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Urethane−Urea Copolymers Containing Siloxane Linkages: Enhanced Temporal Stability and Low Optical Loss for Second-Order Nonlinear Optical Applications

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ABSTRACT: This paper presents a class of nonlinear optical (NLO) urethane−urea copolymers, where dimethylsiloxane linkages of different length are incorporated into the polymer main chain. For comparison, a urethane−urea polymer having virtually no siloxane units has also been prepared. Results show that for copolymers with siloxane linkages poled samples have exceptional orientational stability, consistent in part with strong hydrogen-bonding effects. By the introduction of siloxane linkages, low optical loss materials suitable for device-quality applications have been obtained. The low optical loss can be attributed to the relatively lower number density of C−H bonds in the polymer matrix. Simultaneous realization of enhanced temporal stability and lower optical loss has been achieved in a single polymer system.

Introduction

Investigation of polymeric nonlinear optical (NLO) materials has long been of scientific interest and is a technologically important research subject.[1−5] Polymeric NLO materials have large susceptibilities, fast response times, and good mechanical and physical properties and are amenable to systematic molecular modification.[6] Despite these advantages, NLO polymers exhibit a major disadvantage when compared to inorganic materials in terms of NLO temporal stability. For the second-order NLO polymers prepared utilizing an external electric field to achieve acentric ordering of chromophores, the resulting NLO signal is thermodynamically unstable, especially at elevated temperatures. Obviously, stabilization of the poling-induced noncentrosymmetric lattice is a critical challenge for device applications.

Another key requirement imposed on the polymeric materials involves low optical loss at telecommunication wavelengths (1.3 and 1.55 μm). It has been found that the intrinsic absorption of chromophores and polymers is a major component of such loss.[4] The loss can be limited by shifting C−H overtone vibartional absorption toward longer wavelengths by replacing hydrogen atoms with heavier atoms such as deuterium or halogens, essentially chlorine or fluorine.[7] So far, however, such substitution is not a trivial undertaking from a synthetic standpoint. Thus, improvement of optical loss has proceeded more slowly than improvement of optical nonlinearity.[8,9]

Device-quality NLO polymers must achieve a combination of good processability, high poling efficiency (large electrooptic coefficient (r_{33})), and low optical loss. In this regard, polyfunctionalized polyurethanes have been intensely investigated in recent years and have shown great potential in the fabrication of prototype devices.[10−12] They have offered a reasonable number density of high $\mu\beta$ chromophores, high poling efficiency, good solubility, and good solvent resistance as well as easy preparation and processing. During the course of preparation of polyurethanes, we also found that simultaneous realization of such properties is not always attainable and that the poling efficiency and optical loss of the resulting materials are very sensitive to changes in processing conditions.

To further enhance the properties of this class of polymers, we have developed a new methodology that introduces urea groups and dimethylsiloxane units simultaneously into the main chains of polyurethanes. A series of urethane−urea copolymers containing siloxane linkages of different length have been prepared to explore the role of variable length siloxane linkages, and they have shown improved temporal stability, low optical loss, and good solubility in common organic solvents. In this paper, we report detailed studies of the synthesis and characterization of the copolymers, as well as the thermal properties, the second-order nonlinearity, and other physical properties of the synthesized polymeric materials. The results of the optical loss measurements will also be discussed.

Experimental Section

General Methods. ^{1}H NMR spectra were recorded on a Bruker-250-FT-NMR spectrometer, and the chemical shifts were referenced relative to TMS. Elemental analyses were performed by Atlantic Microlab Inc. Thermal gravimetric analyses (TGA) and differential scanning calorimetry (DSC) studies were conducted on Shimadzu TGA-50 and Perkin-Elmer DSC-7 instruments at a heating rate of 5 °C/min, respectively. The UV−vis spectra were obtained on a Perkin-Elmer Lambda-4C UV/vis spectrophotometer. Gel permeation chromatography (GPC) analyses were carried out on a Perkin-Elmer model 200 HPLC system using polystyrene as the standard and chloroform as the eluent.

