Orientational Relaxation of Transversely Aligned Nonlinear Optical Dipole Moments to the Main Backbone in the Linear Polyurethane

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ABSTRACT: This paper presents the orientational relaxation of nonlinear optical (NLO) chromophore in a linear polyurethane of T-polymer based on 4-[(2-hydroxyethyl)amino]-2-(hydroxymethyl)-4′-nitroazobenzene (T-AZODIOL) and aromatic diisocyanate of tolylene 2,4-diisocyanate (TDI). T-polymer has the feature that NLO dipole moment is aligned transverse to the main chain. A remarkable difference of the orientational relaxation of NLO dipole moments was observed between the samples corona-poled at 80 and 94 °C. The time-dependent decay curve of second-order nonlinear susceptibility is fitted well by a Kohlrausch−Williams−Watts stretched exponential function. The relaxation time of T-polymer poled at 94 °C is 3 orders of magnitude larger than that poled at 80 °C, and the relaxation time for the sample poled at 94 °C is over 50 years at room temperature. The second-order nonlinear susceptibility of the sample poled at 94 °C is twice larger than that poled at 80 °C. Thermally stimulated discharge current measurement for the sample poled at 94 °C clearly indicates the broad current flow due to the segmental molecular motion and the sharp current flow due to the reorientation of NLO dipole moment at higher temperature which is significantly related to the effective transition temperature for SHG activity. The remarkable stability of second harmonic generation activity for the sample poled at 94 °C is ascribed to the smaller free volume for the sample poled at 94 °C and/or the orientational retaining of the aligned NLO chromophores by space charges formed in terms of the charges injected at 94 °C.

Introduction

One of the features of organic and polymeric nonlinear optical (NLO) materials is the large electro-optic coefficients due to large second-order nonlinearity. Polymeric NLO materials have significant potential for the optical devices application such as the electro-optical modulator. However, several problems must be overcome to achieve the fabrication of NLO and electro-optic (EO) devices for actual use. Some of these are good long-term thermal stability of the NLO or EO effect, good structural and chemical stability, and low optical propagation losses. As for the long-term thermal stability of NLO and EO effects, it is important to study the nature of the orientational relaxation of NLO dipole moments in the polymer matrix and its relation to the structural factors of the materials. The resultant knowledge can be feedback to the creation or development of the novel orientationally stable NLO polymeric materials. Among them, a few approachs are proposed: One approach is the use of cross-linking to suppress the reorientation of NLO chromophore due to the segmental molecular motion of polymer matrix.[1−5] Another approach is the utilization of high glass transition temperature (T_g) material, such as polyimide.[6,7]

Recently, we have synthesized a new type of linear polyurethane (T-polymer) with NLO azobenzene chromophore whose dipole moment is aligned transverse to the main chain backbone and another linear urethane polymer (L-polymer) with NLO dipole chromophore incorporated in the main chain backbone.[8,9] The resultant poled T-polymer shows the large second-order nonlinearity of $d_{33} = 1.6 \times 10^{-7}$ esu (67 pm/V) with good thermal stability at the ambient conditions.[8,9] This polymer is amorphous with a high density of NLO chromophore moieties and can be fabricated to an optically transparent thin film by spin-casting or solvent casting. As pointed out by the previous work,[10] the NLO chromophore in this arrangement can be easier to orient by an external electric field than in structures where the dipole moments are pointing along the polymer backbone. Namely, the system whose NLO dipole moments aligned transverse to the polymer backbone requires less deformation of the main chain backbone on orienting the dipole moment to the poling field direction than does the system whose NLO dipole moment is incorporated along the polymer backbone.

In this paper, the orientational relaxation of NLO dipole moments in the T-polymer corona-poled at two different temperatures is studied from the time-dependent decay of the second harmonic generation (SHG) activity at the several elevated temperatures. The resultant orientational relaxation of the aligned NLO chromophore is discussed in relation to the structural factor of the effective transition temperature for SHG activity.

