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Polyurea with Large Positive Birefringence for Second Harmonic Generation

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ABSTRACT: The second-order nonlinear optical properties of four polyureas with large positive birefringence are presented. The temporal stability of the poling-induced orientations at different temperatures were estimated by in-situ second harmonic generation (SHG) measurements. For the polyurea prepared from aliphatic diamines, the optical transparency was down to 300 nm. The most interesting aspect of these polyureas is in their refractive indices: the refractive indices of TE modes before poling are higher than those of TM modes. This indicates that the polymer chains were stretched along the substrate surface. This work represents the first example of an increase of poling-induced refractive indices in TE modes.

Introduction

The nonlinear optical properties of poled polymeric materials have drawn considerable interest in recent years as potential candidates for applications in electro-optic modulators, switches, and frequency converters.[1] However, for these materials to be used as a second harmonic generation (SHG) device, a couple of requirements such as the suitable transparency range, high NLO coefficients, long-term temporal stability, low optical propagation loss, and phase matching characters for light at the fundamental and second harmonic frequencies should be satisfied. It is difficult to fulfill all these requirements simultaneously. In the past decade, many polymers with large second-order nonlinear coefficients have been developed for NLO applications.[2−4] But the chromophores containing a strong electron-donating group and electron-withdrawing group at the ends of a π-conjugated system have charge-transfer absorption in the visible range. As a result, these polymers are not suitable for the frequency doubling in the UV−visible region.

We found that main-chain poly(arylamine)s with two directional charge-transfer chromophores possess positive birefringence;[5,6] i.e., the indices of refraction in the film plane are larger than those in the film normal direction. Such positive birefringence may be used to realize phase matching in a poled polymer as in the case of bulk single crystals. The poly(arylamine)s have high refractive index dispersions, and the refractive dispersions between fundamental and second harmonic wavelengths cannot be offset by the positive birefringence; therefore bulk phase matching is impossible. In polyurea (PU), the urea groups have a large dipole moment (4.9 D),[7] and can be aligned by poling to produce noncentrosymmetric structures. Pyroelectricity and piezoelectricity of PU films prepared by vacuum deposition polymerization (VDP) have been reported.[8,9] These data are comparable to poly(vinylidene fluoride) (PVDF), and the impressive aspect of PU films for these applications is their stability at high temperatures. The nonlinear optical properties of aromatic PU synthesized by VDP and from solution polymerization have been reported by Takezoe et al.,[10] Hikita et al.,[11] and Nalwa et al.[12] Though PU thin films do not have large nonlinear optical coefficients, they show a cutoff at a very short wavelength and a good temporal stability of the poling-induced orientation is attractive.

To realize bulk phase matching in poled polymers, we have synthesized a number of new polyureas by using 4,4′-diphenylmethane diisocyanate with aromatic and aliphatic diamines. These polymers possess positive birefringence that can be used for phase matching. In this paper we present the synthesis, the characterization, and the linear and nonlinear optical properties of several main-chain polyureas.

Experimental Section

Sample Preparation. 4,4′-Diphenylmethane diisocyanate was dissolved in *N*-methyl-2-pyrrolidone (NMP) at a concentration of about 10% by weight in a three-necked flask equipped with a nitrogen inlet. An equimolar amount of diamine dissolved in NMP (10 wt %) was rapidly added to the stirred diisocyanate solution under a nitrogen atmosphere at room temperature. The formation of PU using aliphatic diamine is strong exothermic process. The mixture was stirred at room temperature for 2 h and then diluted with NMP. After filtering, the polymer was precipitated out by pouring the reaction mixture into water. Further purification was done by extraction in a Soxhlet extractor with water. The products were dried overnight in a vacuum oven. The obtained polymers were colorless powders. For the PU prepared from aromatic diamines, the NMP solution was heated at 80 °C for 24 h. The purification process is similar to the PU prepared by using aliphatic diamine. The chemical structures of polymers were confirmed by elemental analysis and nuclear magnetic resonance spectroscopies. The synthesis scheme is shown in Figure 1.

U1. Anal. Calcd for $C_{28}H_{36}N_4O_2$: C, 73.04; H, 7.83; N, 12.17. Found: C, 72.56; H, 7.81; N, 12.02. ^{13}C NMR (DMSO-d_6): δ 154.0, 138.2, 133.8, 128.2, 117.6, 45.2, 44.6, 43.9, 40.5, 33.8, 32.7, 28.6.

