OFFICE OF NAVAL RESEARCH

GRANT N0014-90-J-1148

R&T Code 4132016

Scientific Officer: Dr. Kenneth Wynne

Technical Report No. 96-08

Synthesis and Optical Properties of Polyureas with Azoaromatic Groups in the Main Chain

by

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Submitted to

Macromolecular Chemistry and Physics

University of Massachusetts Lowell
Department of Chemistry
Lowell, Massachusetts

February 6, 1997

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. AGENCY USE ONLY *(Leave blank)*

2. REPORT DATE
February 6, 1997

3. REPORT TYPE AND DATES COVERED
technical; 01JUNE 96 to 30SEPT97

4. TITLE AND SUBTITLE
Synthesis and Optical Properties of Polyureas with Azoaromatic Groups in the Main Chain

5. FUNDING NUMBERS
C: N00014-90-J-1148
R&T Code: 4132016
Dr. Kenneth J. Wynne

6. AUTHOR(S)
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University of Massachusetts Lowell
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8. PERFORMING ORGANIZATION REPORT NUMBER
1148-96-08

9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)
Office of Naval Research-Physical S&T Division, ONR 331
Department of the Navy
Arlington, Virginia 22217-5000

10. SPONSORING / MONITORING AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES

12a. DISTRIBUTION / AVAILABILITY STATEMENT
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12b. DISTRIBUTION CODE

13. ABSTRACT *(Maximum 200 Words)*

We report the synthesis and optical properties of two different polyureas containing azo units in the main chain. The polymers were synthesized from the reaction between a diisocyanate and a diaminoazo compound (4,4'-diaminoazobenzene) with good yield. These polyureas had glass transition temperatures around 197°C and the films of these polymers showed an absorption maximum at 380 nm due to the azo chromophore. Upon polarized laser irradiation at 488nm, dichroism was optically induced in these main-chain azoaromatic polymers with a fairly high glass transition temperature. In addition we observed a degree of polar order by corona poling and a build up of second harmonic signal. It is conjectured that the induced order results mainly from an alignment of azo units through *trans-cis trans* isomerization, as well as from the molecular rearrangement of the polyurea backbone. We further observed regularly-spaced surface relief gratings on the polyurea film upon exposure to an interference pattern of polarized argon laser beams. Large scale molecular migration in this high Tg polymer at room temperature has been achieved for the first time.

14. SUBJECT TERMS
Polyureas; azo units; main chain; diiscyanate;diaminoazo compound;polarized laser irradiation; dichroism; corona poling; second harmonic; trans-cis-trans isomerization; surface relief gratings.

15. NUMBER OF PAGES
24

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT
UNCLASSIFIED

18. SECURITY CLASSIFICATION OF THIS PAGE
UNCLASSIFIED

19. SECURITY CLASSIFICATION OF ABSTRACT
UNCLASSIFIED

20. LIMITATION OF ABSTRACT
UL

Standard Form 298 (Rev. 2-89)
Prescribed by ANSI Std. Z39-18
298-102

Synthesis and Optical Properties of Polyureas with Azoaromatic Groups in the Main Chain

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SUMMARY:

We report the synthesis and optical properties of two different polyureas containing azo units in the main chain. The polymers were synthesized from the reaction between a diisocyanate and a diaminoazo compound (4,4'-diaminoazobenzene) with good yield. These polyureas had glass transition temperatures around 197 °C and the films of these polymers showed an absorption maximum at 380 nm due to the azo chromophore. Upon polarized laser irradiation at 488nm, dichroism was optically induced in these main-chain azoaromatic polymers with a fairly high glass transition temperature. In addition we observed a degree of polar order by corona poling and a build up of second harmonic signal. It is conjectured that the induced order results mainly from an alignment of azo units through *trans-cis-trans* isomerization, as well as from the molecular rearrangement of the polyurea backbone. We further observed regularly-spaced surface relief gratings on the polyurea film upon exposure to an interference pattern of polarized argon laser beams. Large scale molecular migration in this high T_g polymer at room temperature has been achieved for the first time.

Introduction

Polymers containing azoaromatic groups have drawn much attention as materials for photonic applications, as photoresponsive materials in opto-electronics, image processing, and nonlinear optics.1),2) The azoaromatic linkages can be incorporated into the backbone of the polymer3),4) or in the side chain5),6) A number of researchers have investigated *trans-cis* photoisomerization of the azobenzene group in the side chain of the polymer, resulting in a photo-induced change of the optical properties of the polymer.5-9) Among these studies, photo-induced orientation of azobenzene units in polymer matrices has received a great deal of attention.10),11) It is generally accepted that repeated *trans-cis-trans* isomerization processes induce the alignment of the molecules in a direction perpendicular to the polarization of the writing beam.12-17) More recently, surface relief gratings have been fabricated in side chain azopolymer films through such repeated *trans-cis-trans* isomerization upon illumination with an interference pattern. Fairly large scale migration of polymer chains in these azo polymers was observed well below T_g.5),18),19)

Several attempts have also been made to incorporate azo units in the polymeric main chain.20-22) Polyamides, polyesters, and polyethers have been synthesized from difunctional azo units using interfacial or solution polymerization techniques.23-26) Kumar *et al.*,27),28) for example, prepared polyureas containing azo groups in their main chain and investigated the *cis-trans* photo- and thermal isomerization of these materials in solutions. However, there has been no report on photo-induced orientation of main-chain azoaromatic polymer films. Relatively slow *cis-trans* isomerization has been reported from solutions of the rigid main-chain polymers. It has been presumed that the expected even slower isomerization process in the films will significantly retard such an orientation mechanism.