Results

Polymer Samples. T-polymer was prepared from 4-[(2-hydroxyethyl)amino]-2-(hydroxymethyl)-4′-nitroazobenzene (T-AZODIOL)[11] with aromatic diisocyanate 2,4-tolylene diisocyanate (TDI) whose chemical structures are shown in Figure 1. T-polymer has a NLO chromophore whose one head is embedded in the polymer backbone and the dipole moments extend transverse to the main chain. Differential scanning calorimetry (DSC) measurement showed that T-polymer has a glass transition temperature, T_g, at 57 °C as shown in Figure 2. This T_g is not necessarily a measure of the SHG activity loss as described later.

Thermal Stability of SHG Activity. Figure 3 shows the SHG activity profiles of d_{33} vs annealing temperature (solid curve in the figure) and d_{33} vs poling

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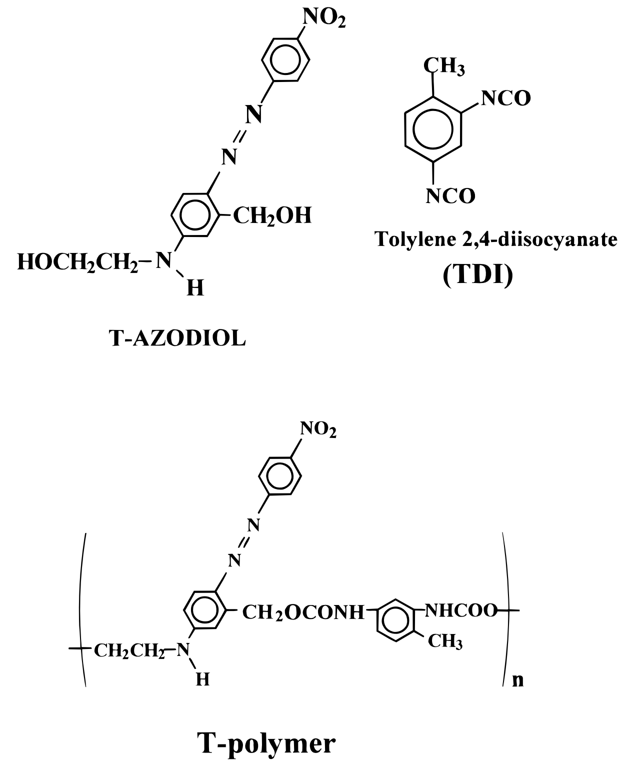

Figure 1. Structural formulas and codes of monomers and polymer.

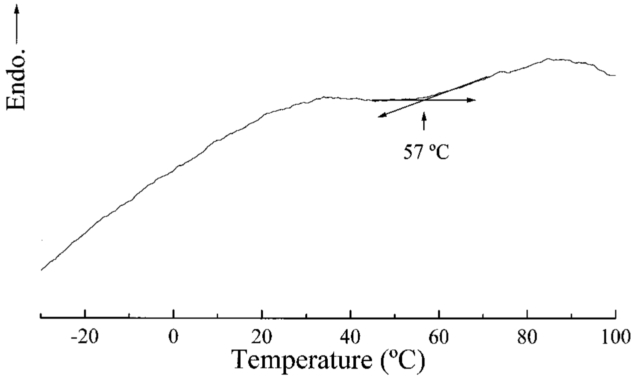

Figure 2. DSC profile of T-polymer.

temperature (dashed curve in the figure). In the poling process, the sample film was subjected to 94 or 80 °C annealing for 1 h and then cooled down to the glass transition temperature as settled and then to room temperature under blowing air. The dependence of d_{33} on the poling temperature shows a two-step increase of d_{33}, where the first plateau is in the vicinity of 80 °C and the second plateau is above 90 °C. Value of d_{33} for T-polymer corona-poled at 94 °C is approximately two times larger than that poled at 80 °C. In the annealing process, T-polymer poled at 94 °C (closed circle in the figure) does not show a significant loss of SHG activity until the large activity loss occurs at the temperature around 85 °C, whereas SHG activity for T-polymer poled at 80 °C (closed square in the figure) was significantly lost at the temperature above 70 °C.

