Synthesis and Properties of Polyetherurethane Pendant with Azo-dye by N-Substitution

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SYNOPSIS

Polyurethane elastomers pendant with azo-dye were prepared by N-substitution by a two-step process. First, the polymer is metalated by sodium hydride, and then the prepared urethane polyanion is treated with ω-bromohexyloxyphenyl-p-nitroazobenzene. The polyurethanes were characterized by NMR, UV, FTIR, GPC, DMA, X-ray, and polarized optical microscopy. The reaction caused cleavage of some allophanate bond degradation and narrower MW distribution. As the substitution degree increased, the hydrogen bonds in polyurethane diminished and phase mixing with azo-dye was enhanced. Photoisomerization of the pendant azo-dye was also observed. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Organic azo-dye is one of a type of important materials recently introduced in modern technologies, structurally due to its specific visible spectra absorption, strong chromophore orientation, and photothermal isomerization which cause azo-dye to be able to used as dye lasers, nonlinear optics, and liquid crystallines in academic as well as industry applications.

The systems were incorporated the azo-dye as part of a side chain to the backbone by Ringsdorf and other groups.[1] These polymers have the advantage that a high chromophore concentration they can be incorporated into the polymer system without crystallization, phase separation, or the formation of concentration gradients and even the relaxation process might be dramatically slower because the motions of the chromophore are hindered by its attachment to the polymer. Recently, a review concentrated on the chemical nature of the polymer systems identified as promising second-order nonlinear optical materials in that most of them are concerned with azo-dye directly linked to the polymer backbone. Among the polymer systems, encouraging results have been reported for polyurethane derivatives.[2]

The incorporation of functional azo-dye diol or diamine as a chain extender can produce a polyurethane block copolymer with a pendant azo-dye on the hard segment.[3] Such a dye-containing polyurethane elastomer may possess both characteristics of the dye and thermoplastic elastomer properties which are expected to import a wide range of service temperature due to the semirigid hard segment as well as to the anisotropic optical, electrical, and mechanical responsible materials.[4] However, this system could suffer from the disadvantage that the urethane hydrogen bonding may interfere with the chromophore orientation of the azo-dyes. Instead, a N-substitution reaction was chosen to synthesize azo-dye derivations of polyurethane in this investigation.

EXPERIMENTAL

Materials

The model polyurethane (PU) was commercial Pellethane 2363 80A provided by Dow Chemical which is based on methylene diphenyl diisocyanate, 1,4-butanediol, and polytetramethylene oxide (M_n = 981) with a molar ratio of 3 : 2 : 1, respectively, and was extracted with toluene for 24 h before use. ω-Bromohexyloxyphenyl-p-nitro-azobenzene was prepared as described in the literature[5] (mp 86.8°C). Dimethylformamide was purified by distillation and stored over molecular sieves of 3 Å. Sodium hydride

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Table I N-substitution of Polyurethane

Designed Degree of Substitution	Experimental DS[a] (mol %)	From UV[b] (Wt %)
PU-0	0	0
PU-25	13.6	12.1
PU-50	39.3	28.5
PU-100	91.1	48.1

[a] Degree of substitution.
[b] λ_{max} = 380 nm.

was from Aldrich, 60 wt % in paraffin oil, and used as received.

Polymer Synthesis

To a solution of 15 wt % PU dissolved in dry DMF, a calculated amount of sodium hydride suspended in DMF was added with stirring, at a temperature not exceeding 0°C. After the evolution of H_2 ceased, the appropriate amount of ω-bromohexyloxyphenyl-

p-nitroazobenzene in DMF was added to the mixture. After another 4 h of stirring, distilled water was added dropwise to the mixture to precipitate the polymer. The polymer was extracted in a Soxhlet with ethanol to remove DMF and unreacted starting material, and the product was dried in a vacuum.

Polymer Characterization

^{1}H-NMR spectra were recorded on a Bruker AM-500 spectrometer in a solution of deterated tetrahydrofuran. Chemical shifts (δ) are given in ppm with tetramethylsilane as a standard.

UV-visible absorption spectra were recorded with a Shimadzu UV-240 spectrophotometer. The pure solvent was placed in the reference beam. Photoisomerizations were carried out by irradiation with a 350 W high-pressure xenon lamp.

