \times 10 mm \times 0.2 mm specimens, and the applied stress was 2.5 MPa. The samples were displaced for 10 min and allowed to recover for 20 min. The microtensile specimens (three each) for stress–strain analysis were cut to 40 mm \times 10 mm and were kept for conditioning at a temperature of $20 \pm 2^\circ\text{C}$ and a relative humidity of $65 \pm 2\%$ for 24 h before testing. The specimens conformed to ASTM D 6385. The tensile testing was performed with an Instron 4501 universal testing machine (Canton, MA) at a crosshead speed of 100 mm/min.

Synthesis of the dihydrazides

The dihydrazides were synthesized from the respective dicarboxylic acids according to procedures already reported.^{22,23}

Synthesis of 4,4'-azobis(benzoylazide)

4,4'-Azobis(benzoylazide) was synthesized from 4,4'-azobis(benzoic acid)²⁴ with acid chloride,²⁵ and the detailed procedure is available in the literature. A typical procedure for the preparation of the azide was as follows. To 0.01 mol (1.7 g) of acid chloride in acetic acid kept at 0–5°C with an ice pack, 0.04 mol (2.6 g) of sodium azide was added portionwise over a period of 0.5 h under a nitrogen atmosphere. The resulting slurry was stirred for an additional 4 h at room temperature and then was filtered under suction. The reddish-orange precipitate was washed several times with water for the removal of excess sodium azide and then with methanol and was dried in a desiccator *in vacuo*. Recrystallization from carbon tetrachloride/light petroleum yielded reddish-orange crystals of the acyl azide that melted with decomposition around 120°C. The recrystallized compound was stored in a refrigerator to prevent decomposition before use. The yield was 1.92 g (60%). Unlike other acyl azides, which

TABLE I
Codes, Compositions, and Intrinsic Viscosities of PUS

| Polymer code | Polymer composition | Molar ratio | | | HSC (%) | Intrinsic viscosity |
|--------------|------------------------|--------------------|--------|-----------------|---------|---------------------|
| | | Azide ^a | Polyol | CE ^b | | |
| pg2ad20 | PTMG 2000, adh, azide | 1.54 | 1 | 0.54 | 20 | 1.71 |
| pg2ad40 | PTMG 2000, adh, azide | 3.44 | 1 | 2.44 | 40 | 1.56 |
| pg2ad60 | PTMG 2000, adh, azide | 7.24 | 1 | 6.24 | 60 | 1.56 |
| pg2od20 | PTMG 2000, odh, azide | 1.62 | 1 | 0.62 | 20 | 1.65 |
| pg2sb20 | PTMG 2000, sbdh, azide | 1.48 | 1 | 0.48 | 20 | 1.68 |
| pg2td20 | PTMG 2000, tdh, azide | 1.56 | 1 | 0.56 | 20 | 1.82 |
| pg6ad60 | PTMG 650, adh, azide | 2.62 | 1 | 1.62 | 60 | 1.12 |
| pc5ad40 | PCL 530, adh, azide | 1.20 | 1 | 0.20 | 40 | 1.12 |
| pc5ad50 | PCL 530, adh, azide | 1.60 | 1 | 0.60 | 50 | 1.08 |
| pc5ad60 | PCL 530, adh, azide | 2.21 | 1 | 1.21 | 60 | 0.92 |
| pc2ad40 | PCL 2000, adh, azide | 3.44 | 1 | 2.44 | 40 | 1.77 |

^a Azide = 4,4'-azobis(benzoyl azide).

^b Chain extender (CE) = odh, adh, sbdh, and tdh (oxalyl, adipoyl, sebacoyl, and terephthaloyl dihydrazide).

decomposed at room temperature, this acyl azide was inert and could be stored in a refrigerator before use for several days. The decomposition temperature of the azide was ascertained by TGA of a mixture of the azide and polyol (poly[tetramethylene oxide]glycol (PTMG 2000)). A sudden weight loss around 120°C indicated the decomposition temperature of the azide.

IR (KBr): 2130, 2175 (vs, N₃), 1680 cm⁻¹ (vs, C=O).
¹H-NMR (CDCl₃, δ): 7.92–8.02, 8.18–8.23 (phenyl).