U2. Anal. Calcd for $C_{21}H_{24}N_4O_2$: C, 69.23; H, 6.59; N, 15.38. Found: C, 68.56; H, 6.70; N, 15.15. ^{13}C NMR (DMSO-d_6): δ 154.2, 138.2, 134.0, 128.4, 117.8, 47.2, 45.3, 40.3, 31.1, 28.3.

U3. Anal. Calcd for $C_{20}H_{24}N_4O_2$: C, 68.18; H, 6.82; N, 15.91. Found: C, 68.03; H, 6.83; N, 15.90. ^{13}C NMR (DMSO-d_6): δ 155.4, 138.2, 133.9, 128.0, 118.2, 45.8, 40.2, 35.9, 22.2.

U4. Anal. Calcd for $C_{27}H_{22}N_4O_2$: C, 65.06; H, 4.42; N, 11.24. Found: C, 65.41; H, 4.46; N, 11.27. ^{13}C NMR (DMSO-d_6): δ 151.9, 144.2, 137.8, 137.4, 135.7, 134.8, 134.1, 128.8, 128.6, 127.9, 118.9, 118.3, 117.9, 112.9, 40.2.

To measure the infrared spectra of PU, a free standing film was used. It was prepared by casting the solution of PU in NMP on a glass slide. After drying in a vacuum oven, the

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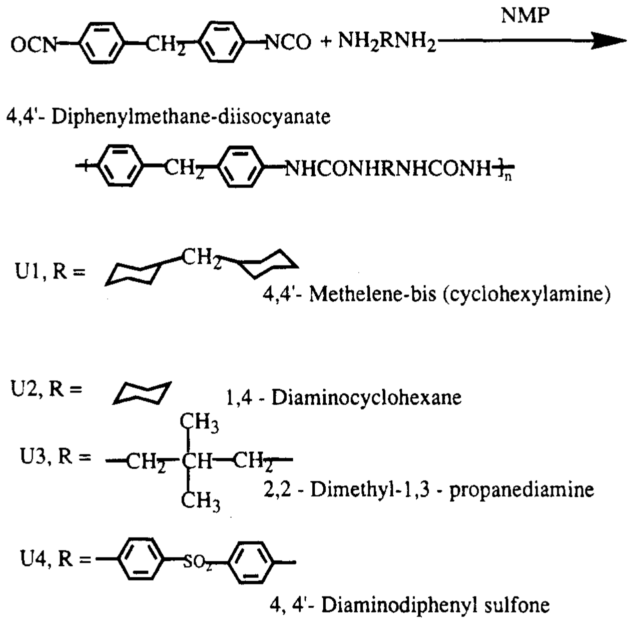

Figure 1. Schematic diagram of the synthesis of polyurea.

films can be separated from the glass substrate. The thicknesses of the films are in the range 5–15 μm.

Linear Optical Properties. Thin films for refractive index and SHG measurements were prepared by spin coating. By variation of the spinner speed and/or the concentration of the polymer solution, different thicknesses between 0.5 and 2 μm could be obtained. The refractive indices of the samples were measured by using the prism coupling method[13,14] described previously. Laser light (He–Ne laser, 0.6328 μm; Nd:YAG, 1.064 μm; or the second harmonic wave of the Nd:YAG laser through a frequency-doubling single crystal KTP, 0.532 μm) polarized parallel or perpendicular to the surface of the film was coupled with an FD21 prism into the polymer films. At a certain incident angle θ, coupling occurred and minima in the reflected light were observed. From the coupling angles for different modes the refractive indices and thicknesses of films were determined simultaneously.

The absorptivities of PU films spin coated on ITO glass substrates were measured by using a UV–visible spectrometer (JASCO), and the amorphous characters were confirmed by wide angle X-ray diffraction using free-standing films.

Poling and SHG Measurement. To produce noncentrosymmetric structures, a corona-poling technique was used. The film was slowly heated at a temperature of 165 °C that was maintained constant during the poling process, a high positive (5–7 kV) voltage was applied to the top needle electrode, and an evaporated aluminum layer was used as the ground electrode. The two electrodes are about 1 cm apart. After 30 min, it was gradually cooled to room temperature under the stress of an applied electric field.

The SHG measurements of poled samples were carried out with an Nd:YAG laser operating at 1.064 μm. The setup has been described previously.[3b] The laser beam passed through a series of ND filters and a variable polarizer was focused onto the samples by a lens; the SHG signal was guided through a series of interference filters to separate the fundamental wave and was focused onto a photomultiplier tube. A reference signal was generated using SHG from a Y-cut quartz crystal and the relative SHG strength was used for the calculation of NLO coefficients of poled PU.