Materials. All of the chemicals were purchased and used as received unless otherwise stated. The solvents were purified

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by distillation under reduced pressure over anhydrous magnesium sulfate and dried further over molecular sieves before being used. The NLO chromophore, 4-*N*,*N*′-bis(2-hydroxyethyl)amino-4′-nitroazobenzene (DR-19), studied in the experiments described here was synthesized according to the published literature procedures.[13] The diamino monomers were acquired following Kakkar's methods with some modifications.[14]

1,3-Diethylamino-1,1,3,3-tetramethyldisiloxane (1b). To a solution of 4.28 g (20 mmol) of 1,3-dichloro-1,1,3,3-tetramethyldisiloxane in 80 mL of anhydrous diethyl ether was added over 15 min 10 mL of diethylamine under argon at 0 °C. During the addition, a white precipitate was formed, and the resulting mixture was stirred for another 2 h. The filtrate was collected to yield 3.97 g of a colorless liquid, **1b**, by bulb-to-bulb distillation at 0.8 mmHg pressure (72%). ^{1}H NMR-($CDCl_3$, ppm): δ 2.85(q, 8H, CH_2); 1.00(t, 12H, CH_3); 0.17(s, 12H, $Si(CH_3)_2$). Anal. Calcd for $C_{12}H_{32}N_2OSi_2$: C, 52.11; H, 11.66; N, 10.13. Found: C, 52.35; H, 11.76; N, 10.28.

1c was prepared by the same method as the preparation of **1b**; yield, 63%. ^{1}H NMR ($CDCl_3$, ppm): δ 2.91(q, 8H, CH_2); 1.07(t, 12H, CH_3); 0.20 (s, 12H, $Si(CH_3)_2$); 0.09 (s, 12H, $Si(CH_3)_2$). Anal. Calcd for $C_{16}H_{44}N_2O_3Si_4$: C, 45.23; H, 10.44; N, 6.59. Found: C, 45.46; H, 10.57; N, 6.78.

1,3-Bis(4-aminophenoxy)-1,1,3,3-tetramethyldisiloxane (2b). 1.42 g (13 mmol) of *p*-aminophenol dissolved in 60 mL of THF was added dropwise to a solution of 3.5 g (12.7 mmol) of 1,3-diethylamino-1,1,3,3-tetramethyldisiloxane dissolved in 40 mL of THF under argon. The resulting mixture was stirred for 10 h at 50 °C, and the solvent was removed by rotary evaporation. Then, the residue was extracted cautiously with chloroform/hexane (volume ratio 1:5) at 0 °C. The extracted solution finally provided 2.70 g (61%) of **2b** as a clear yellow viscous oil after the removal of solvent. ^{1}H NMR ($CDCl_3$, ppm): δ 6.67 (d, 4H, $J = 8.5$ Hz, C_6H_4); 6.58 (d, 4H, $J = 8.5$ Hz, C_6H_4); 3.40 (br, 4H, NH_2); 0.17 (s, 12H, $Si(CH_3)_2$). Anal. Calcd for $C_{16}H_{24}N_2O_3Si_2$: C, 55.14; H, 6.94; N, 8.04. Found: C, 55.26; H, 6.81; N, 8.17.

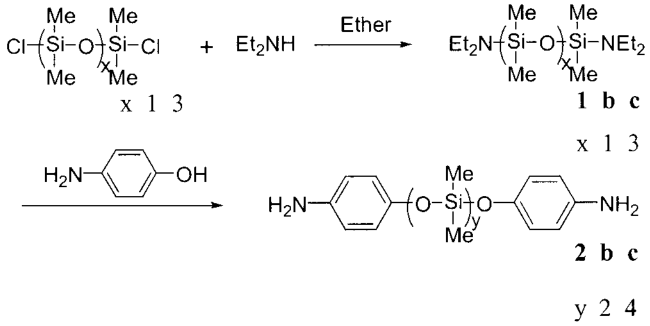
2c was prepared by the same method as the preparation of **2b**; yield, 63%. ^{1}H NMR ($CDCl_3$, ppm): δ 6.65 (d, 4H, $J = 8.5$ Hz, C_6H_4); 6.47 (d, 4H, $J = 8.5$ Hz, C_6H_4); 3.65 (br, 4H, NH_2); 0.22 (s, 12H, $Si(CH_3)_2$); 0.10 (s, 12H, $Si(CH_3)_2$). Anal. Calcd for $C_{20}H_{36}N_2O_5Si_4$: C, 48.35; H, 7.30; N, 5.64. Found: C, 48.60; H, 7.24; N, 5.79.