Synthesis of PUSs

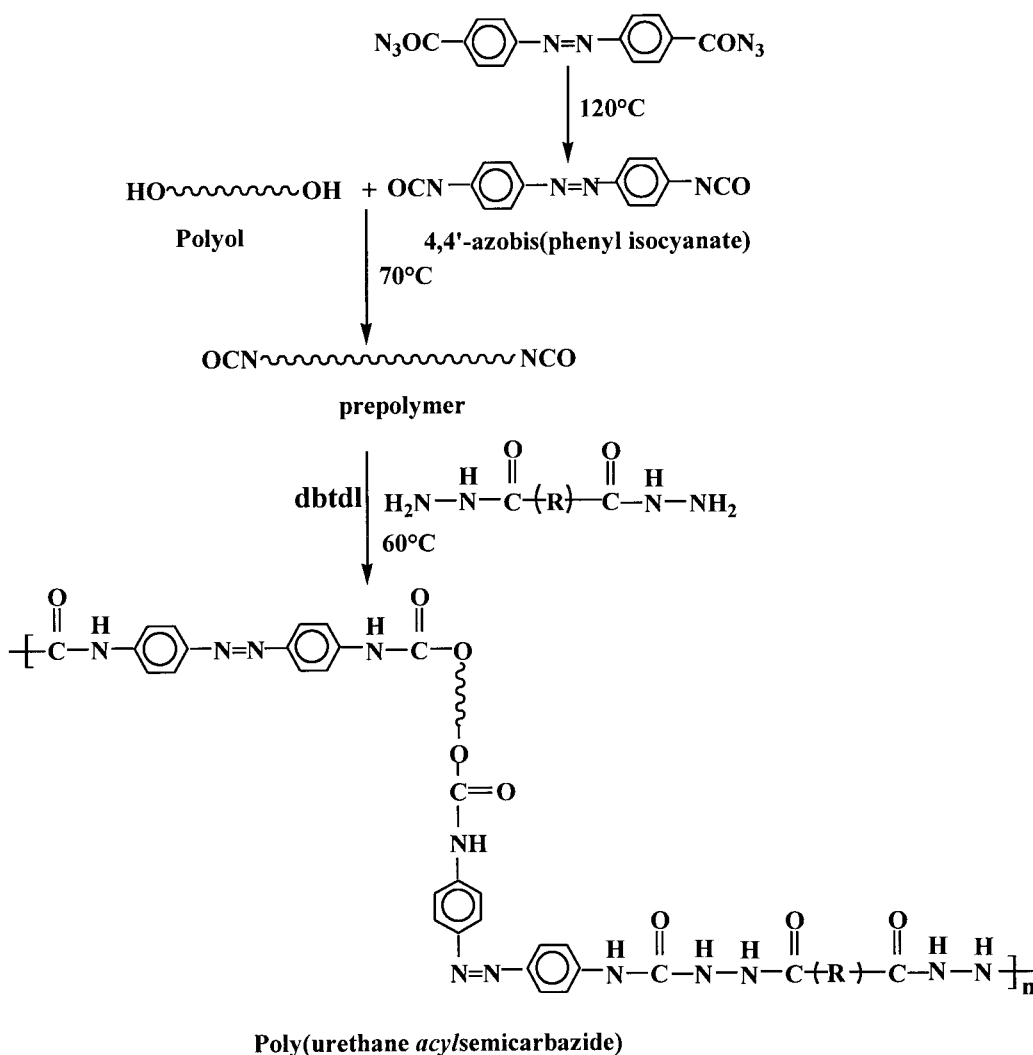
To a stoichiometric amount of polyol placed in a round-bottom flask fitted with a stirrer and a nitrogen inlet, solid azide was added. The temperature was raised to 120°C, and the reaction mixture was stirred well and maintained at that temperature until the liberation of N₂ was complete; this yielded the isocyanate (ca. 5–10 min). The temperature was lowered to 60°C, and the polymerization was carried out until the theoretical NCO content was reached (as determined by *n*-butylamine titration). The prepolymer was dissolved in dry DMAc, and the temperature was lowered to 50°C. The dropwise addition of a dihydrazide solution in DMSO to the prepolymer was performed at room temperature with stirring followed by the addition of dibutyltin dilaurate (DBTDL). The temperature was raised slowly to 60°C, and the mixture was stirred until the completion of the reaction, which was indicated by the disappearance of the isocyanate peak in the IR spectrum. The reaction mixture was poured into water, and the precipitate was washed well with water and then methanol several times to remove the solvent completely. The polymers were dried in a vacuum desiccator for 2 days. Solutions of the polymer (10%) in DMAc were poured into silicon troughs and dried in an oven at 60–70°C for 24 h to yield clear, tough, orange films.

RESULTS AND DISCUSSION

Table I provides the codes, compositions, and intrinsic viscosities of the polymers. The first two letters of the code represent the polyol, and they are followed by the first digit of the molecular weight of the polyol. This is followed by the first two letters of the chain extender and the HSC. For example, pg2ad20 represents a polymer prepared from PTMG 2000 and adipoyl dihydrazide with a 20% HSC. The intrinsic viscosities of the polymers decreased with increasing HSC, and this was due to the lowering of the molecular weight with an increasing NCO/OH molar ratio. Scheme 1 details the steps involved in the PUS synthesis.

FTIR spectroscopy

A representative IR spectrum (ATR) of the films obtained from solutions of PUS in DMAc is given in Figure 1. The presence of >NH and >C=O stretching of urethane and semicarbazide linkages is confirmed by the presence of bands around 3350 and 1730 cm⁻¹. An increase in HSC leads to an increase in the intensity of both the >NH and >C=O stretching bands, reflecting the increase in the concentration of urethane and semicarbazide groups. Ester polyol based PUSs show a very intense C=O peak that is due to the ester linkages in the polyol (soft segment). Multiple peaks around 2940–2800 cm⁻¹ correspond to CH₂, which is very strong for polyether-based polymers. The band around 1436 cm⁻¹ corresponds to an aromatic azo >N=N< linkage, whereas that around 1600 cm⁻¹ is due to an aromatic CH stretching vibration. The peak at 1100 cm⁻¹ corresponds to C—O—C stretching of PTMG units. The presence of urethane linkages confirms the formation of the polymer, whereas the presence of the N=N stretching vibration around 1500 cm⁻¹



where $\text{R} = (\text{CH}_2)_x$, $x = 0, 4, 8$



polyol = PTMG 650,2000

PCL 530, 2000

Scheme 1

shows the incorporation of azo groups during the prepolymerization stage itself, confirming the decomposition of azide to isocyanate, and the further reaction of the isocyanate functionality with OH groups of the polyol, leading to termination of the prepolymer with isocyanate end groups (as confirmed by the peak around 2270 cm^{-1} corresponding to the NCO stretching vibration).

TGA

The onset points of degradation of various compositions are given in Table II; representative TGA curves of the

PUs are given in Figure 2, and their derivatives are shown in Figure 3. All the polymers exhibit a two-step degradation pattern, the first step of which may be due to the decomposition of the $\text{N}=\text{N}$ linkage. Although the incorporation of semicarbazide linkages into the PU backbone leads to increased thermal stability ($\sim 100^\circ\text{C}$), the variation in the composition seems to have little effect on the thermal stability of the systems.

This behavior is due to the thermal stability being connected to the dissociation of the least thermally stable chemical groups, in this case urethane and azo linkages, which dissociate around $200\text{--}250^\circ\text{C}$.²⁶ As HSC increases from 20 to 60%, the thermal stability of