For in-situ SHG measurements, the samples were poled inside a self-developed closed temperature-controlled oven having optical windows and equipped with a needle electrode. The samples were heated and poled at the same time while the SHG intensity was monitored. In the experiment, the sample was kept at 50° to the incident beam. The SHG signal was increased as the temperature increased to a certain value and then decreased due to the increasing ionic conductivity. For all these PU, the poling temperatures were selected according to the in-situ SHG experiments. The decay of poling-induced orientation at several different temperatures for each sample was also studied by in-situ SHG measurement.

Table 1. Molecular Weights of Polyurea

code	$10^{-4}M_n$	$10^{-4}M_w$	M_w/M_n
U1	3.6	12.0	3.3
U2	5.5	16.9	3.0
U3	3.7	9.3	2.5
U4	1.1	1.5	1.4

Results and Discussion

Synthesis and Characterization. A number of methods have been reported for the synthesis of polyureas,[15] such as using diamines with phosgene, diamines with dicarbamyl halides, or diamines with carbonates. Reaction of diamines with diisocyanates in solution or by vacuum deposition has the advantage that no byproducts are produced. Since no byproduct was evolved in the diisocyanate–diamine reaction, the most simple solution method was employed for the preparation of polyurea. *N*-Methyl-2-pyrrolidone (NMP) was used as the reaction solvent. Other polar aprotic solvents such as *N,N*-dimethylacetamide (DMAc), dimethyl sulfoxide (DMSO), *N,N*-dimethylformamide (DMF), and so on can also be used. The molecular weights of these polyureas obtained from gel permeation chromatography (GPC) are listed in Table 1. From these data, we can see that polyureas prepared by using aliphatic diamines have molecular weights relatively higher than that obtained by using aromatic diamine. This is related to the reactivity of different diamines. The reactivity of aliphatic diamine toward diisocyanate was significantly higher than that of aromatic diamine with the sulfonyl group. The difference of chemical reactivity should be attributed to the basicity and the electric effect of the amines.[16] It is well-known that the diamine–diisocyanate reaction proceeds by nucleophilic attack of the amine nitrogen on the carbon atom of the isocyanate group, followed by a proton transfer that stabilizes the adduct.[17] Aliphatic diamines are more basic than aromatic diamines and, thus, are generally more reactive. The electron density of the amine nitrogen in the aromatic diamine is smaller than that of aliphatic diamines, thus hindering their nucleophilic attack on the carbon atom of the isocyanate group. The larger polydispersity of PUs prepared using aliphatic diamines can also be attributed to their higher reactivity.

The structure of the synthesized polymers was confirmed by elemental analysis and infrared (IR) and nuclear magnetic resonance (NMR) spectroscopy. The IR spectra obtained from free-standing U1 polymer films before and after poling are shown in Figure 2. From the IR spectra, we can see some peaks of absorption were shifted by poling [for example, N–H stretching (3337 to 3333 cm^{-1}), N–H deformation (1547 to 1550 cm^{-1}), carbonyl stretching (1653 to 1651 cm^{-1}), C–N stretching (1226 to 1236 cm^{-1}), and C–H stretching (cyclohexane ring, 2924 to 2928; 2851 to 2870 cm^{-1}); and the peak (at 1448 cm^{-1}) due to the in-plane bend of the cyclohexane ring almost disappeared after poling], but some other peaks were unchanged, such as the benzene ring stretching peak (1599 cm^{-1}). These differences are due to the conformer changing of cyclohexane spacer groups by electric poling. Such a phenomenon has not been reported in the literature for NLO polymers and will be further discussed in relation to refractive indices.

X-ray Spectra and Transparency. Wide angle X-ray diffraction spectra of the films obtained from