Polymer PUU 1. In the first step, 1.65 g (5 mmol) of DR-19 (**3**) and 3.26 g (10.5 mmol) of dianisidine diisocyanate (**4**) were added to a round-bottom flask containing 60 mL of anhydrous dioxane under a nitrogen atmosphere. After heating for 2 h at 70 °C, the solution was cooled to room temperature slowly. The remaining dianisidine diisocyanate could be recrystallized from the flask, cooled to 0 °C, and filtered off under nitrogen. In the second step, 1.15 g (5 mmol) of 4,4′-(isopropylidene)dianiline dissolved in 15 mL of dioxane was added into the reaction mixture over 20 min. Stirring was continued for 3 h at 90 °C, and the viscosity of the solution increased greatly during this period. The resulting polymer was precipitated from methanol and filtered. Following this, the polymer was washed several times with deionized water and methanol. The filter cake was dried in a vacuum oven at 70 °C, affording a red polymer (4.41 g, 73%).

PUU 2 and **3** were synthesized by the same procedures as that described above. Only at the last step, the siloxane-containing diamino monomers, **2b** and **2c**, were used to replace 4,4′-(isopropylidene)dianiline, respectively.

Thin Film Preparation and Electric Poling. Polymer solutions in 1,2-dichloroethane were filtered through 0.2 μm syringe filters and then spin-cast onto indium−tin oxide (ITO) coated glass slides. The films were vacuum-dried and stored in a drybox before electric poling and NLO measurement. A corona poling stage, using an ITO-grounded corona-discharge setup, with a tip-to-plane distance of ca. 1 cm, was used to pole the films at elevated temperatures. The poled films were then cooled to room temperature in the presence of the applied electric field.

Scheme 1. Synthesis of Diamino Monomers



Second-Order Nonlinearity Measurements. Electrooptic coefficients (r_{33}) were measured via an attenuated total reflection (ATR) technique.[15] A mode-locked, Q-switched Nd:YAG laser with a pulse width of <10 ns and repetition rate of 10 Hz was used as the fundamental light (1.064 μm). A Y-cut quartz crystal was used as the reference sample. The second-harmonic signal was detected and amplified by a photomultiplier tube. After amplification it was averaged and converted to digital signal for computer processing.

Temporal stability of dipole alignment was determined by monitoring the decay of the second-harmonic signal as a function of temperature. Optical loss data were measured at 1.3 μm using the "immersion" technique.[16] Silicon wafers coated with gold were used as the substrate for optical loss measurements.

Results and Discussion

Synthesis of Materials. The diamino monomers, **2b** and **2c**, were prepared from the corresponding diaminosiloxane derivatives and *p*-aminophenol according to Scheme 1. It is known that siloxanes can be synthesized by various routes,[17−19] and this preparation follows an acid−base hydrolytic method; i.e., aminosilanes (R'_3Si-NR_2, R′ and R = Me, Et) react with organic compounds containing acidic protons. For example, the reaction of (trimethylsilyl)diethylamine, $Me_3Si-NEt_2$, with *p*-aminophenol produced *p*-aminotrimethylsilyphenol in almost quantitative yield.[18] The starting aminosiloxanes were easily synthesized from their dichlorosiloxane derivatives with excess amount of diethylamine in ether solutions.

Synthesis of polymers was achieved by a two-step reaction as shown in Scheme 2. Prepolymer **5**, a diisocyanate containing urethane groups, was prepared from diol **3** (DR-19) which has a NLO-active group, and dianisidine diisocyanate **4**, following the literature method with some modifications.[20] An excess amount of dianisidine diisocyanate was necessary to ensure the rapid formation of prepolymer **5** and prevent the further polymerization of **5**. Then, the prepolymer, bearing isocyanate terminal groups, further reacted with the diamine in the last step to give the urethane−urea copolymer. To remove trace amounts of ionic impurities, which may increase the conductivity of the film, thus decreasing the poling efficiency during subsequent electric field poling, the polymers were purified from methanol and deionized water several times before use.