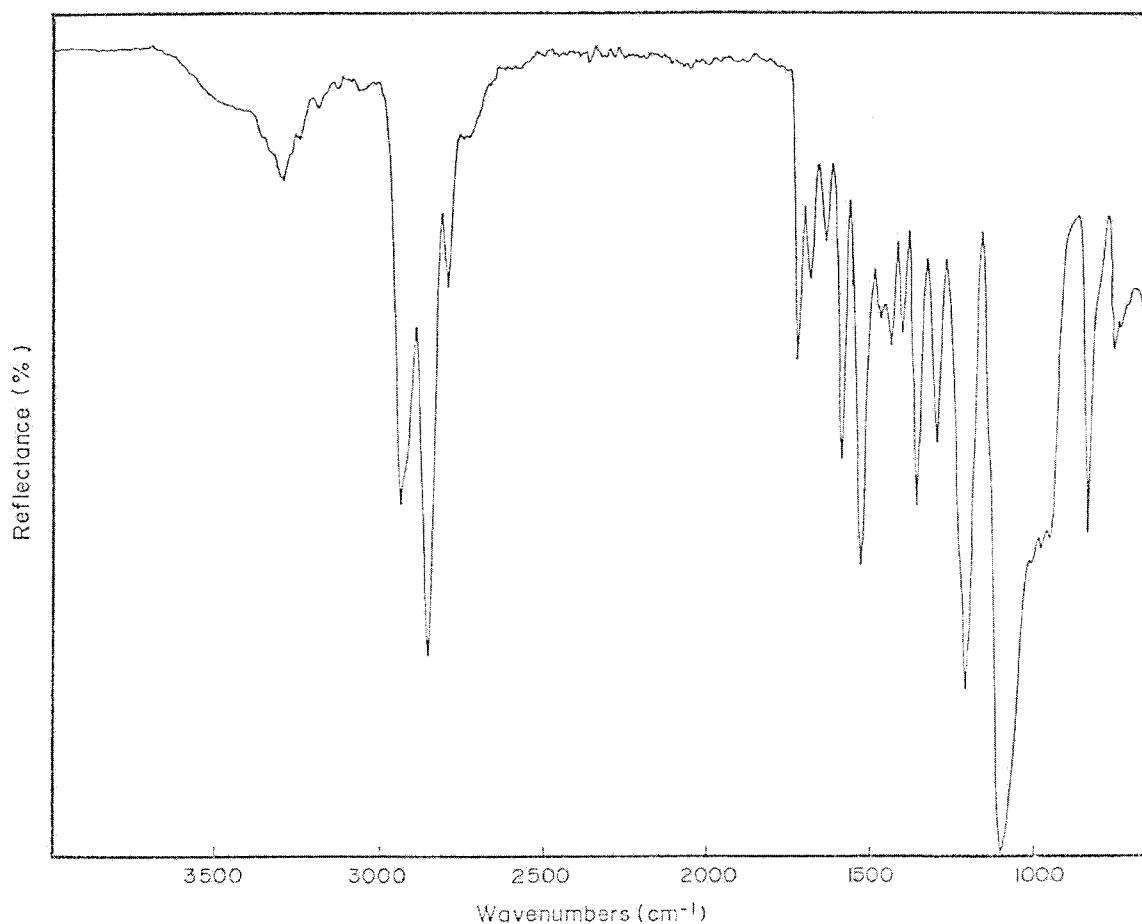


Figure 1 Representative ATR-FTIR spectrum of PUS pg2od20.

the polymer does not change much, but the intensity of the derivative peak of the first transition (corresponding to the cleavage of the azobenzene group) increases. This may be attributed to the increasing number of azobenzene groups with increasing HSC.

Differential scanning calorimetry (DSC)

Figure 4 provides representative DSC scans of the samples, and all the data are summarized in Table II. The polyurethanes generally exhibit three transition

TABLE II
Thermal Properties of PUS

| Polymer code | TGA (°C) | | DSC (°C) | | | |
|--------------|----------|----------|-----------|-----------|-------------------------|---------------|
| | I onset | II onset | $T_{g,s}$ | $T_{m,s}$ | $T_{m,h}^a$ | Exotherm peak |
| pg2ad20 | 324.6 | 408.7 | -32.6 | 23.8 | 50.6 | 322.3 |
| pg2ad40 | 324.4 | 404.2 | -54.9 | 23.9 | 57.9 | 332.4 |
| pg2ad60 | 333.1 | 410.5 | -61.4 | 9.8 | 100.2 | 337.7 |
| pg2od20 | 336.7 | 407.0 | — | 26.9 | 52.4 | 323.6 |
| pg2sb20 | 329.3 | 407.0 | -36.3 | 26.1 | — | 309.4 |
| pg2td20 | 316.8 | 411.9 | -20.5 | 25.9 | 63.7 | 329.7 |
| pg6ad60 | 336.2 | 416.1 | -15.3 | — | 72.9 | 339.2 |
| pc5ad40 | 313.6 | 443.9 | -2.2 | 34.3 | 48.5, 74.3 ^b | 334.2 |
| pc5ad50 | 324.0 | 446.1 | 0.6 | — | 71.1 | 330.1 |
| pc5ad60 | 333.2 | 460.9 | 5.5 | — | 62.5, 94.5 ^b | 336.9 |
| pc2ad40 | 313.6 | 449.1 | -40.5 | 27.4 | 79.2 | 328.7 |

^a Endotherms correspond to the disruption of urethane macroglycol bonds.

^b Two endotherms observed.