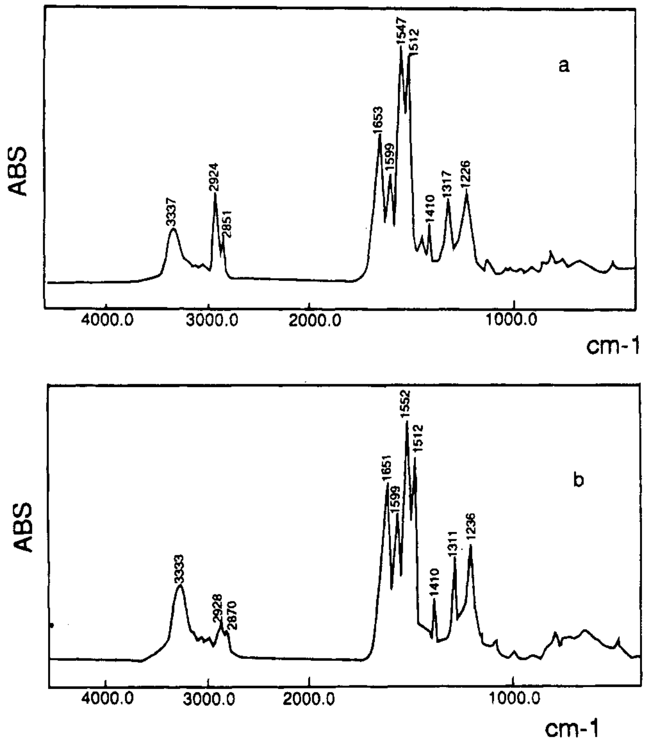

Figure 2. FTIR spectrum of the U1 free-standing film before (a) and after poling (b).

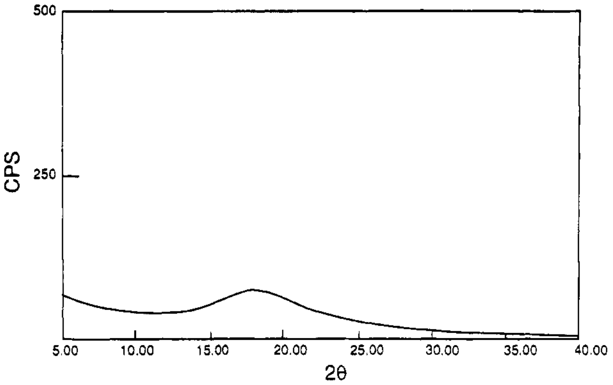

Figure 3. Wide angle X-ray spectrum of the U1 standing film.

nickel-filtered Cu Kα radiations were used to confirm the amorphous characters of these polyureas. The wide angle X-ray diffraction spectrum of the U1 free-standing film is shown in Figure 3. The results demonstrated that these polymers are completely amorphous. Figure 4 shows the transmission spectrum of the U1 polymer spin coated on an ITO glass substrate in the range 200–800 nm. The shortest transmission wavelength of this polymer is near 300 nm.

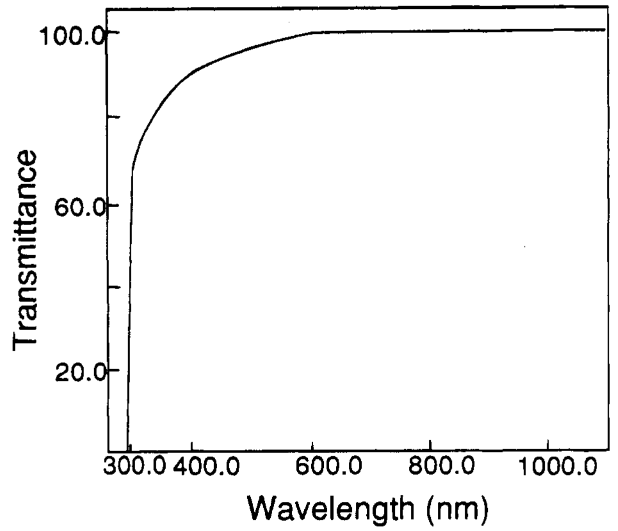

Figure 4. Transmission spectrum of the U1 polymer film spin coated on an ITO glass substrate.

Table 2. Refractive Indices of Polyurea before and after Poling

		unpoled		poled	
polymer	wavelength (μm)	^{n}TE	^{n}TM	^{n}TE	^{n}TM
U1	0.532	1.6052	1.5834	1.6363	1.6124
	0.6328	1.5962	1.5761	1.6188	1.6001
	1.064	1.5762	1.5644	1.5969	1.5821
U2	0.532	1.6152	1.6012	1.6454	1.6348
	0.6328	1.6089	1.5949	1.6351	1.6230
	1.064	1.5838	1.5762	1.6120	1.6026
U3	0.532	1.6223	1.6127	1.6215	1.6157
	0.6328	1.6091	1.5995	1.6081	1.6021
	1.064	1.5919	1.5833	1.5910	1.5861
U4	0.532	1.7088	1.6715	1.7013	1.6774
	0.6328	1.6872	1.6564	1.6785	1.6591
	1.064	1.6577	1.6340	1.6518	1.6359