Good solubility is essential to process these polymers into optical quality thin films by spin-coating. Polymers **PUU 1**−**3** were soluble in most organic solvents, such as dichloromethane, chloroform, 1,2-dichloroethane (DCE), and tetrahydrofuran (THF). The solubility was found to be in a decreasing order **PUU 3** > **2** > **1** in DCE. This trend is consistent with the increase of the Si−O bonds, and such an increase in the length of the

Scheme 2. General Reaction Route and Structures of the Synthesized PUUs

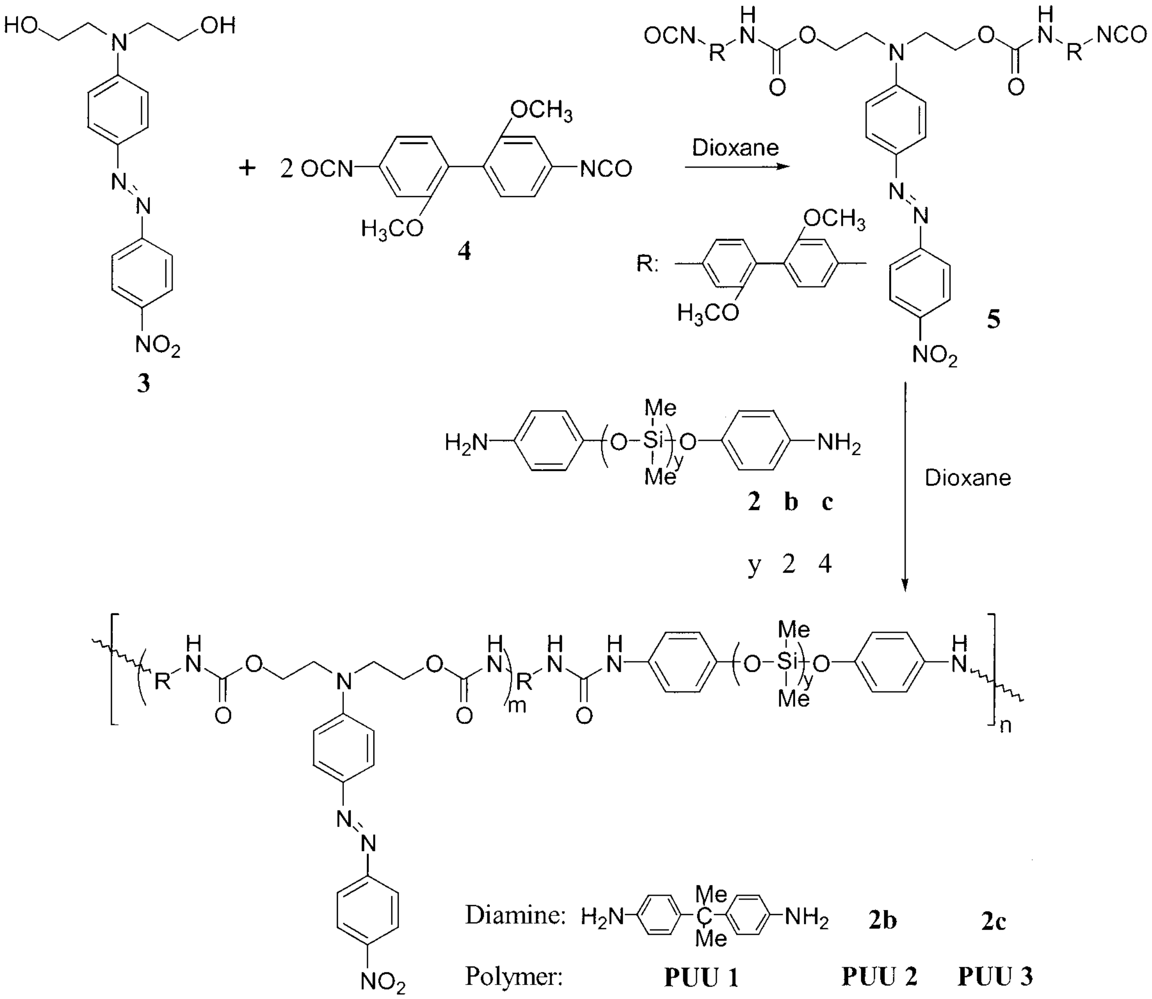


Table 1. Physical Properties of Urethane−Urea Copolymers

polymer	λ_{max} (nm) solvent[a]	λ_{max} (nm) film	M_w/M_n [b]	T_g (°C)[c]	T_d (°C)[c]
PUU 1	488	474	40 300/26 200	147	304
PUU 2	487	471	41 100/23 800	133	298
PUU 3	487	473	39 400/24 500	119	296

[a] Measured in the 1,2-dichloromethane solution. [b] Weight- and number-average molecular weight of polymers. [c] In nitrogen (5 min/°C). T_d is the temperature when 5% weight loss was observed in N_2.

dimethylsiloxane linkage can efficiently improve the solubility. Because of the good solubility in organic solvents, the molecular weights of the polymers could be determined by gel permeation chromatography (GPC) based on polystyrene standards. **PUU 1**, for example, has a weight-average molecular weight M_w of 40 300 with a polydispersity of 1.54. The M_w's of **PUU 2** and **3** were 41 100 and 39 400, and the corresponding polydispersity was 1.73 and 1.61, respectively. These molecular weights are sufficient for electrooptic applications.

The wavelengths of maximum absorption (λ_{max}) of the three polymers in the solid state and in the DCE solutions are listed in Table 1. Their λ_{max}'s showed little difference both in the solid state and in the solution. This can be atttributed to the similiarity of polymer main chain structure and to the fact that the Si−O linkage leads to little change in the dielectric constant of the urethane−urea copolymer.