Infrared survey spectra were recorded with a Nicolet 170X. One hundred scans at a resolution of 2 cm^{-1} were signal-averaged before Fourier
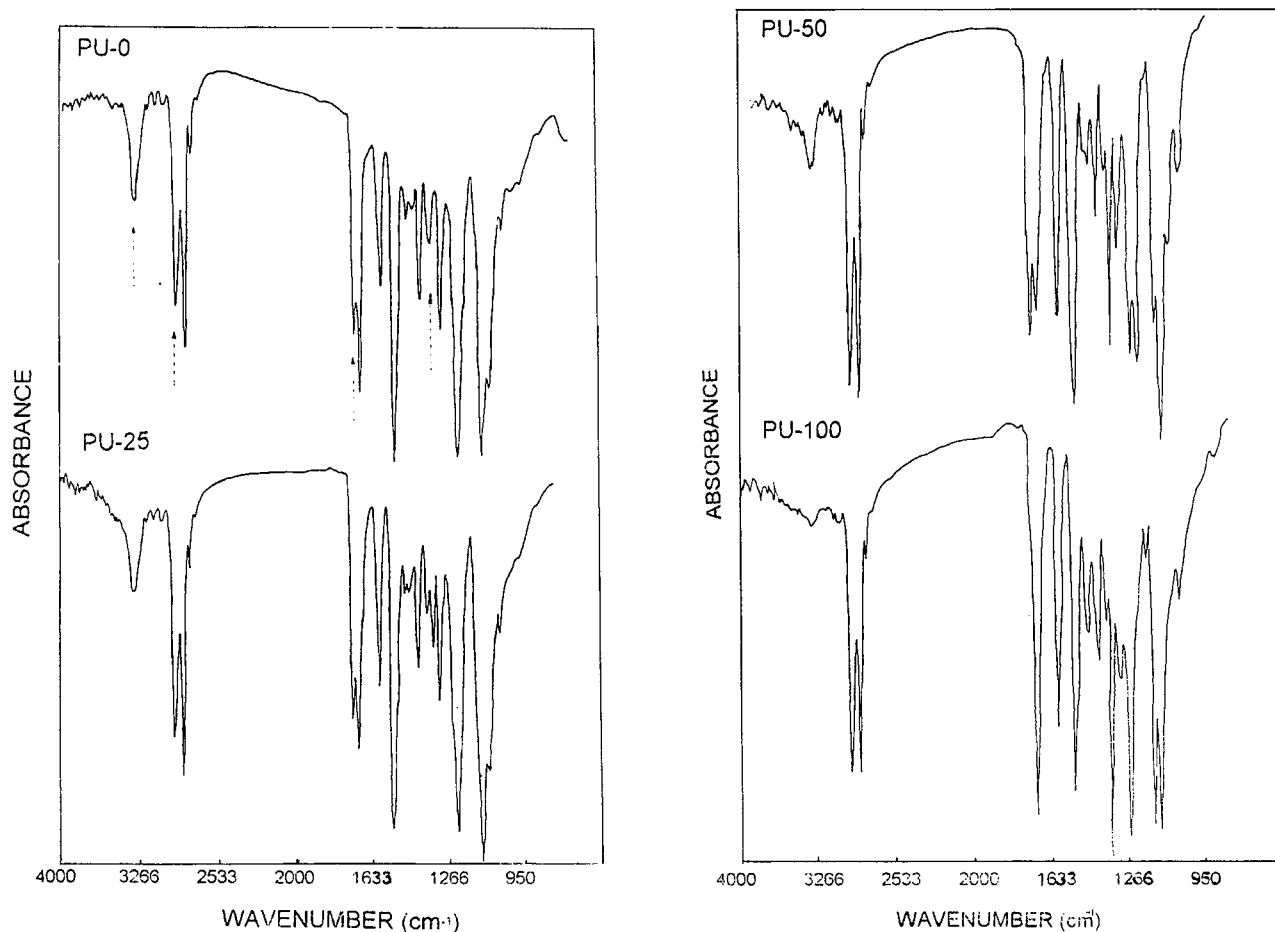
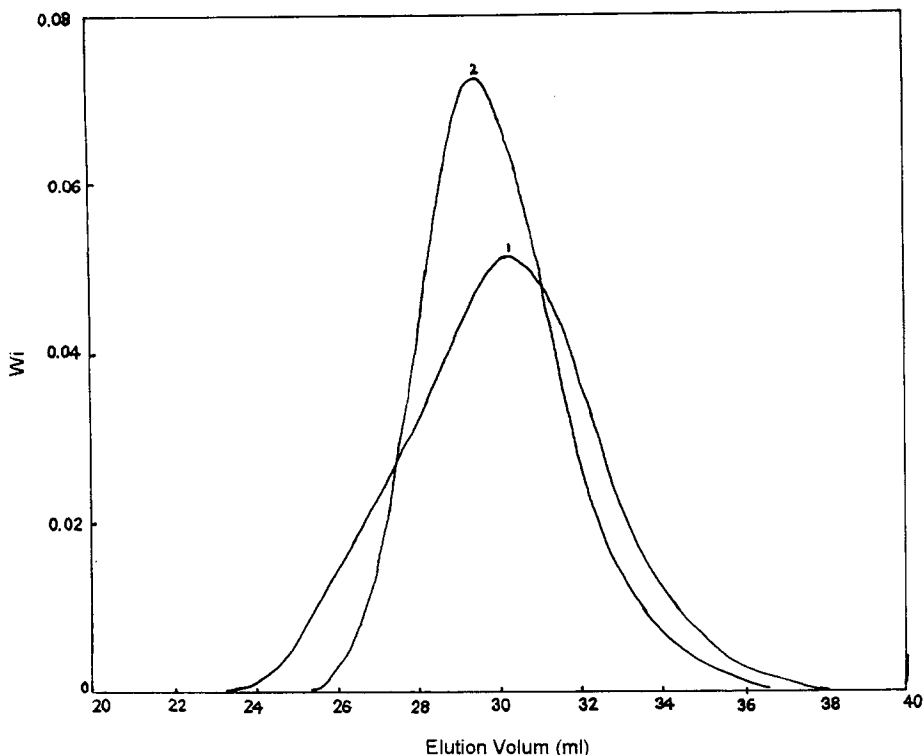