Refractive Indices and Birefringence. Refractive indices are required for the determination of phase-matching conditions and for the calculation of nonlinear optical coefficients. Several phase-matching methods have been developed on the basis of the nature of refractive indices, such as the phase matching by birefringence in single crystal,[18] phase matching by the anomalous dispersion of refractive indices in some special systems,[19] and phase matching by modal dispersion in thin films.[20] The refractive indices of poled polymer films are generally measured by using attenuated total reflectance and prism coupling methods (m-line method).[21-24] In our experiment, the refractive indices of polymers were measured by the m-line method in a slab waveguide configuration; the results are listed in Table 2. From these data, we can see that the refractive indices of the U4 polymer are remarkably higher than those of the other three PU. The refractive indices of a substance are determined by its constitute molecular structure. In our experiment all of these PU were synthesized by using the same diisocyanate, the main structure difference of synthesized PU is determined by the diamines. For U1, U2, and U3, aliphatic diamines were used, the obtained PU have good transparency, their transmission wavelength was down to 300 nm. For U4, an aromatic diamine with an acceptor group was used, and a longer cutoff wavelength (350 nm) was observed. The refractive indices of this polymer are also apparently larger than those of other PU.

The birefringence of a substance is defined as the difference of refractive indices of ordinary ($n_{\parallel}$) and extraordinary ($n_{\perp}$) refractive indices.[25] The value of birefringence was determined by the orientation of chromophores and the steric constrains in the films. A number of birefringence properties of polymers have been reported in the literature. Prest and Luca[26] reported that solution-cast polymeric films of polycarbonate (PC) and poly(oxy-2,6-dimethyl-1,4-phenylene) (PODMP) preferentially align the polymeric chain backbone in the plane of the films, and the sign of the birefringence depends on the drying process. Recently, Boese et al.[27] found poly(*p*-phenylenebiphenyltetracarboximide) exhibits an extraordinarily large anisotropy in the refractive indices with in-plane index $n_{\parallel} = 1.806$ and the out-of-plane index $n_{\perp} = 1.589$ at 1064 nm, and the in-plane dielectric constant is also larger than that in the film normal direction. The positive birefringence of poled NLO polymers was reported very recently by Wang and Guan.[28] They found while there is a large birefringence in an unpoled accordion main-chain polymer, 1,2-benzyl-1,2-cyclohexyl-bridged syndioregic α-cyanocinnamamide (BCSC), no SHG intensity was detected. On the other hand, after corona poling, the SHG from the BCSC appears, although the birefringence is decreased. A similar phenomenon has also been found in our previous experiments in studying the NLO main-chain polymers with lambda-type charge-transfer chromophores when the spacer group is a long and flexible group. After poling, the sign of birefringence changed from plus to minus and large SHGs were obtained in poly(arylamine)s.[5]

Table 2 shows that all the refractive indices of the TE mode are larger than those of the TM mode of the unpoled PU, indicating that the main chain is stretched along the substrate plane. The refractive indices of the TE and TM modes of the U1 and U2 polymers were increased by corona poling. To our knowledge, such a poling-induced refractive index increase of the TE mode has not been reported in the literature (generally, after poling, the dipole of the chromophores will be moved along the poling direction, the refractive indices of the TM mode will increase, and the refractive indices of TE mode will decrease compared to the unpoled samples). The unusual refractive index change may be related to the conformer changing of the spacer groups induced by corona poling in these two polymers. There are two possible conformers in cyclohexane: the chair and twist-boat conformers. Equilibrium exists between these two forms. Before poling, the less constrained chair conformer is favored. The energy barrier between the chair conformer and the twist-boat conformer is 11 kcal/mol. During the corona process, the intense field generated at the needle tip creates ions with the same polarity as the needle. The reactive ions accelerate toward the ground film and accumulate near the surface region, generating a very high magnitude electric field across the film. When $\mu E > \Delta E$ (μ is the dipole moment of the chromophore, E the surface voltage on film plane, and ΔE the energy barrier between the two conformers), the constrained twist-boat conformation can be induced. Along with such conformer changing, the orientations and dipoles of polymer chains will be changed; therefore, the refractive indices of both TE and TM modes will also be changed. The other two polyureas (U3 and U4) have no such refractive indices increasing since there is no conformer changing of spacer groups by corona poling.

The free-standing films (U1, U2, and U3) can be drawn at higher temperatures. The value of positive birefringence will be further increased. By using this method, we have realized a bulk-phase-matched second harmonic generation (SHG) in the U1 polymer. The detailed description of the phase-matching experiment will be published elsewhere.