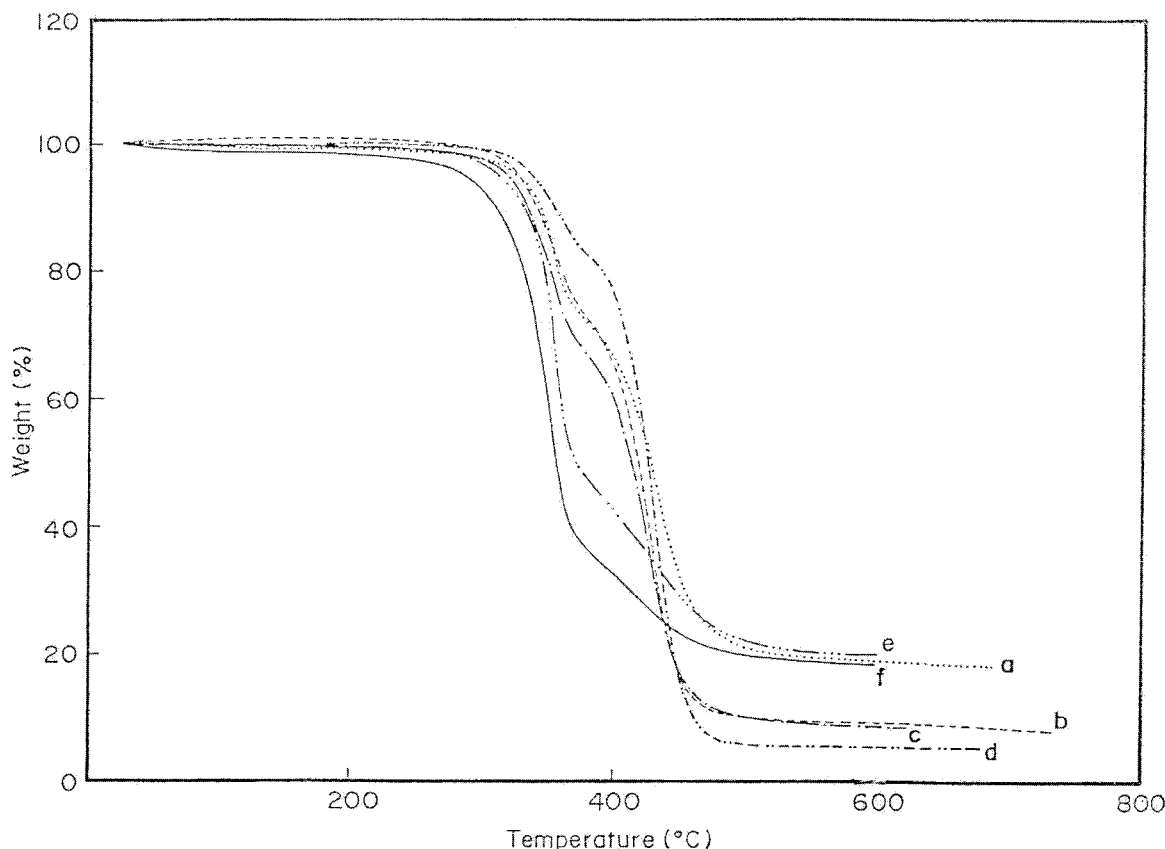


Figure 2 Representative TGA curves of PUSs: (a) pg2ad60, (b) pg2ad40, (c) pg2ad20, (d) pg2od20, (e) pg6sb60, and (f) pg6ad60.

regions detected by DSC. The polymers with 20 and 40% HSCs (pg2ad20 and pg2ad40) have a glass-transition temperature (T_g), whereas for the polymer with a 60% HSC, T_g is insignificant. Exothermic peaks can be observed around 300–330°C, which arose because of the decomposition of azo linkages. The intensity of the exothermic peaks increases with increasing HSC (azo content). In addition to the sharp exothermic peaks, endotherms can be detected at temperatures below 100°C and can be ascribed to the disruption of urethane–macroglycol bonds.²⁷

For a fixed polyol and chain extender when HSC is varied, T_g of the soft segment ($T_{g,s}$) varies. Although ether PUSs exhibit a decrease in T_g because of phase separation (Fig. 4), ester PUSs exhibit an increase in T_g because of phase mixing. When the polyol and HSC are fixed and the chain extender is varied, $T_{g,s}$ remains the same, whereas T_g of the hard segment ($T_{g,h}$) can be observed for polymers prepared with sebacoyl dihydrazide as a chain extender. When the HSC, polyol type, and chain extender are fixed and the polyol molecular weight is increased, $T_{g,s}$ decreases. When the other parameters are fixed and the polyol type is varied, ether polyol based PUSs have a lower $T_{g,s}$ than the ester type. The extensive hydrogen bonding in the ester type contributes to phase mixing and, therefore, a higher $T_{g,s}$.

UV-vis spectroscopy

Figure 5 shows representative absorption spectra of a polymer (pc2ad40) obtained from solutions of the polymer in DMAc. The spectrum of the unirradiated solution is due to the trans form, and the peak at 410 nm can be ascribed to the trans form. Continuous irradiation of a solution with UV light (~366 nm) led to a spectrum with weak absorption in the range of 500–600 nm with isobestic points. When the dilute solutions of the polymers irradiated with UV light at 366 nm were irradiated with visible light or kept in the dark, they returned to the initial state. The kinetics of trans–cis isomerization were studied through the plotting of the relative absorbance (A_t/A_0) versus the time (min), where A_0 and A_t are the absorbances before irradiation and after irradiation for different time intervals t with UV light, respectively. The rates of isomerization do not vary much with the chemical structure of the polymer backbone and the azo group concentration.

The kinetics of the cis–trans-relaxation backprocess of azo chromophores in polymer solutions were followed through the monitoring of the changes in the absorbances corresponding to the π – π^* transition. The solutions of the polymer in DMAc were initially irradiated with UV light for an hour (366 nm) and then

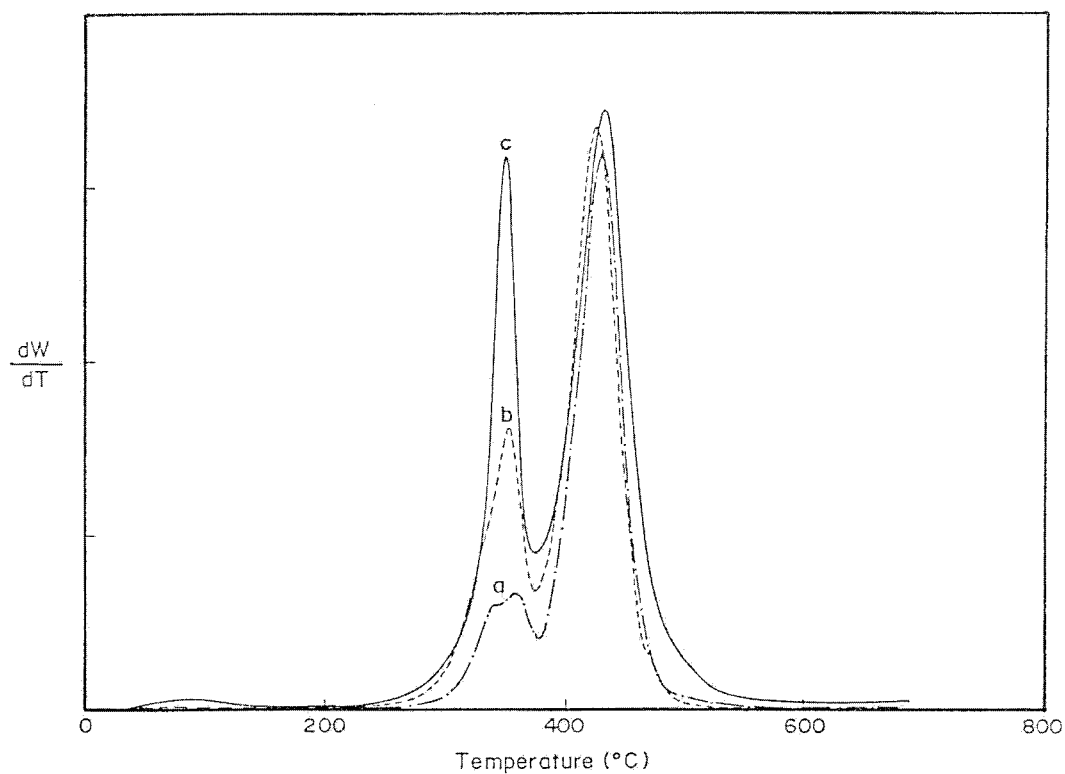


Figure 3 Derivative thermograms of polymers with various HSCs: (a) pg2ad20, (b) pg2ad40, and (c) pg2ad60.