Recently nonlinear optical (NLO) properties of poled polymeric materials have received a great deal of interest for potential applications as electro-optic (EO) modulators, switches, and frequency doublers.29) Certain material requirements need to be satisfied by polymers if they are to be used in second-order NLO devices. In addition to large and rapid optical nonlinearity, they need to possess long-term thermal stability and low optical loss. For second harmonic generation applications, transparency in the visible region to short wavelengths is desired. A higher T_g is expected to lead to improved stability of the poled order.29)

It was reported that the urea groups in polyurea have a large dipole moment of 4.9 D,30) which could be aligned by electric poling to induce noncentrosymmetric structures. Although the polyureas studied possessed only modest NLO coefficients, they have the advantage of low cut-off wavelength and good temporal stability of the poling-induced NLO activity.31)

The objectives of this research are to prepare polyureas containing azo units in the main chain via the reaction of diisocyanate and 4,4'-diaminoazobenzene, and to investigate optical properties of the polymer films. The azo groups in the main chain with rigid spacers are expected to lead to a high T_g polymer. Incorporation of the ureas and azo groups into the polymer structure may lead to enhanced NLO properties. We present the synthesis, characterization, NLO properties, and optically induced orientation of polyureas in this paper. In addition, we report the formation of surface relief gratings on a main-chain azoaromatic polymer film for the first time.

Further studies on other optical properties will follow in a subsequent publication.

Experimental part

Materials and reagents

Toluene-2,4-diisocyanate and isophorone diisocyanate were used as received from Aldrich Chem. Co. Inc. Deuterated methyl sulfoxide (DMSO-d_6) was used as received from Aldrich Chem Co. Inc. The polymerization medium, 1-methyl-2-pyrrolidone (NMP, 99+% anhydrous) was also purchased from Aldrich and used as received. All chemicals were used without further purification except where noted.

Synthesis of 4,4'-diaminoazobenzene

The diamine monomer with azo unit, 4,4'-diaminoazobenzene, was synthesized according to the literature procedure.32) The monomer was purified via column chromatography with silica gel using an eluent (ethyl acetate : *n*-hexane = 1 : 1, *v/v*%).

IR (KBr) : 3338 (m; NH_2), 3100 (w; aromatic CH), 1625 (s; NH),
1592 (s; aromatic C=C), and 1149 cm^{-1} (s; C-N)

^{1}H NMR (DMSO) : d = 7,65 (d; H^4), 6.75 (d; H^4), and 5.20 (s; H^4)

Polymerization

Polyureas were synthesized by means of polyaddition reactions between diisocyanate and diamine monomers under nitrogen purge. The polymers were precipitated from the polymerization medium, NMP, in methanol after polymerization. The polymers were washed thoroughly with methanol and acetone to remove unreacted diisocyanates or diamines.

4,4'-diaminoazobenzene (1 g, 4.71 mmol) was reacted with toluene-2,4-diisocyanate (0.77 g, 4.40 mmol) in 17 ml NMP at 90 °C for 12 hr. The polymer obtained was a dark yellow powder (1.56 g, 92 % yield). The polymerization reaction between 4,4'-diaminoazobenzene (1 g, 4.71 mmol) and isophorone diisocyanate (0.97 g, 4.40 mmol) was carried out in 22 ml NMP at 95 °C for 48 hr to afford a dark yellow powder (1.49 g, 78 % yield).

Characterization

FT-IR spectra were recorded on a Perkin-Elmer 1760X FT-IR spectrometer using KBr pellets, and the FT-Raman spectra were obtained from a Perkin-Elmer 1700X FT-Raman spectrometer. ^{1}H NMR spectra were taken from a Bruker ARX-250 spectrometer operating at 250MHz. Absorption spectra were recorded on a Perkin-Elmer Lambda 9 UV-VIS-NIR spectrophotometer.

Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were carried out using a Du Pont Thermal Analysis Model 2000 equipped with a Model 2950 TGA and a Model 2910 DSC. TGA data were obtained in flowing nitrogen at a heating rate of 20 °C/min. DSC thermograms were obtained under nitrogen atmosphere at a heating rate of 10°C/min.

Film casting, poling, and second harmonic generation (SHG) measurement

Thin films of synthesized polyureas were spin-coated onto glass slides using 5-10 wt% dimethyl formamide (DMF) solutions to prepare 0.4 - 0.6 μm thick films. **Thickness of the films were measured by ellipsometry.** The spin-coated films were dried in a vacuum oven at 70 °C for 48 hr.