Second Harmonic Generation. Figure 5 shows the relationship of SHG intensity vs temperature for the U1 polymer. The SHG appeared at 65 °C, significantly increased from 140 °C, and reached the highest value in the range 165–170 °C. When the temperature was higher than 180 °C, the SHG intensity began to decrease since ionic conductivity was induced. The poling time was also determined by in-situ SHG measurement. Figure 6 shows the relationship between the SHG intensity of U1 vs time with a poling temperature of 165 °C. After a period of 20 min, the SHG intensity reaches a plateau, and after that, the SHG is not related to time. The SHG experiment was done to evaluate the nonlinear optical coefficients of PU polymers. The Maker fringes for both the s- and p-polarized fundamental and p-polarized second harmonic of U1 polymer are shown in Figure 7. Here θ is the angle between the propagation direction and the normal to the film surface. The SHG intensity is zero at 0° and grows symmetrically around this angle, indicating that after poling the average dipole moment of the polymer is perpendicular to the film surface. The SHG signal from a Y-cut quartz crystal was used as a reference for calculating the second harmonic coefficient.

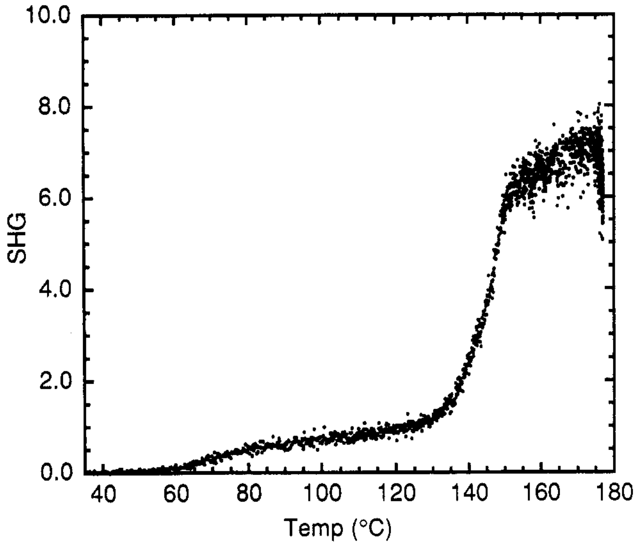

Figure 5. In-situ measurement of SHG intensity vs temperature for the U1 polymer.

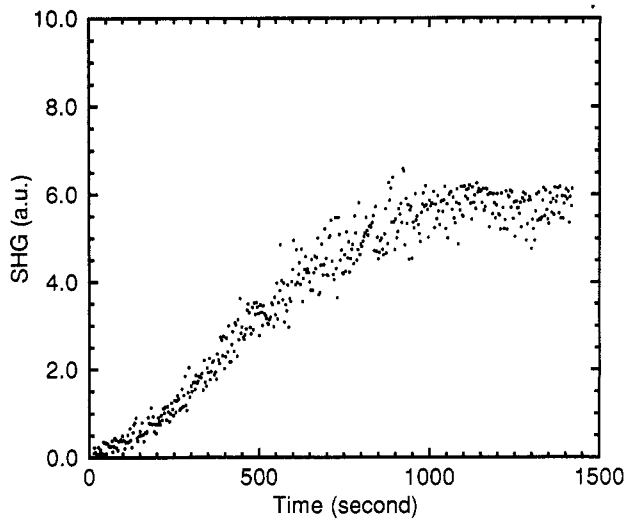

Figure 6. Relationship between SHG intensity and poling time at a poling temperature of 165 °C of the U1 polymer.

The SHG intensity $I_{2\omega}$ is equal to[29,30]

$$I_{2\omega} = (512\pi^3/A)t_g^{\,4}t_\omega^{\,4}T_{2\omega}d_p^{\,2}I_\omega^{\,2}[1/(n_\omega^{\,2} - n_{2\omega}^{\,2})^2] \sin^2 \psi(\theta) \quad (1)$$

where $I_{2\omega}$ is the transmitted SH wave intensity, I_ω is the incident fundamental wave intensity, A is the beam area, d_p is the product of appropriate SH coefficients with angular factors resulting from the projection of the nonlinear polarization components onto the direction of $E_{2\omega}$ in the film, t_ω and $T_{2\omega}$ are the transmission factors,

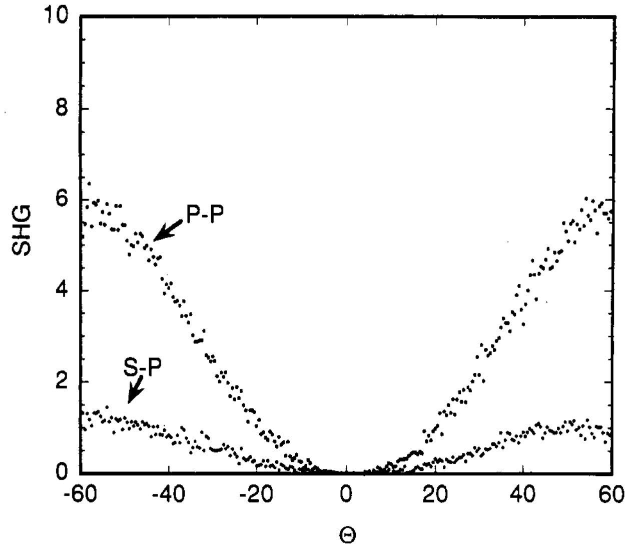

Figure 7. Maker fringe of the U1 polymer with both P-P and P-S polarizations.