Figure 1 IR spectra of N-substitution PUs.

Figure 2   Molecular weight of (1) PU-0 and (2) PU-50.

transformation. All IR spectra covered the range 400–4000 cm^{-1}.

The molecular weight and distribution were obtained by a Waters high-pressure gel permeation chromatography (GPC) assembly (Model M590 pump μ-Styragel columns of 10^5, 10^4, 10^3, 500, and 100 Å, refractive index detector). Elution counts were calibrated by well-defined polystyrene standards. THF solutions were used and the flow rate was 2 mL/min.
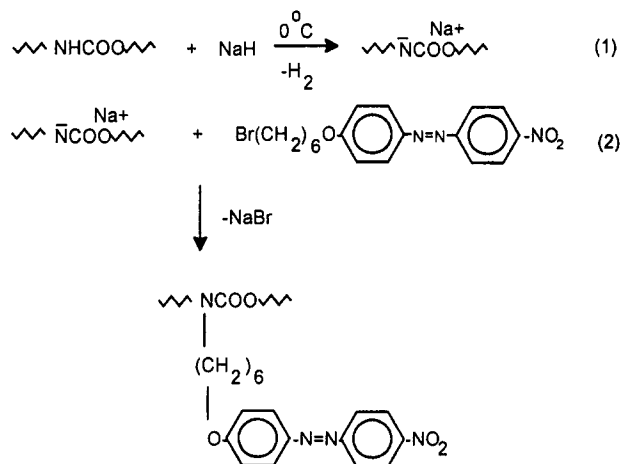
Dynamic mechanical data were obtained using a DDV-II-C apparatus that was controlled by a computer. All measurements were carried out under a nitrogen purge at a frequency of 110 Hz with a constant heating rate of 2 K/min.

X-ray measurements were made using monochromatic CuKα radiation (λ = 1.5418 Å) and a Nicolet Xentronics two-dimensional position-sensitive and a data system. Data were collected for 20 min, and background scans of equivalent duration were subtracted to remove background scatter. The two-dimensional data were then azimuthally averaged to generate intensity vs. 2θ scans.