A corona-poling technique was used to impart noncentrosymmetric order in the film.29) The spin-coated film was slowly heated above the glass transition temperature (T_g) of the polymer. During the poling process the temperature was kept constant. A high voltage (4-6kV) was applied to the wire electrode. After 1hr the film was gradually cooled to room temperature under the applied electric field.

The SHG measurements on poled films were performed with a Q-switched Nd:YAG laser (Quantel 660A) at 1064 nm.33) A *p*-polarized incident beam was passed through the sample. The angle of incidence was 10°. The transmitted fundamental wave was blocked using $CuSO_4$ solution. A narrow band interference filter centered around 532 nm was used to allow the SH beam to pass. The SH signal was detected by a photomultiplier tube (PMT), then amplified and averaged in a boxcar integrator (Stanford Research SR-250).

Measurement of photo-induced orientation

Films of polyureas were irradiated for 30 min with a linearly polarized argon laser beam at 488nm. The beam intensity was 50 mW/cm^2. The polarized UV spectra were recorded by means of a Perkin-Elmer Lambda 9 UV-VIS-NIR spectrophotometer.

Surface relief grating formation

Holographic gratings were recorded under ambient condition by a simple interferometric apparatus at 488nm using an argon ion laser with an intensity of 55mW/cm^2. The schematic setup of the grating experiment has been reported elsewhere.18),19) The surface structure of the gratings on the polymer films was investigated by atomic force microscopy (AFM, Autoprobe

Cp, Park Scientific Instruments) under ambient conditions before and after the holographic gratings were recorded. An 80 μm scanner was used in the contact mode. A microlever of force constant 0.05 N/m was used. A scan rate of 2 Hz was employed.

Results and discussion

We synthesized two kinds of polyureas with aromatic or aliphatic cyclic spacers. We employed a simple literature method that avoids side reactions during the polymerization process to obtain polyureas containing azo units in the main chain. To prevent a possible crosslinking reaction on the secondary amine (-*NH*-CO-*NH*-) of the urea linkage a slight excess of diamine was used. The polymers were powdery and soluble in polar aprotic solvents such as DMSO, DMAc, DMF, and NMP. Scheme 1 shows the polymerization reaction of polyureas.

We confirmed the structure of the synthesized polymers with IR spectroscopy. The IR spectra are shown in Fig. 1. The N-H stretching band at 3352 cm^{-1}, carbonyl stretching at 1656 cm^{-1}, and C-N stretching at around 1220 cm^{-1} are clearly seen in both spectra. We also confirmed the existence of azo groups in the main chain from the peak at around 1445 cm^{-1} in the Raman spectrum.

Thermal properties of the polyureas were examined by means of TGA and DSC. As shown in Table 1 the onset temperatures of thermal decomposition of **PU1** and **PU2** are 312 and 333 °C, respectively, under nitrogen atmosphere. Both polymers have T_gs around 197 °C. The relatively high T_g of the polymers is attributed to the structure of main chain polyureas containing conjugated aromatic ring and aliphatic cyclic structures in the backbone, giving considerable stiffness to the polymer. All the polymers were amorphous and no first order transitions in the DSC thermograms were observed.

Excellent optical quality films of the polyureas were obtained from solutions of DMF with a concentration of 5-10 wt% by means of spin coating. The solutions showed deep yellow color. Fig. 2 shows the absorption spectra of 4,4'-diaminoazobenzene in acetone, and films of polymers **PU1** and **PU2**. The monomer 4,4'-diaminoazobenzene showed an absorption maximum (λ_{max}) at 400 nm. In the case of the **PU1** film, the λ_{max} was observed at 380 nm, and that for the **PU2** film at 377 nm. These maxima result from the π-π^* transition of the azobenzene units. We also synthesized a polyurea from isophorone diisocyanate and 1,4-phenylenediamine, that is a polyurea without azo linkages in its main chain. It did not show any λ_{max} in the visible region.

To induce a noncentrosymmetric structure in the polyurea films, corona poling was carried out above the T_g of the polyureas. We employed a poling temperature of 210-215 °C. Both the polymers showed the absorption maxima to be blue-shifted and decreased after the poling process **(Fig. 2 (b) and (c))**. The SHG experiment was carried out to evaluate the NLO coefficients of the poled films of polyureas containing azo units. The SHG intensity is zero at 0° incidence and increases symmetrically around this angle indicating that after poling the average dipole moment of the polymer is perpendicular to the film surface.