The glass transition temperatures (T_g) of these polymers, determined by differential scanning calorimetry (DSC), follow the order **PUU 1** > **2** > **3**. By comparing with the dimethylsiloxane units, we conclude that T_g decreases with the incorporation of siloxane linkages and an increase in its length. A slightly lower T_g is expected presumably due to the flexibility of the dimethylsiloxane units, which may lead to a rotation along the backbone and cause faster relative motion among polymeric main chains.[14] Furthermore, we found that the T_g of polyurethanes without any siloxane linkages is much lower than that of **PUU 1** as expected. For example, the T_g of cross-linked polyurethane using DR-19 and TDI as monomers and triethanolamine as the cross-linker was in the range 100−120 °C,[24] much lower than that of **PUU 1** (141 °C). In contrast, the former has the same level of T_g as **PUU 3** containing four repeated siloxane linkages. It is also worth noting that the data given Table 1 show little differences in the T_d values for the synthesized copolymers differing in the main chain structure. Although the introduction of the dimethylsiloxane units does reduce the T_g of the resulting polymer, it does not cause dramatic attenuation of thermal stability. In other words, it is the combination of the rigidity of Si−O bonds and the strong hydrogen-bonding effect between the urethane−urea carbonyls that is responsible for their high thermal stability.

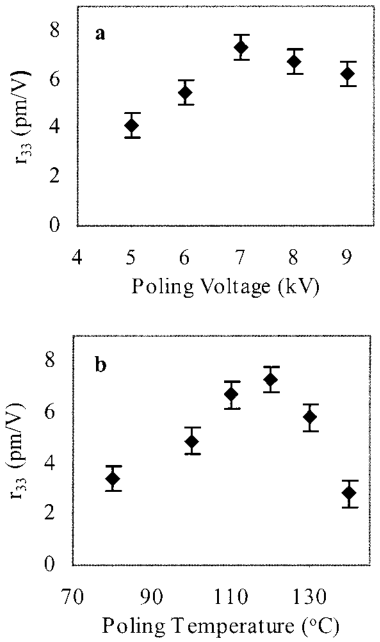


Figure 1. Poling conditions of **PUU 2**. (a) The poling voltage-dependent profile of r_{33}. The poling temperatures and time were fixed to 120 °C and 30 min, respectively. (b) The poling temperature-dependent profile of r_{33}. The poling temperature was varied from 80 to 140 °C.