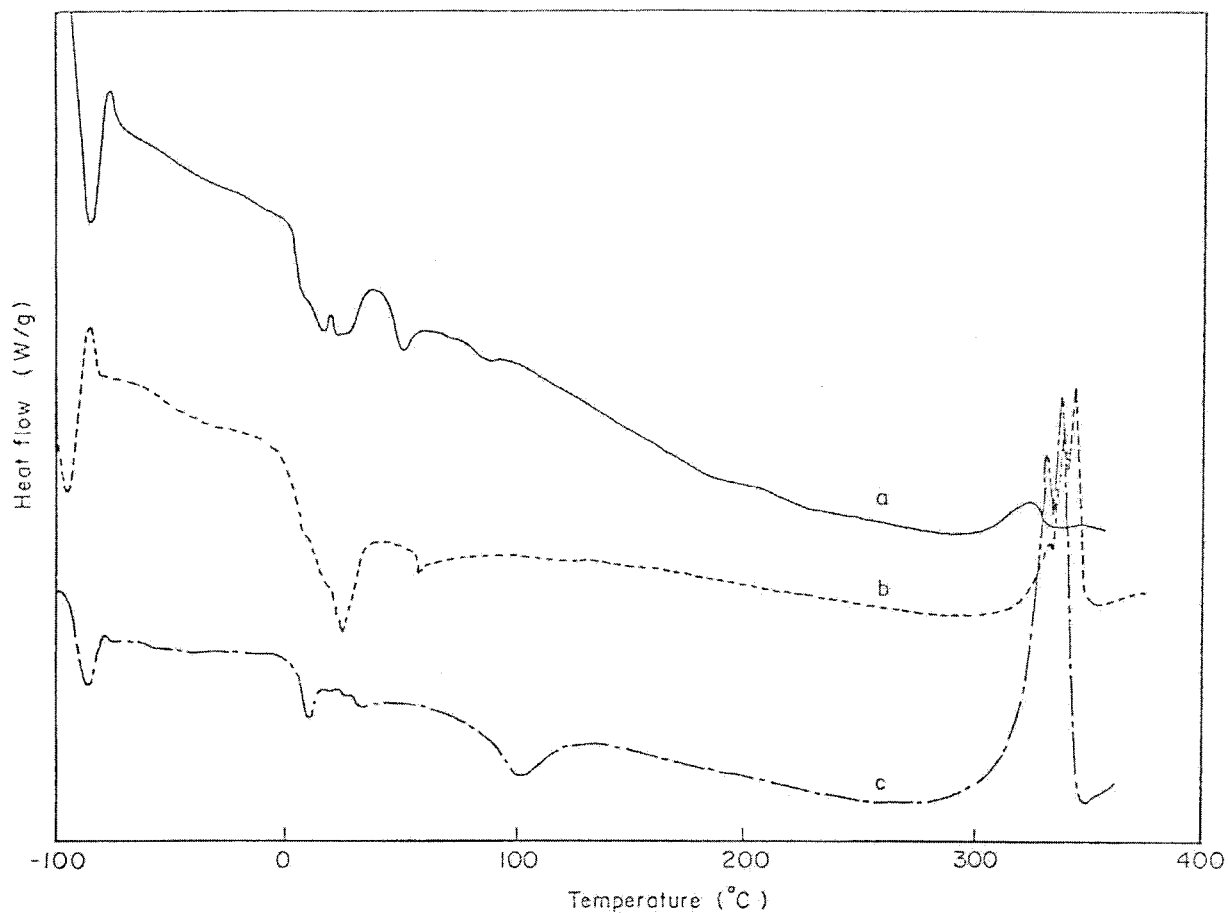


Figure 4 DSC curves of PUSs containing different HSCs: (a) pg2ad20, (b) pg2ad40, and (c) pg2ad60.

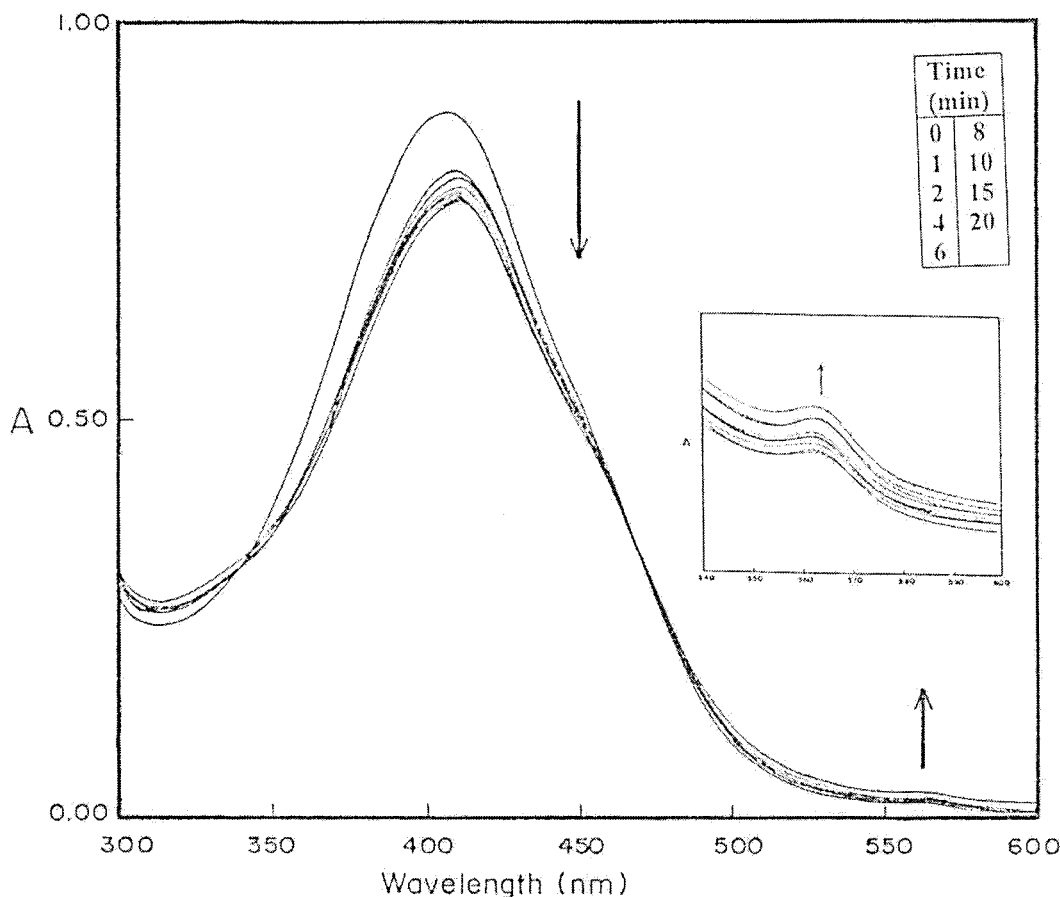


Figure 5 Representative absorption spectra of PUS pc2ad40 at various irradiation times.