t_g is the transmission factor of the fundamental light through the glass substrate, and n_ω and $n_{2\omega}$ are the refractive indices of PU at the fundamental and second harmonic wavelengths, respectively. $\psi(\theta)$ is the angle factor given by

$$\sin^2 \psi(\theta) \sim [(\pi/2)(l/l_0)\{\bar{n}/(N^2 - \sin^2 \theta)^{1/2}\}]^2 \quad (2)$$

where l is the sample thickness, l_0 is the coherence length, θ is the incident angle, $\bar{n} = (n_\omega + n_{2\omega})/2$, and $N^2 = \bar{n}^2 + [(n_\omega - n_{2\omega}/2]^2$. The dp obtained from the p-polarized SH wave intensity with an irradiating p-polarized incident wave is shown by

$$d_p = [d_{33} \sin^2 \theta_\omega' + d_{31} \cos^2 \theta_\omega'] \sin \theta_{2\omega}' + 2d_{31} \cos \theta_\omega' \sin \theta_\omega' \cos \theta_{2\omega}' \quad (3)$$

where the angles θ_ω' and $\theta_{2\omega}'$ are the incident angles that convert from an external to internal angle, $\sin \theta' = (\sin \theta)/n$. The dp obtained from the p-polarized SH wave intensity with an irradiating s-polarized incident wave is shown by

Table 3. Nonlinear Optical Coefficients of Polyurea

code	d_{33} (pm/v)	d_{31} (pm/v)
U1	3.0	1.0
U2	2.4	0.8
U3	2.8	0.9
U4	3.4	1.1

$$d_p = d_{31} \sin \theta_{2\omega}' \quad (4)$$

Using eq 1–4, the nonlinear optical coefficients can be estimated by fitting the measured SHG intensities in both P-P and S-P polarizations compared with Y-cut quartz reference (d_{11} = 0.4 pm/V).

The calculated results are compiled in Table 3. The NLO coefficients of these polyureas are comparable to each other and close to those reported by Takezoe et al.,[10] but smaller than the results reported by Hikita et al.,[11] although their samples and preparation methods were similar to each other.

Optical Loss of Polymer Waveguide. In order to be effective, the polymer should waveguide with low optical loss. The measurement of optical losses in polymeric materials can be done with a variety of techniques. These include some forms of transmission spectroscopy, application of photothermal methods, and direct measurements in the waveguide. In our experiment, the optical losses were determined by direct measuring the scattered light with an optical fiber detector focused on the light streak through a narrow slit system. The optical loss curve plotted by scattering intensity versus the propagation length of the U1 polymer waveguide on glass substrate at 0.6328 μm is shown in Figure 8. The optical loss of 1.26 dB/cm is calculated by a least-squares computer fit of the data to the expression $I = I_0 \exp(-2\alpha\chi)$, where α is the attenuation coefficient in cm^{-1} [α expressed in dB cm^{-1} is equal to (8.68)α expressed in cm^{-1}].