Electric Poling and NLO Measurements. As expected, no NLO signal was observed without the application of an external electric field, which affirms that the dipoles of chromophores in the polymer matrix are initially randomly oriented.[19] Thus, an external electric field (corona poling) was employed to achieve the effective dipolar alignment of the randomly oriented chromopohores. During corona poling, it is important to optimize the poling conditions (poling voltage, poling temperature, and poling time) to obtain a maximum NLO signal. In our case, **PUU 2** was selected to evaluate the dependence of poling-induced second-order nonlinearity on poling conditions. For example, the poling time was fixed for 30 min because the NLO signal no longer increased beyond 30 min. As shown in Figure 1a, the signal is also dependent on the intensity of the applied field; i.e., the r_{33} values increased with the applied voltage to a peak at 7 kV but began to decrease slightly above 7 kV. Likewise, the temperature-dependent profile of the NLO signal can be expressed by Figure 1b. The maximum signal was realized at a temperature of 120 °C. Therefore, the optimum poling conditions were 7 kV for 30 min with a poling temperature of 120 °C. To maintain good quality of the poled films, a stepwise voltage profile was employed (5 kV, 15 min; 6 kV, 15 min; 7 kV, 30 min).

The electrooptic coefficient, r_{33}, was measured by the ATR method[15] using a corona-discharge setup, with a tip-to-plane distance of 1 cm. When the films were poled under the optimum conditions as indicated Table 2, the values of r_{33} of the poled polymers **PUU 1**–**3** were found to be in the range 6–9 pm/V (see Table 2). These values are reasonable for the azo chromophore[21–23] with a relatively low $\mu\beta$ value and the estimated matrix chromophore number density around $\sim(7-8) \times 10^{20}$ cm^{-3}.

Table 2. Nonlinear Optical Properties of Urethane–Urea Copolymers

polymer	loading density (wt %)	poling temp (°C)[a]	r_{33} (pm/V)[b]	optical loss (dB/cm)[c] W/O poling	optical loss (dB/cm)[c] after poling
PUU 1	29.4	135	8.7	4.0	4.5
PUU 2	26.0	120	7.3	1.2	1.8
PUU 3	23.3	95	6.6	0.9	1.3

[a] To achieve the better poling efficiency for all these polymers, a stepwise voltage profile was employed (5 kV, 15 min; 6 kV, 15 min; 7 kV, 30 min). [b] Measured at 1.064 μm with the ATR method. [c] Measured at 1.064 μm with the "immersion" technique.

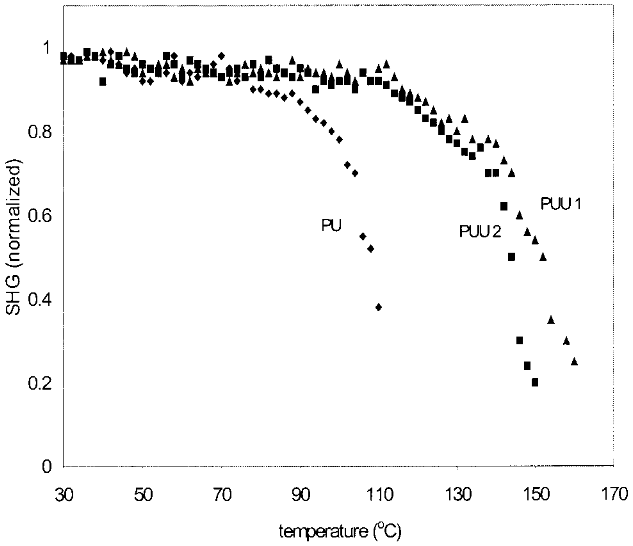


Figure 2. Temporal stability of the polymers **PUU 1** and **2** and thermosetting polyurethane cross-linking prepolymer **5** with triethanolamine (ramping rate: 5 °C/min).