The NLO coefficient, d_{33}, was estimated to be 1 - 6 pm/V at 1064nm, which depended on the applied electric poling field. As expected, the NLO coefficients of these polyureas were found to be smaller than polymers where the NLO activity is derived from azo chromophores that are donor-acceptor substituted. The observed second harmonic generation coefficient was similar to those reported for other polyureas.31)

The absorption at maximum wavelength in the UV-VIS spectrum decreased on poling. The absorbance change is attributed to the orientation of the azo chromophore in the direction perpendicular to the film. The peak was also slightly blue-shifted. The spectral blue shift has been reported for other main-chain polymers.3),34) In the case of side chain azo NLO polymers the spectrum usually red shifts upon poling.35) It is presumed that a preferential orientation as well as a conformational change of the azo groups has occurred due to the electric field poling. In the poling process, the neighboring polar urea groups are expected to align under the applied field. The decrease in absorbance at λ_{max} on poling suggets that alignment of non-polar azo units has occured in conjunction with the alignment of the urea groups. Even though the alignment of non-polar azo units is observed it appears that this alignment did not contribute to enhance the NLO properties.

Thin films of **PU1** and **PU2** overcoated on glass slides were irradiated by a linearly-polarized argon laser beam at 488 nm for 30 min. As shown in Fig. 3, significant dichroism was optically induced by the writing beam in both films. After irradiation, absorbance in the direction parallel to the polarization of the writing beam (perpendicular to the chromophore orientation, $A_\perp$) was much lower than that in the perpendicular direction (parallel to the chromophore orientation, $A_{//}$), and absorbance of both samples were lower than those of pristine polyureas. The dichroic ratios, $D = A_{//} / A_\perp$, of **PU1** and **PU2** were 1.052 and 1.158, and order parameters, $S = (D - 1) / (D + 2)$, were 0.017 and 0.050, respectively (Table 2). Photo-induced dichroism was considered to be due to the alignment of azobenzene groups resulting from repeated *trans-cis-trans* isomerization process as previously studied in side-chain azo polymers.5-10) The degree of orientation was quite comparable to the values obtained for side-chain polymers from the dichroic ratio.5),6) The T_gs of these polyurea polymers are much higher than those reported for side-chain polymers where dichroism studies under laser illumination have been carried out.1) Further, absorption of the films at the wavelength of the writing beam (488 nm) is significantly lower. It is remarkable that the observed optically-induced orientation process in these polyureas is so efficient. The orientation was very stable under ambient conditions and could be erased by heating the films close to T_g.

We have also observed that stable surface relief gratings18),19) could be inscribed on these polymer films at room temperature.36) Fig. 4 shows the three dimensional view of surface relief gratings on the **PU1** film as recorded by atomic force microscopy (AFM). The polymer film was exposed for 30 min to an interference pattern generated by circularly-polarized argon laser beams.37) **A necessary step in the formation of surface relief grating is the orientation of the azo groups under the irradiation of laser beam. The oriented polarizable chromophores and hence the polymers are subjected to a force field in the in homogenous light pattern leading to the surface relief grating formation.18,19,37)** It is noticeable that surface gratings could be inscribed on the main-chain azoaromatic polymer under ambient condition in spite of the high T_g. Regular grating structures with large surface modulation depth were observed. The surface modulation depth was about 440 Å, which was over 10 % of the pristine film thickness and the grating spacing was about 900 nm. Detailed investigations are still in progress and shall be reported elsewhere.

Conclusion

In this study, we have presented the synthesis, characterization, and optical properties of two polyureas containing azo groups in the main chain. The polymers were amorphous and soluble in polar aprotic solvents. The optically induced orientation of the azo units in the main chain was observed despite the relatively high T_g of the polymers. In addition, although the absorption of the polyurea films at the wavelength of writing beam was very low, we observed very efficient and stable photo-induced orientation of azo chromophores. The second-order nonlinear optical coefficients of poled **PU1** and **PU2** were in the range of 1 - 6 pm/V. The symmetric azo chromophores in the polyureas do not play an important role in enhancing the nonlinear optical properties. Upon exposure to an interference pattern of polarized argon laser beam significantly below T_g, surface relief gratings with a surface modulation depth of over 440 Å could be fabricated on the polymer film.

Acknowledgment

Financial support from ONR and NSF-DMR are gratefully acknowledged.

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Figure Captions and Table Legends