Optical texture was studied with a Leitz-350 polarizing optical microscope equipped with a Linkam hot stage and a Polaroid camera. The sample was molten in thin layers between slide glasses at about 450 K and cooled down to room temperature under shear.

RESULTS AND DISCUSSION

Model polyurethane was used to carry out N-substitution according to the following scheme[6]:

$$\sim\!\!\sim NHCOO\!\!\sim\!\!\sim \ +\ NaH \xrightarrow[-H_2]{0^\circ C} \sim\!\!\sim \overset{-}{N}COO\!\!\sim\!\!\sim \overset{Na^+}{} \qquad (1)$$

$$\sim\!\!\sim \overset{Na^+}{\overset{-}{N}COO}\!\!\sim\!\!\sim \ +\ Br(CH_2)_6O\!\!-\!\!\bigcirc\!\!-\!\!N\!\!=\!\!N\!\!-\!\!\bigcirc\!\!-\!\!NO_2 \qquad (2)$$

$$\downarrow \ -NaBr$$

$$\sim\!\!\sim NCOO\!\!\sim\!\!\sim$$
$$|$$
$$(CH_2)_6$$
$$|$$
$$O\!\!-\!\!\bigcirc\!\!-\!\!N\!\!=\!\!N\!\!-\!\!\bigcirc\!\!-\!\!NO_2$$

Sodium hydride was used in the first step of the above scheme to abstract the labile urethane proton. In the next step, the prepared urethane polyanion acts as a nucleophile in the bromine substitution in the molecule of the azo-dye-containing alkylhalogenide, forming pendant polyurethane with azo-dye.

To compare the effects of substitution degree on the physical properties of PU, three different levels
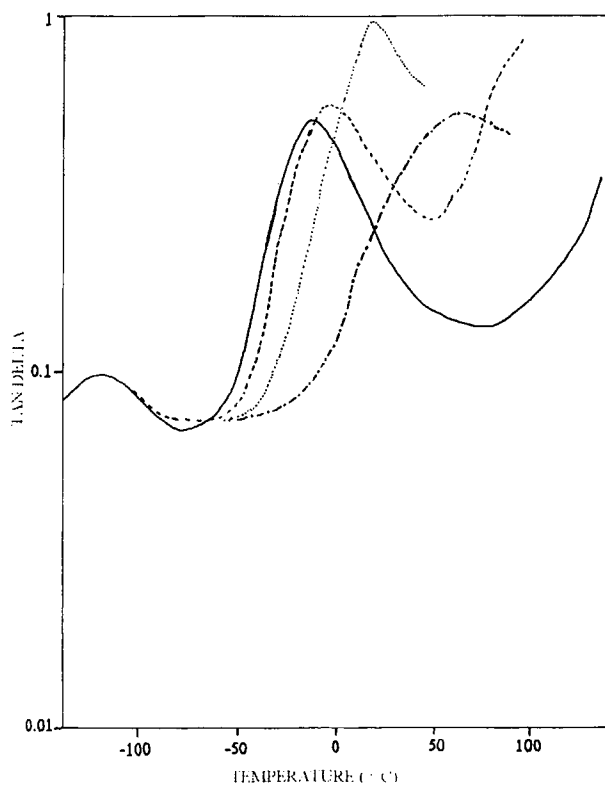
Figure 3 Dynamic mechanical spectrum of N-substitution PU: (———) PU-0; (— —) PU-25; (· · · ·) PU-50; (— · — ·) PU-100.

of substitution were synthesized. The results are listed in Table I. The results show that the yield of substitution was satisfied by this reaction. We suppose that the molar extinction coefficient of azo-dye-containing alkylhalogenide is equal to that of polymers within experimental error.

¹H-NMR Analysis

The structures of the prepared N-substitution PU were confirmed by ¹H-NMR. In the NMR spectrum of the maximum substitution PU, the signal of the urethane proton (NH—CO—O) at 8.51 ppm totally disappeared, as expected, while a new signal appeared at 7.84–7.90 ppm
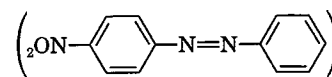
and 8.26 ppm
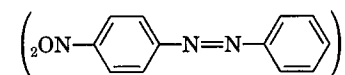
The lack of a signal for the NH proton and the presence of signals for nitroazobenzene was proof of the N-modification of the PU. In the spectra of the partial substitution PU, the appearance of the corresponding signals for the nitroazobenzene was observed, while the signal for the urethane proton was of decreased intensity.