were kept in the dark. The solutions were withdrawn at regular intervals, and the absorbance was measured. In all the cases, the chromophore returned to the initial state, but after a long time of 40–45 h, the rates of relaxation, as calculated from the slope of $\ln(A_\infty - A_0)/(A_\infty - A_t)$ versus the time plot, were similar. Here A_∞ is the absorbance after irradiation for an infinite time. The isomerization proceeded according to first-order kinetics. The incorporation of the azobenzene moiety into the backbone of the polymer chain appears to have little effect on the ease with which the reaction takes place. Further, the isomerization rate of the polymer is independent of the concentration of azobenzene residues in the chain.

Photoviscosity measurements

Several kinds of polymer systems that exhibit changes in their viscosity upon irradiation with UV light have been developed.^{27,28} The inherent viscosities (1 g/dL solutions of the polymers in DMAc) before and after irradiation with UV light for 3–4 h at 366 nm were determined in the presence of visible light. No photoviscosity effect was observed in these cases; that is, the viscosities of the solutions before and after irradiation

were the same. Generally, the viscosity of polymers with long and flexible methylene chains is hardly reduced by photoillumination. The absence of a photodecrease in the viscosity of polymer solutions suggests that the flexible chains of PTMG and polycaprolactone diol (PCL) act as strain absorbers. The conformational change induced by the isomerization of the azobenzene residue is relaxed in the connecting flexible chains of the polyol, and so no change is observed in the shape of the polymer. Therefore, variations of the HSC, polyol molecular weight and type, and length of the chain extender do not have an effect on the photoviscosity.

DMA

Table III lists the dynamic mechanical results of polymers with various compositions. When HSC is increased for a fixed polyol and chain extender, $T_{g,s}$ increases for ester polyol based PUS but decreases for ether polyol based systems. An increase in HSC leads to phase mixing in ester PUS but leads to phase separation in ether PUS. The $\tan \delta$ value corresponding to $T_{g,s}$ decreases with an increase in HSC (Fig. 6), and the initial storage modulus values increase with increas-

TABLE III
Static and Dynamic Mechanical Results for PUS

| Polymer code | DMA | | Stress-strain | | Young's modulus (MPa) |
|--------------|----------------------------------|--------------|------------------------|----------------|-----------------------|
| | $T_{g,s}$ ($^{\circ}\text{C}$) | Tan δ | Tensile strength (MPa) | Elongation (%) | |
| pg2ad20 | -37.9 | 0.343 | 3.6 | 559 | 3.8 |
| pg2ad40 | -47.4 | 0.280 | 5.0 | 379 | 6.5 |
| pg2ad60 | -58.3 | 0.147 | 9.5 | 160 | 12.9 |
| pg2od20 | -40.3 | 0.203 | 10.8 | 1306 | 2.3 |
| pg2sb20 | -43.9 | 0.169 | 3.2 | 336 | 4.6 |
| pg2td20 | -43.7 | 0.252 | 3.2 | 740 | 3.3 |
| pg6ad60 | -12.7 | 0.120 | 15.5 | 37 | 134.3 |
| pc5ad40 | -19.1 | 0.240 | 10.5 | 115 | 70.5 |
| pc5ad50 | -13.0 | 0.144 | 14.4 | 70 | 96.6 |
| pc5ad60 | 16.4 | 0.119 | 17.5 | 20 | 188.4 |
| pc2ad40 | -30.0 | 0.226 | 6.1 | 424 | 38.0 |

ing HSC; this indicates increasing rigidity. When the polyol and HSC are fixed at 2000 and 20%, respectively, and the chain extender is varied, $T_{g,h}$ can be observed; for pg2sb20, this may be due to the mobility of the flexible methylene chains in the hard segments.

When the molecular weight of the polyol is increased and the other factors are fixed, $T_{g,s}$ decreases and tan δ values corresponding to the lower transition increase. High-molecular-weight ester polyol (PCL 2000) based polymers show a hump around 20 $^{\circ}\text{C}$ cor-

responding to the crystalline melting point of the soft segment. Moreover, T_g of the polymers based on ester polyols is higher than that of ether polyol based PUS because of the additional hydrogen bonding in the ester groups, which leads to phase mixing.

Stress-strain analysis

The stress-strain values of polymers of various compositions are given in Table III. With a fixed polyol