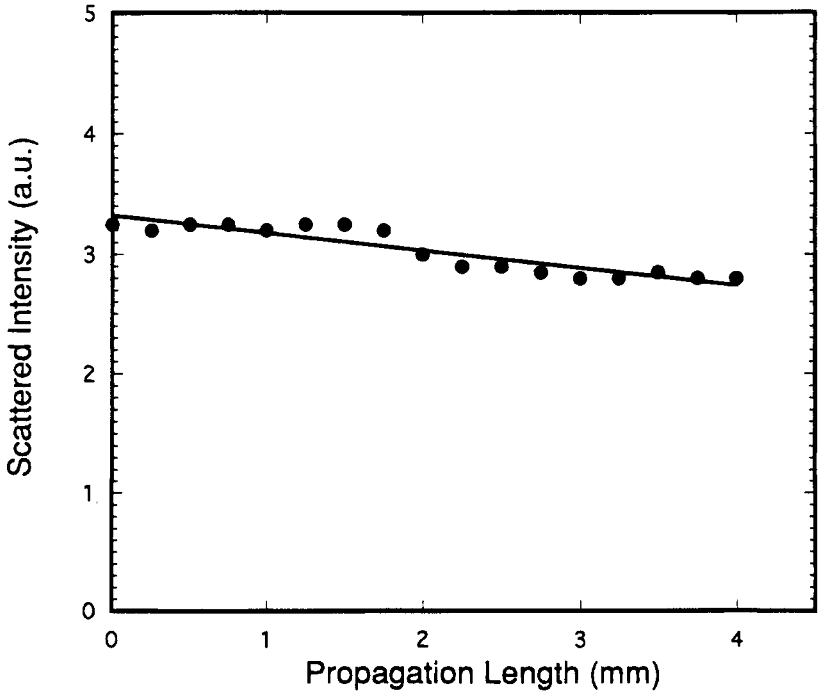

Figure 8. Scattered intensity vs propagation length for the U1 polymer spin coated on glass substrate.

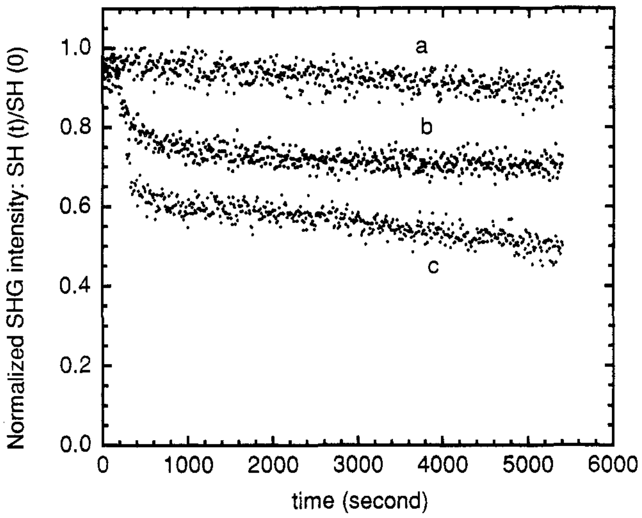

Figure 9. Temporal profile of SHG of the U1 polymer at different temperatures after the poling field was removed: (a) at 25 °C; (b) at 80 °C; (c) at 140 °C.

Thermal Stability of Poling-Induced SHG. One critical problem of poled polymer for nonlinear optical application is the thermal stability of poling-induced orientation, especially at higher temperatures. To investigate the SHG stability, in-situ SHG experiments were performed. The U1 polymer was heated to 165 °C and kept at this temperature for 30 minutes; then the temperature was brought down to 140, 80, and 25 °C, respectively, and the poling field was removed. At each temperature a new sample was used. The relationship of SHG intensity versus time is shown in Figure 9a–c by monitoring the SHG intensity continuously at a fixed angle ($\Phi = 60°$) at 25, 80, and 140 °C, respectively. The effect of polarity and atmosphere on the SHG intensity decay in guest–host polymers and the possible mechanisms of surface and space-charge effects have been studied by Torkelson et al.[31] They found that the temporal stability of the SHG intensity for films poled with a positive corona increases from air to nitrogen to helium since the positive charges on the film surface can be neutralized by negative ions in the air. The SHG intensity decay in poled polymers is a combined effect of surface charge and the loss of chromophore orientation after the poling field is removed. Recently, Wang and Guan[32] showed that the decay of the SHG intensity can be impeded by increasing the poling field strength E_p over a threshold field E_s and with a long poling time in guest–host polymers, but initial fast decay is still apparent when compared with the following slow decay. In the current study, films were poled by using positive corona discharge in the air; the data shown in Figure 9 were taken without attempting to wipe off the surface charges induced by corona poling. The initial rapid decrease of the SHG intensity at short time is apparently temperature dependent and is followed by a gradual decay. The initial rapid SHG decay may be related to the disappearance of surface charge and the relaxation of orientation, but at present we have not measured the surface voltage decay after corona poling. Except for the initial fast decay in a short period, the temporal stability of poling-induced SHG of the polyureas is apparently better than those of some NLO dye-grafted polymers.[33]

Conclusions

In the present study, we have reported the synthesis, characterization, and second harmonic generation of a series of main-chain polyurea. These polymers are amorphous with positive birefringence. Refractive indices increasing in TE modes by corona poling were first observed to our knowledge in NLO polymers. The obtained second-order nonlinear optical coefficients of d_{33} of these PU were in the range 2–4 pm/V at 1064 nm. The cutoff wavelength of PU with aliphatic spacer groups is ~300 nm and the optical loss at 632.8 nm is ~1.2 dB/cm. These polymers can be considered to be candidates having potential for second-order nonlinear optical devices in the UV–visible regions.

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References and Notes

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