Infrared Spectroscopy

The IR spectrum shows changes in the bonding characteristics of the hard-segment urethane carbonyl groups at 1700 cm⁻¹ for bonded groups, 1730 cm⁻¹ for free groups, and for the NH— group at 3317 cm⁻¹ (NH stretching) (Fig. 1). In the spectrum of the maximum substitution, the peak of 3317 cm⁻¹ almost disappeared while new bands, characteristic
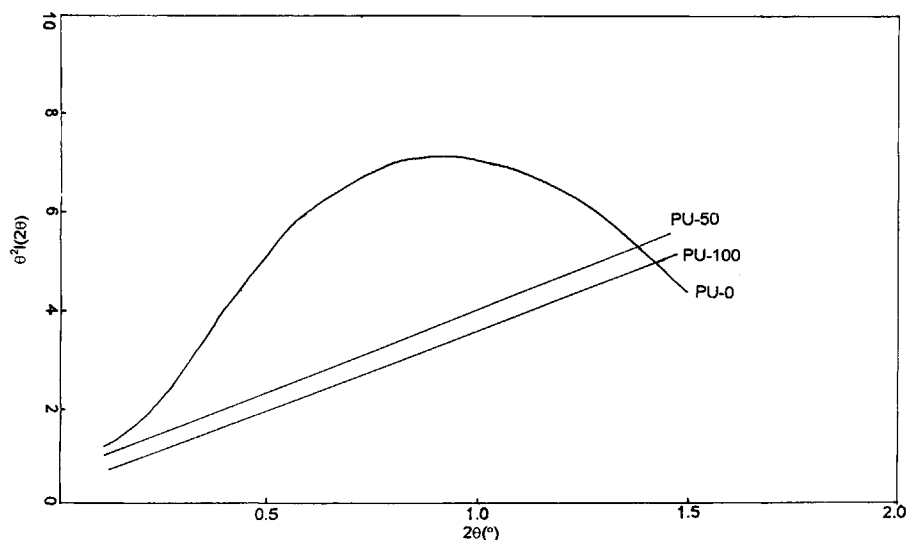

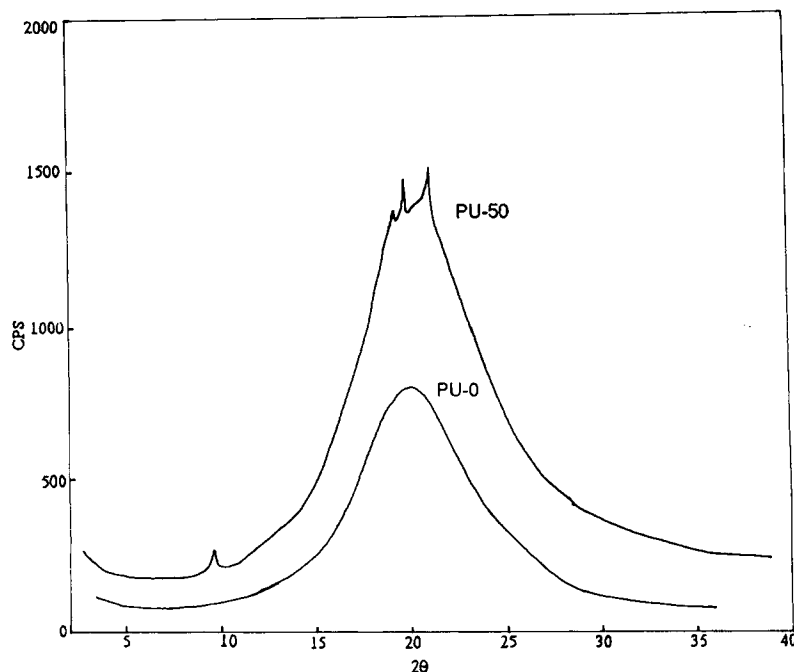**Figure 4** SAXS of PU-0, PU-50, and PU-100 at room temperature.