Scheme 1. Synthesis and structures of polyureas

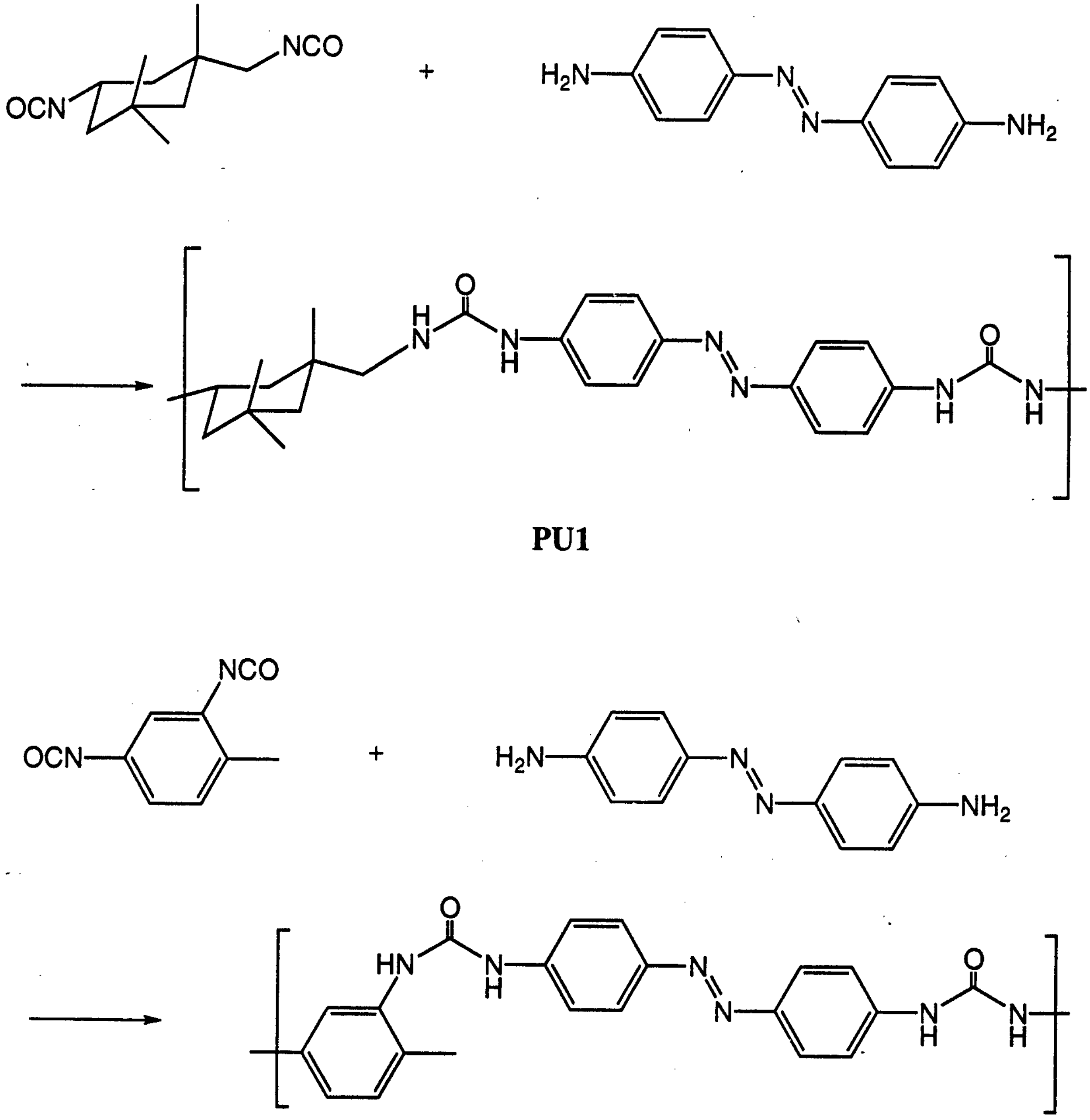
Fig. 1. FT-IR spectra of **PU1** (a), and **PU2** (b).

Fig. 2. Absorption spectra of 4,4′-diaminoazobenzene (a), **PU1** (b), and **PU2** (c). The upper curves are the absorbance for unpoled films and the lower ones are the absorbance for poled films.

Fig. 3. Polarized absorption spectra of **PU1** (a) and **PU2** (b). The upper curves are the absorbance for pristine samples, the middle ones are the absorbance for light polarized parallel to the chromophore orientation, and the lower ones are the absorbance for light polarized perpendicular to the chromophore orientation.