The real time NLO stability of the polymer film as a function of temperature provides information on the maximum device processing temperature that the film can withstand and allows a quick evaluation of the temporal and thermal stability of the material. The polymers **PUU 1** and **2** were heated at a rate of 5 °C/min and exposed to the air during the measurements. As shown in Figure 2, the NLO signal for **PUU 1** was stable until the temperature reached 135 °C, while **PUU 2** stable until 123 °C. This is a significant improvement over the other cross-linked thermosetting polyurethanes, which usually remained stable until approximately 95 °C.[24] Compared with any cross-linked polyurethane, there exists strong hydrogen bonding in the urethane–urea polymer matrix, which plays the cross-linking role so that the dipole orientation after electric poling can be stabilized. Thus, the introduction of the urea groups could effectively enhance the orientational stability of the aligned NLO chromophores. The higher temporal stability for **PUU 1** over **PUU 2** is probably attributable to the relatively higher T_g of the former. **PUU 1** has no siloxane linkages, but **PUU 2** contains two siloxane units.

Optical Loss. Practical applications require low optical loss for the materials in the wavelength region of application. It is generally acknowledged that the factors influencing the observed losses are of intrinsic and extrinsic origins. The intrinsic loss is likely dominated by the C–H overtone stretching vibrations and by combinations of overtone and deformation. To determine the intrinsic absorption losses of the polymers discussed here, we first measured the optical losses of unpoled materials. As shown in Table 2, the siloxane-containing polymers **PUU 2** and **3** have the substantially lower optical losses than **PUU 1**. This result can be rationalized by calculating the number density of C−H bonds.[25] The number density of C−H bonds in a polymer matrix is expressed by the following equation:

$$N = \frac{\rho n_{\mathrm{C-H}}}{M_{\mathrm{unit}}} \qquad (1)$$

where N is the number density of C−H bonds (mol/cm^3), ρ is the density of polymer (g/cm^3), $n_{\mathrm{C-H}}$ is the number of C−H bonds per repeat unit, and M_{unit} is the molecular weight of a single repeat unit. By calculating the number density of C−H bonds, we found that $N_{\mathrm{PUU1}} > (N_{\mathrm{PUU2}} \cong N_{\mathrm{PUU3}})$. Obviously, the introduction of Si−O linkages, which results in reducing the number density of C−H bonds in the backbone structure, plays a key role in lowering the optical loss of materials. Furthermore, this low optical loss is probably due to the transparency of Si−O linkages in the IR−vis region.

On the other hand, the extrinsic factor inducing the optical loss is mainly from the electric field poling process.[5] When the film is under the influence of the poling field, the poling process may lead to surface damage of the film and/or phase separation of chromophores, thus increasing optical loss to some extent compared to the unpoled sample, as indicated in Table 2. Electric field poling induces inhomogeneity of the film, which usually causes the scattering of the incident light, and further induces an increase of optical loss.[12]

Inhomogeneities formed during polymerization may also raise the optical losses. Nevertheless, in our case, we believe that this contribution is negligible considering the high reactivity between $-\mathrm{NH_2}$ and $-\mathrm{NCO}$ groups. To further exclude this kind of loss, precise control of polymerization is crucial, and all these polymers were prepared carefully under the same conditions, such as reaction time, temperature, environment, etc. After a systematic study of several factors, an optical loss as low as 0.6 dB/cm was obtained at 1.3 μm.

Conclusion

We have presented a class of processable NLO urethane−urea polymers, where the dimethylsiloxane linkages of different length are incorporated into the polymer main chain. These polymers can be efficiently poled by an electric field and exhibit reasonable second-order nonlinearities (comparable to the values observed for other polymers containing the same chromophore). The temporal stability of the poling-induced macroscopic order can be greatly enhanced by the introduction of urea groups. They have also demonstrated low optical loss at 1.3 μm, which indicates that the incorporation of siloxane units might be a useful means of adjusting the number density of C−H bonds in the polymer matrix and thus reducing the loss of the resulting materials.

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