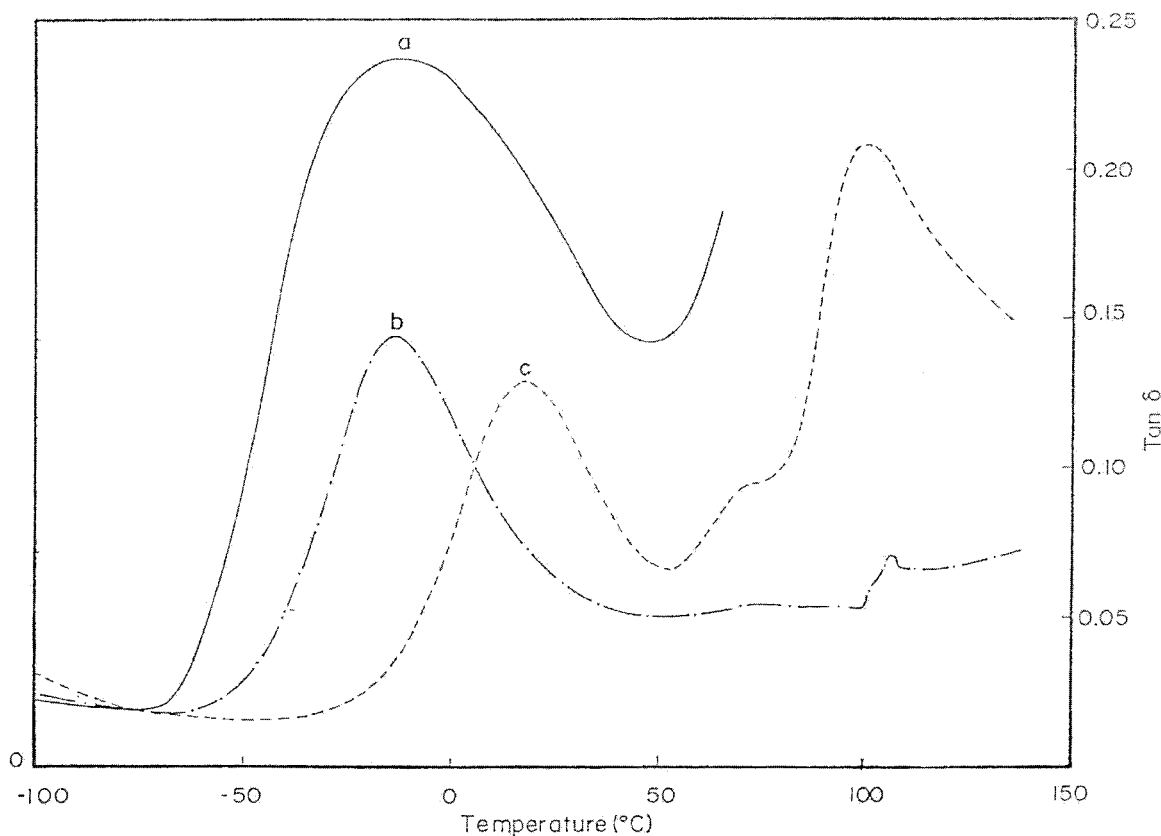


Figure 6 Effect of the HSC on the dynamic mechanical properties of (a) pc5ad40, (b) pc5ad50, and (c) pc5ad60.

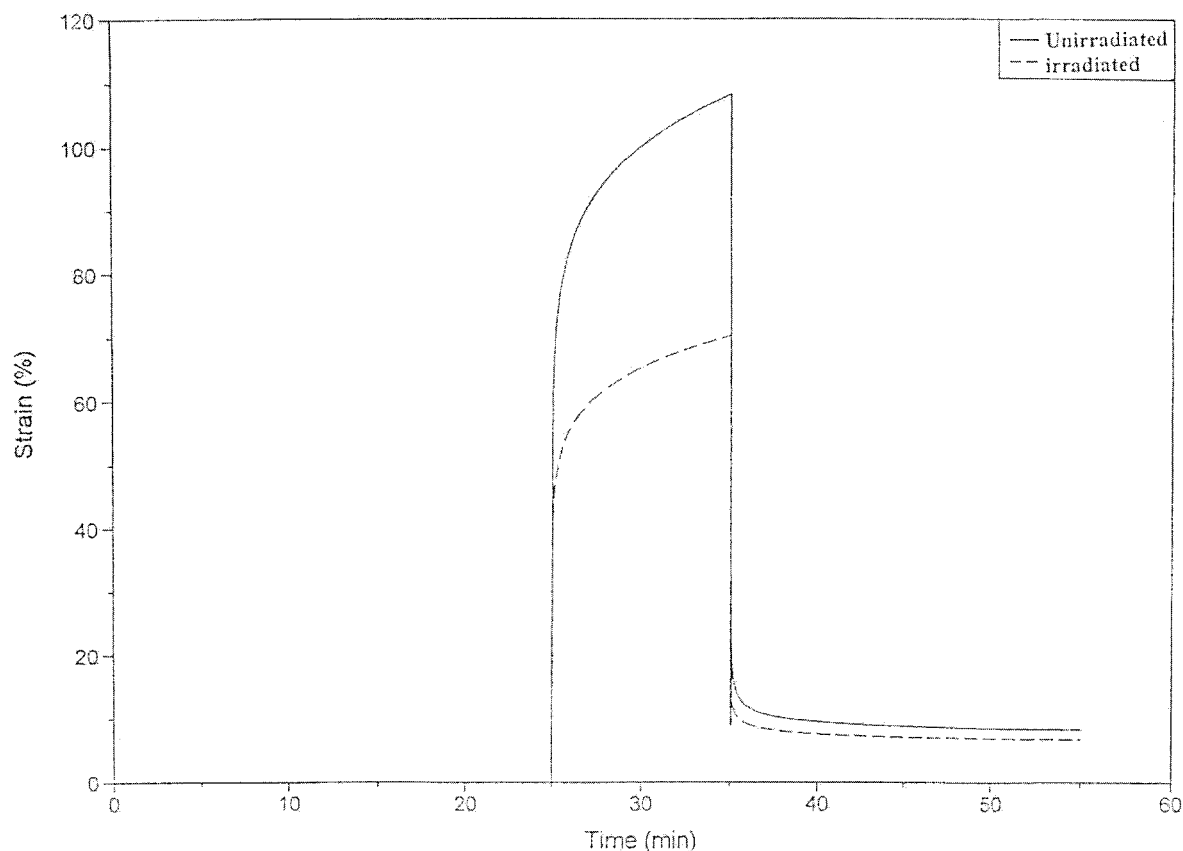


Figure 7 Creep-recovery curves of irradiated and unirradiated samples of pg2od20.

molecular weight (PTMG 2000 and PCL 530) and a fixed chain extender (adipoyl dihydrazide), when HSC is increased, the tensile strength increases and the elongation decreases. This is because the soft segment contributes to the elongation and the hard segment contributes to the tensile strength. As for polyols of two different molecular weights, at a fixed HSC, the low-molecular-weight-polyol-based polymers exhibit better tensile strength, and the high-molecular-weight-polyol-based PUSs exhibit better elongation. With the HSC and chain extender fixed, the polyol type is varied. PCL has better tensile properties because of the additional hydrogen bonding in the ester groups, which leads to a phenomenon called *strain-induced crystallization*. The nature of the chain extender seems to have no effect on the tensile properties of the polymers.

Creep-recovery studies

The DMA creep-recovery curves for the polymer samples resemble the response predicted by the Burgers model, suggesting that the macroscopic viscoelasticity of the polymer can be understood in terms of this model. The large time-independent, virtually instantaneous strain upon an impulsive increase in the stress

indicates elastomeric behavior with a weak Hookean constant. The weaker the Hookean constant is, the larger the initial fast displacement is. After the weak Hookean spring reaches the maximum displacement, the polymer shifts through the curvature of the Voight region to the Newtonian region. The creep response is time-dependent and indicates the yielding of the polymer to stress through the reorganization of its internal microscopic structure. The creep rate of the polymer is indicative of the stability of its elastomer structure. The creep-recovery curves of irradiated (6 h of irradiation) and unirradiated samples are shown in Figure 7. The photostationary state is attained after about 6 h of irradiation, and thereafter the extent of deformation is the same; that is, further irradiation with UV light does not alter the extent of deformation.