Figure 5 WAXD scanning of PU-0 and PU-50 at room temperature.

for the $-NO_2$ group and a single carbonyl peak, appeared at 1342 and 1730 cm^{-1}, respectively.

In the spectra of the partially substituted samples, the bands associated with NH and bonded C=O are of decreased intensity, while the free C=O and methylene bands increase. It means that the hydrogen bonds in model PU diminished as the substitution degree increased.

GPC Analysis

To confirm the change of molecular weight during the N-substitution reaction, the molecular weight of the model PU and PU-50 was measured by GPC. Some interesting results are observed in Figure 2. The model PU shows the broad distribution and a shoulder which indicated the high molecular weight fraction. The treated PU for PU-50, however, exhibits a narrow distribution without the shoulder of a high molecular weight fraction and the molecular weight increased, which was in good agreement with the calculated value. This means that there is a negligibly small degradation of model PU because the molecular weight of the resulting polymer would have decreased if degradation of the main chain occurred. It is known that the formation of allophanate and biuret is hard to avoid in the process of PU preparation. The side chains of these products were broken more easily under the sodium hydration as the following scheme shows:
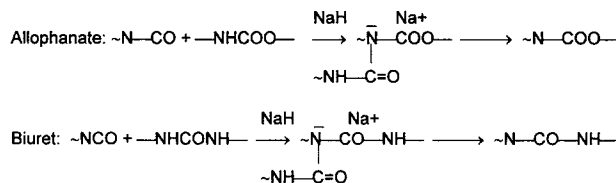
Dynamic Mechanical Thermal Analysis

Rheovibron dynamic mechanical testing was used to study the dynamic moduli (E', E'') and internal friction (tan δ) as a function of temperature for -150 to $150°C$. The PUs are illustrated in Figure 3. Two peaks designated γ and β appear in the tan δ data. The γ peak relaxation at $-125°C$, which is independent of sample composition, is a local mode motion of CH$_2$ sequences in the polyether phase. The β peak corresponds to the glass transition of the polyether-rich soft-segment phase. Different levels of substitution cause the β peak to move to higher temperatures. The PUs for PU-0 and PU-25 exhibited two phases obviously, while PU-50 and PU-100 were too soft to measure a high T_g.

Further confirmation was made by small-angle X-ray scattering (SAXS). SAXS has been probed to study polymer morphology.[7–9] From the smeared SAXS data in Figure 4, a peak or "d" spacing of 54 Å was obtained for sample PU-0 but no shoulder or "d" spacing for sample PU-50 and PU-100. The fact that the spacing is decreased by an increase of the substitution suggests that we are dealing with the
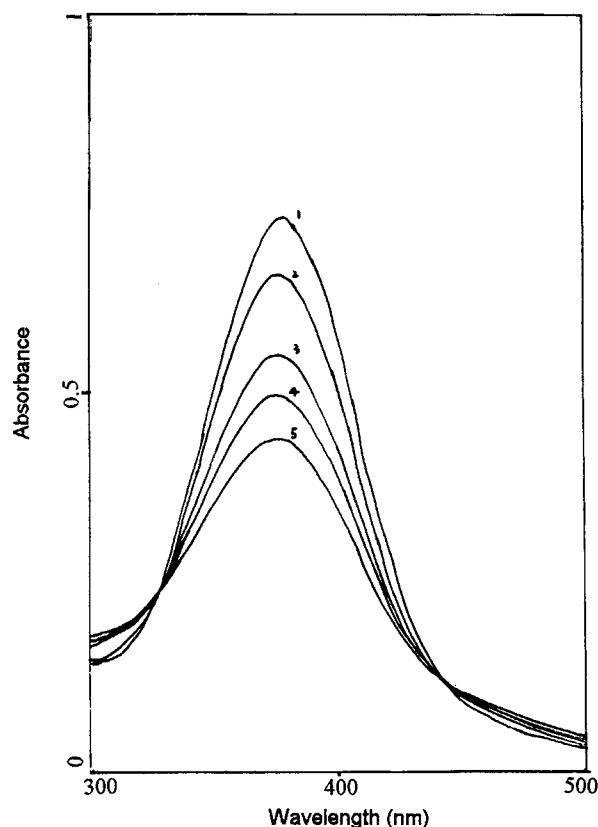
Figure 6   Absorption spectra of PU-100 in DMF after different periods of irradiation at λ = 380 nm: (1) before irradiation; (2) 2 h; (3) 4 h; (4) 6 h; (5) 8 h.