Table 1. Thermal properties of polyureas

Table 2. Dichroic ratios and order parameters of polyureas



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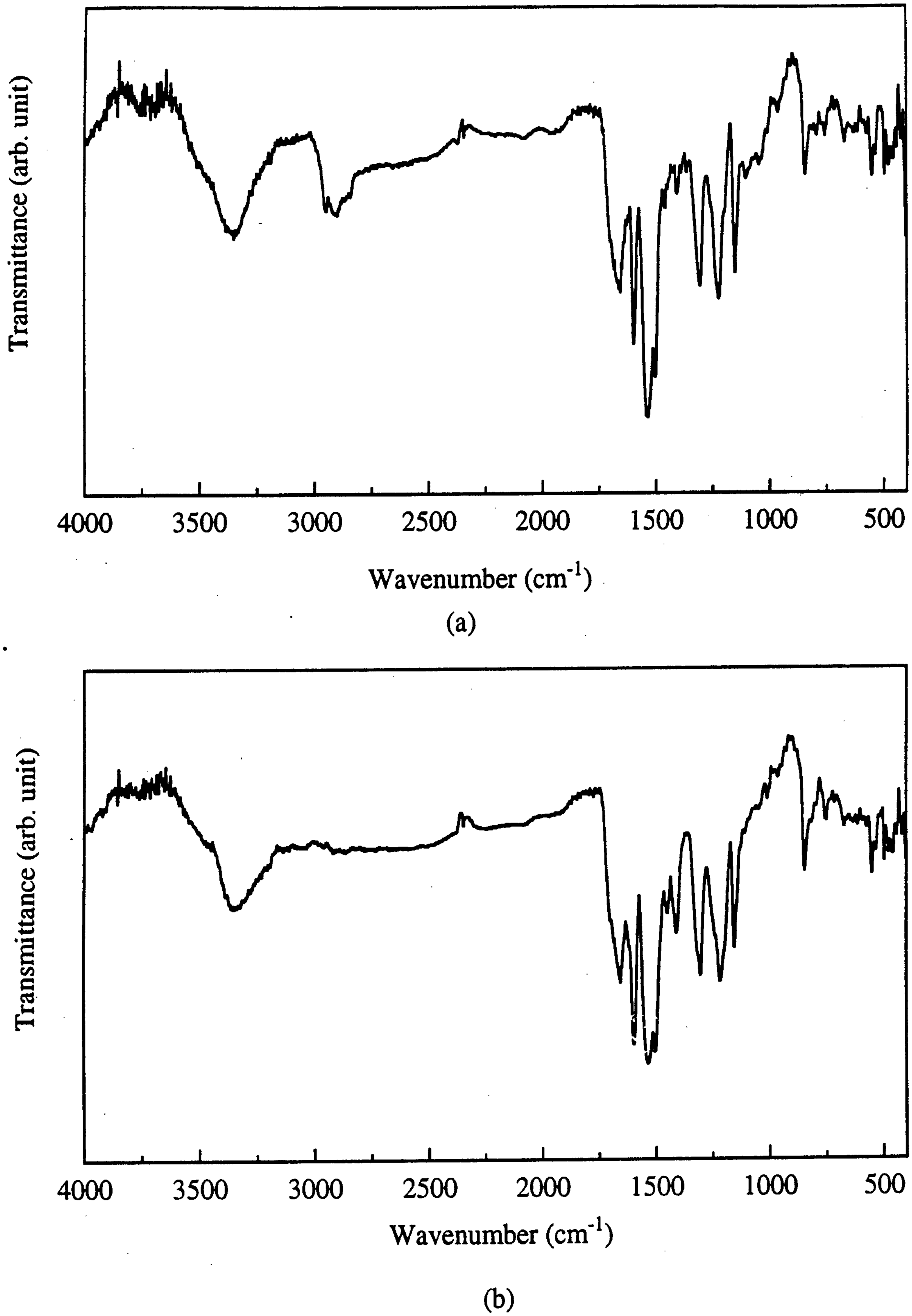
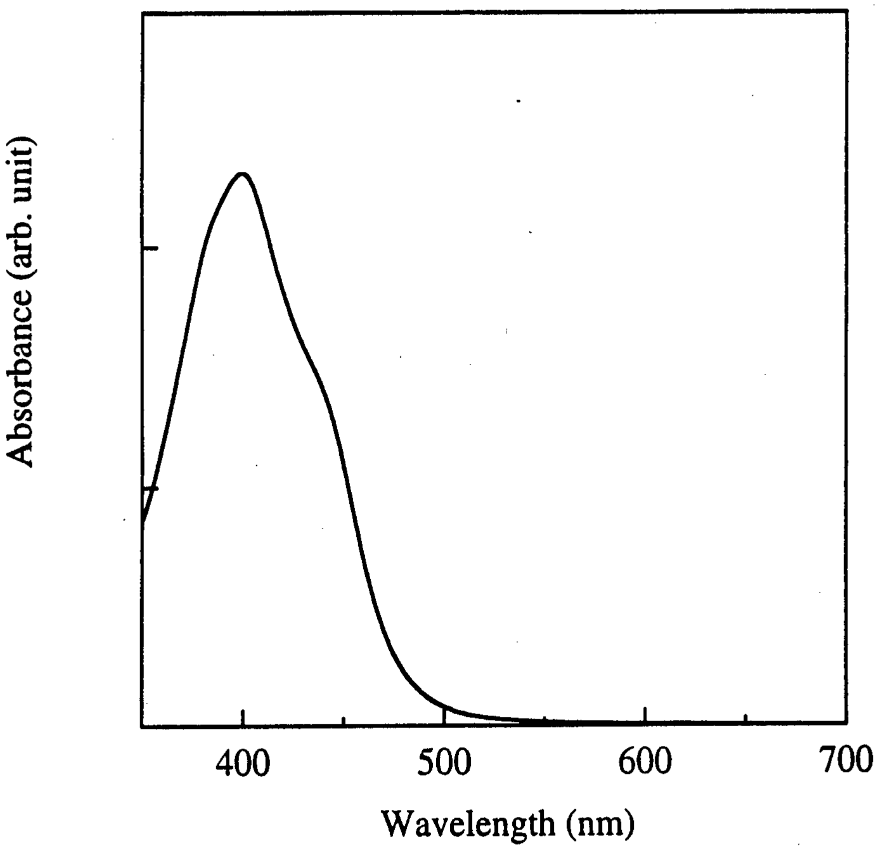
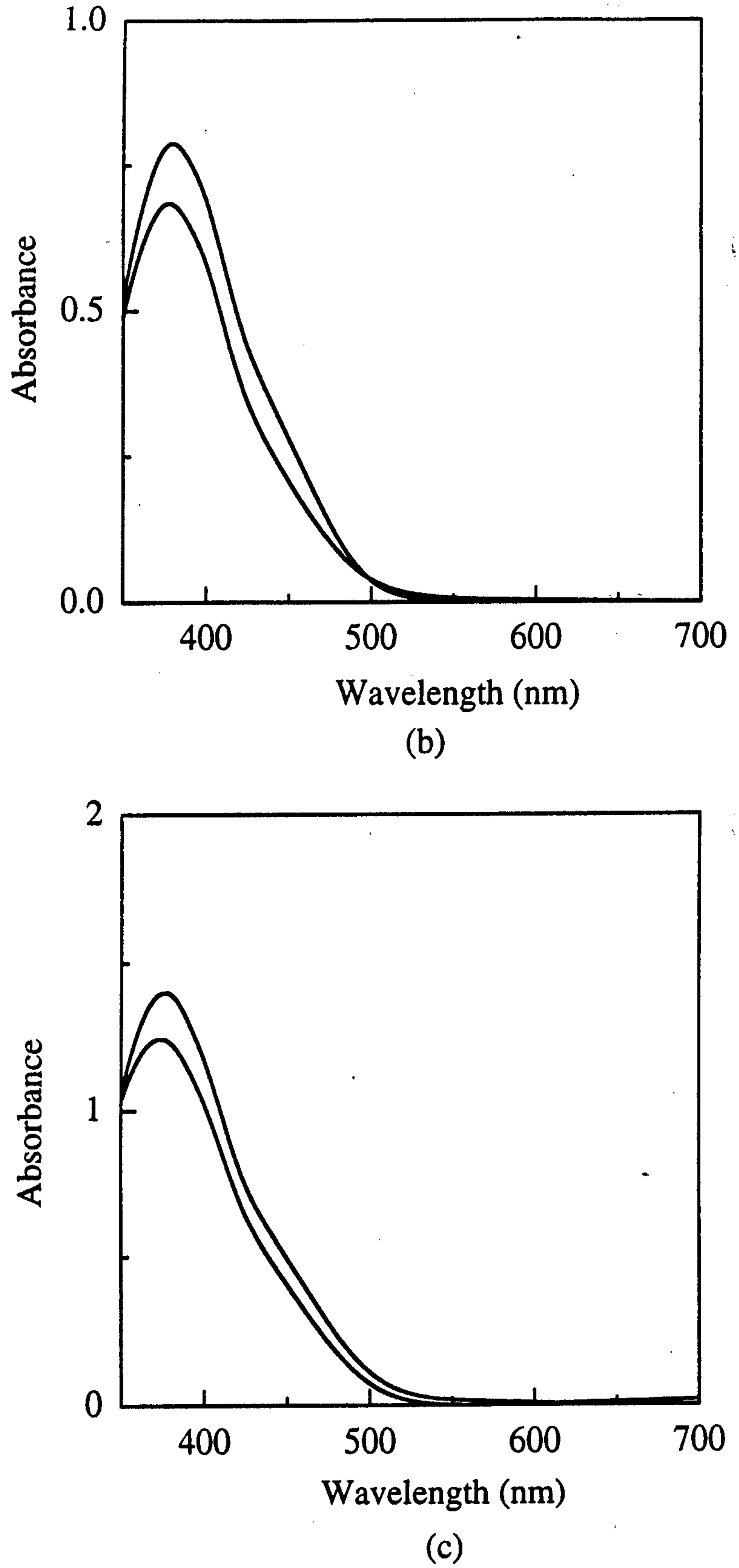