An idealized strain curve in a creep-recovery study shows three distinct regions of behavior related to the initial deformation: a transition zone, an equilibrium region, and a recovery region. During photoisomerization, there is no marked difference in the transition, equilibrium, and recovery zones. However, a marked difference can be seen in the initial deformation. Unirradiated samples undergo a large deformation at a given stress of 2.5 MPa and recover completely. In the unirradiated state, the azobenzene residues are in the

trans form, and the chains are extended. Upon the application of stress, they readily deform. However, irradiated samples exhibit only small deformations, although the recovery is almost 100%. Under irradiation with UV light, the chains undergo coiling because of isomerization from the trans state to the cis state. This in turn is reflected as small deformation when stress is applied because the coiled chains cannot undergo much stretching.

The extent of deformation also varies with the irradiation time; that is, samples undergo less deformation when the irradiation time is increased. With the irradiation time, more chains in the trans form are converted into the cis form, and this leads to the coiling of chains.

CONCLUSIONS

A series of PUSs with photochromic azobenzene groups in the polymer backbone were synthesized by a two-step prepolymer method. Thermal analyses revealed that the thermal stabilities were independent of the HSC and that phase separation occurred in the systems prepared with high-molecular-weight ether polyol. The results were consistent with DMA, which furthered supported the phenomenon of phase separation. The variation of HSC also affected the static mechanical properties: a higher HSC led to increased tensile strength. In addition to UV-vis spectroscopy results, which proved the photosensitive nature, creep-recovery studies confirmed the photomechanical effects resulting from the photoisomerization of polymer chains. However, the rates of isomerization were found to be independent of the chromophore concentration.

References

- Laptii, S. V.; Kercha, Y. Y.; Balitskaya, L. G.; Yurchik, Z. H.; Lebedev, A. F. *Ukr Khim Zh* 1991, 57, 208; *Chem Abstr* 1991, 115, 73416t.
- Gaiduk, R. L.; Kercha, Y. Y.; Yakovenko, A. G.; Bogdanovich, V. A.; Oranskaya, E. I. *Vysokomol Soedin Ser A* 1990, 32, 339; *Chem Abstr* 1990, 113, 24807.
- Grischenko, A. E.; Ruchin, A. E.; Nikolev, V. Y.; Yanchevskii, V. A.; Lebedev, A. F.; Skazka, V. S. *Vysokomol Soedin Ser A* 1984, 26, 2332; *Chem Abstr* 1995, 102, 25356h.
- Salvel'ev, U. V.; Veselov, V. Y.; Grekov, A. P. *U.S.S.R. Pat.* 1,659,429 (1987); *Chem Abstr* 1992, 117, P8729z.
- Vilenskii, V. A.; Kercha, Y. Y.; Shumskii, V. F.; Sukhorukova, S. A.; Grekov, A. P. *Vysokomol Soedin Ser A* 1976, 18, 910; *Chem Abstr* 1978, 88, 106069.
- Fabrenfabriken Bayer A.G. *Fr. Pat.* 1,546,262 (1968); *Chem Abstr* 1969, 71, 51211t.
- Ivashkevich, S. L.; Kozhanova, L. N.; Nozhenko, L. A.; Gorbachev, A. A.; Lishchuku, L.; Grekov, A. P.; Travinskaya, T. V.; Trukhan, G. P. *U.S.S.R. Pat.* 1,687,625 (1991); *Chem Abstr* 1992, 117, 153180t.
- Korenko, L. A.; Yakovenko, A. G.; Kercha, Y. Y. *Ukr Khim Zh (Russ Ed)* 1988, 54, 752; *Chem Abstr* 1989, 110, 8940s.
- Vilen'skii, V. O.; Glieva, G. E.; Goncharenko, L. A.; Kercha, Y. Y.; Sukhorukova, S. A.; Levchenko, N. I.; Grekov, A. P. *Ukr Khim Zh (Russ Ed)* 2000, 66, 56; *Chem Abstr* 2001, 134, 353862.
- Sukhorukova, S. A.; Navrotskaya, R. P.; Grekov, A. P. *Ukr Khim Zh (Russ Ed)* 1986, 52, 540; *Chem Abstr* 1986, 105, 173419h.
- Yanchuk, N. I. *Fiz Khim Osnovy Sinteza Pererab Polim Gor'kii* 1983, 83; *Chem Abstr* 1984, 100, 35199g.
- Stenzenberger, H.-D.; Hummel, D. O. *Angew Makromol Chem* 1979, 82, 103.
- Ewelina, O.; Ryszard, J.; Stanislaw, K. *Eur Polym J* 2002, 38, 1871.
- Natansohn, A.; Rochon, P. *Chem Rev* 2002, 102, 4139.
- Organic Photochromic and Thermochromic Compounds; Crano, J. C.; Guglielmetti, R. J., Eds.; Kluwer Academic: New York, 1999.
- Ebralidze, T. D.; Mumladze, A. N. *Appl Opt* 1990, 29, 44.
- Bai, S.; Zhao, Y. *Macromolecules* 2001, 34, 9032.
- Wang, C. I.; Kuo, Y. M.; Chao, D. Y. *Polym Adv Technol* 2000, 11, 127.
- Kuo, Y.-M.; Ku, K. Y.; Lin, H. C.; Wang, N. H.; Chwang, C. P.; Chao, D. Y. *J Appl Polym Sci* 1998, 69, 2097.
- Al-Salah, H. A. *Acta Polym* 1998, 49, 465.
- Morman, W.; Baharifar, A. *Polym Bull* 1990, 24, 413.
- Campbell, T. W.; Foldi, V. S.; Farago, J. J. *J Appl Polym Sci* 1959, 2, 155.
- Vogel's Text Book of Practical Organic Chemistry, 5th ed.; ELBS: London, 1996; p 703.
- Reid, E. B.; Prichett, E. J. *J Org Chem* 1953, 18, 715.
- Petersen, J. M.; Price, C. C. *Organic Syntheses*; Wiley: New York, 1953; p 33.
- Wu, Y.; Natansohn, A.; Rochon, P. *Macromolecules* 2001, 34, 7822.
- Seymour, R. W.; Cooper, S. L. *Macromolecules* 1973, 16, 48.
- Irie, M.; Menju, A.; Hayashi, K. *Macromolecules* 1979, 12, 1176.
- Menju, A.; Hayashi, K.; Irie, M. *Macromolecules* 1981, 14, 755.