average interdomain spacing as might be expected, although the SAXS spacing obtained is too large to be directly correlated to the domain size.[10] The discussion of the SAXS data would be relatively qualitative. The above DMA and SAXS results showed that the phase mixing was enhanced as the substitution degree increased. This enhanced phase mixing is attributed to the disruptive effect of the pendant chain on the packing of the hard segment and decreased cohesion forces within the hard segment by hydrogen bond loss. It is well known that substitution of the urethane proton in PUs leads to changes in a number of their physicochemical and physicomechanical properties.[11] By reducing the number of the N—H protons, there is decrease in the intermolecular interactions within the hard segment by hydrogen bond loss between the urethane groups. The increase in the soft T_g also indicated enhanced phase mixing with azo-dye incorporation.

Liquid Crystalline Texture or Not?

The alkyloxyphenyl-p-nitroazobenzene is a liquid crystalline compound and shows some liquid crystalline properties in polystyrene side-chain derivatives.[12] For our samples, we observed a rather dif-

fuse birefringent pattern under a crossed Nicols and no sharp striations could be discriminated. In accordance with this observation, the WAXD diagrams of PU-50 showed a rather diffuse curve as shown in Figure 5, being different from the halo of the completely amorphous sample. Partial organization of the molecules, which was attributed to the azo-dye microcrystalline, could not be denied. The WAXD of PU-0 showed that both the hard segment and soft segment were amorphous. Further work is underway.

Photoisomerization

The UV absorption spectrum of azobenzene is known to change when the configuration changes from *trans* to *cis* upon irradiation.[13] Many previous studies[14-16] were concerned with the photochemical and thermal isomerization of azoaromatic residues in the side chains and in the backbone of polymers in the bulk.

We observed similar spectral changes from N-substitution PUs when compounds containing azobenzene in the side chain were exposed to UV (Fig. 6). The intense absorption at 380 nm due to the π–π* transition decreased under irradiation while the intensity increased gradually in the dark. Both *trans-cis* and *cis-trans* isomerizations took place by a photochemical process. The photoisomerization
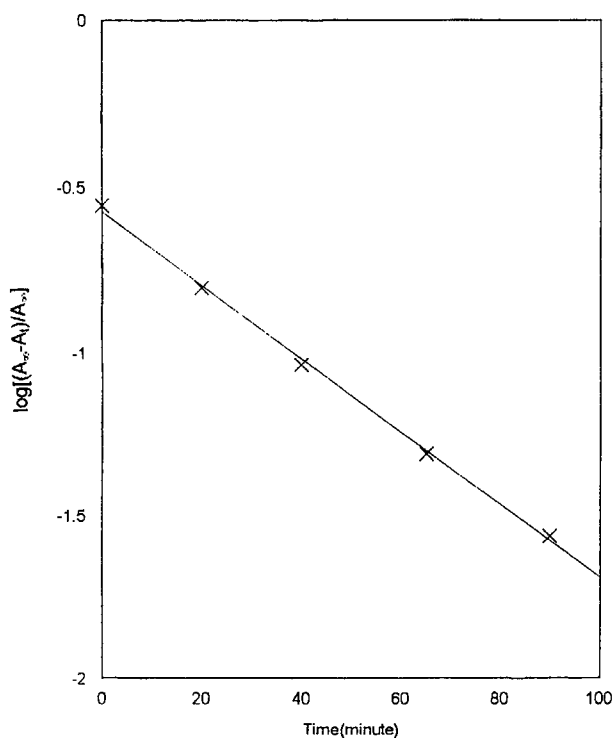

Figure 7   First-order plot of the thermal isomerization of PU-100 in DMF at room temperature after irradiation.

cycle can be repeated without fading. The first-order plot of the thermal isomerization of azobenzene in PU film at room temperature is shown in Figure 7. This is a plot of $\log[(A_\infty - A_t)/A_\infty]$, where A_∞ is the absorbance at $\lambda = 380$ nm before UV irradiation and A_t is that at time t after UV irradiation.

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