Fig. 1. FT-IR spectra of **PU1** (a) and **PU2** (b).



(a)



(b)

(c)

Fig. 2. Absorption spectra of 4,4'-diaminoazobenzene (a), **PU1** (b), and **PU2** (c).

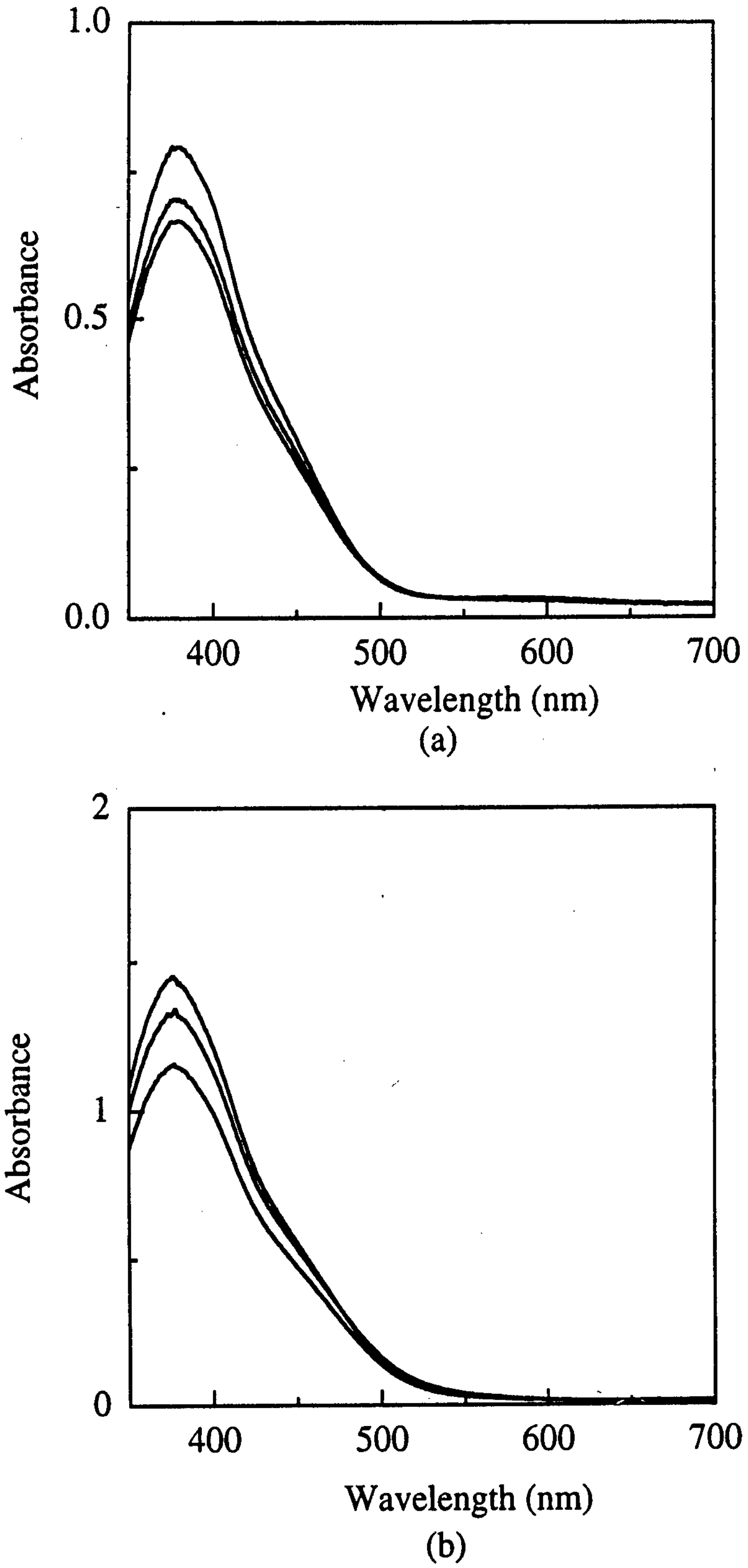


Fig. 3. Polarized absorption spectra of **PU1** (a) and **PU2** (b).

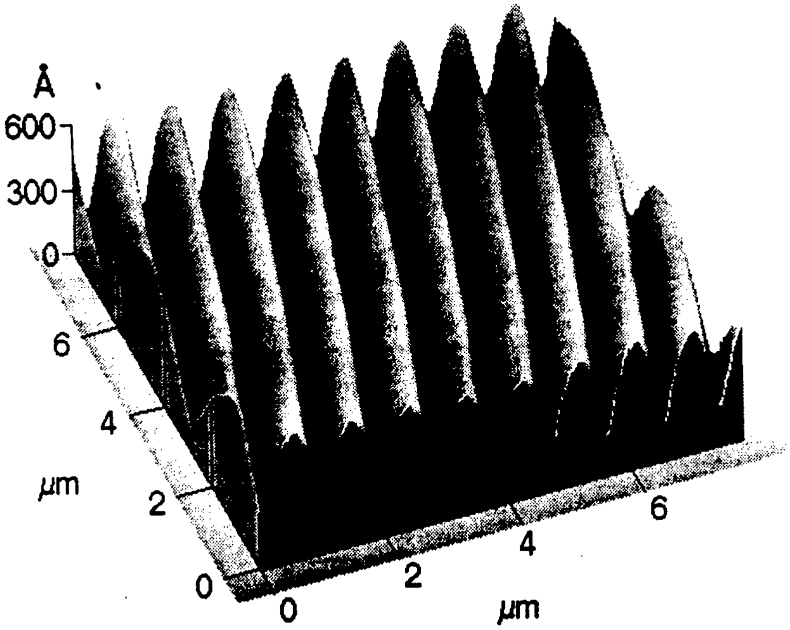


Fig. 4

Table 1. Thermal properties of polyureas

	T_g (^oC)	T_d (^oC)
PU1	197.2	312
PU2	197.6	333

Table 2. Dichroic ratios and order parameters of polyureas

	Dichroic ratio[a)]	Order parameter[b)]
PU1	1.052	0.017
PU2	1.158	0.050

a) Dichroic ratio, $D = A_{//} / A_{\perp}$

b) Order parameter, $S = (D-1) / (D+2)$