Orientational Relaxation of T-polymer Poled at Different Temperatures. The time-dependent decay of the second-order nonlinear susceptibilities d_{33} for T-polymer poled at two different temperatures, 80 and 94 °C, are investigated at various fixed temperatures. To monitor the decay of nonlinear susceptibilities d_{33} at a given fixed temperature, the film was heated up to that temperature at a heating rate of ca. 1 °C/min and successive SHG activity measurements were preformed. The analysis of the decay curves at each temperature provides the orientational relaxation of aligned NLO dipole moments.

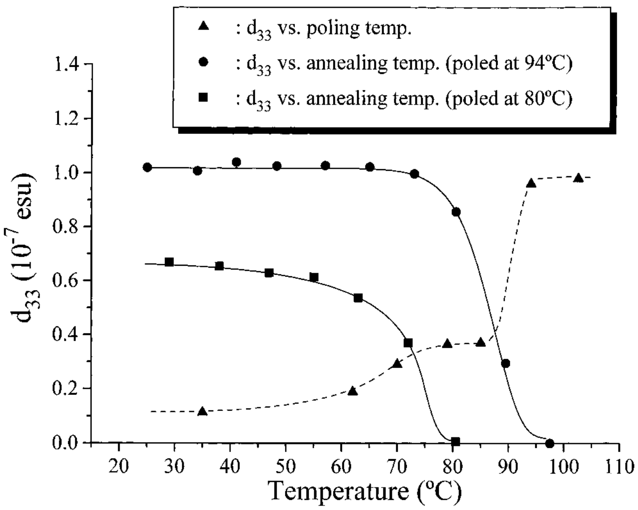

Figure 3. Dependence of SHG coefficients d_{33} on poling and annealing temperatures for T-polymer. In the poling process, the temperature in the horizontal axis is the poling temperature. In the annealing process, the temperature in the horizontal axis is the temperature at which SHG activity is measured.

The observed time-dependent decay of nonlinear susceptibilities d_{33} was nonexponetial. The time-dependent decay of SHG activity due to the reorientation of aligned NLO chromophores in polymers can in general be described by a Kohlrausch−Williams−Watts (KWW) stretched exponential form or by a sum of two exponentials fits, and both are often used to characterize the orientational relaxation of NLO chromophores in the polymers. A sum of two exponential fittings requires three parameters instead of two for the KWW stretched exponential fitting. The time-dependent decay curves for T- polymer are fitted well by both fittings. Figure 4 shows the fitting examples for the relaxation of SHG activity at 80 °C for the sample poled at 94 °C. The physical model involving two distinct exponents of shorter and longer time constants leads to the complexities for characterizing the molecular motion of NLO chromophores in the amorphous polymer matrix. In the present case, a KWW stretched exponential fittings is employed to characterize the relaxation of aligned NLO chromophores in T-polymer

$$d = d_0 \exp(-(t/\tau)^{\beta}) \qquad (0 < \beta \le 1) \qquad (1)$$

where τ is the characteristic relaxation time and β is a measure of width of the distribution of relaxation time and the extent of deviation from a single exponential behavior. When $\beta = 1$, the time-dependent decay corresponds to a single exponential decay profile. The characteristic relaxation time τ is the time required for the system to decay to 1/e of its initial value. Figure 5 shows the KWW stretched exponential fittings (solid curve in the figure) of the time dependence of decay profiles of d_{33} at several elevated temperatures for the sample poled at 94 °C (a) and at 80 °C (b). The vertical axis indicates the d_{33} values normalized by that at $t = 0$, $d_{33}(t)/d_{33}(0)$. Each time-dependent decay curve can be fitted well by the KWW stretched exponential curves with appropriate relaxation time τ and β values as

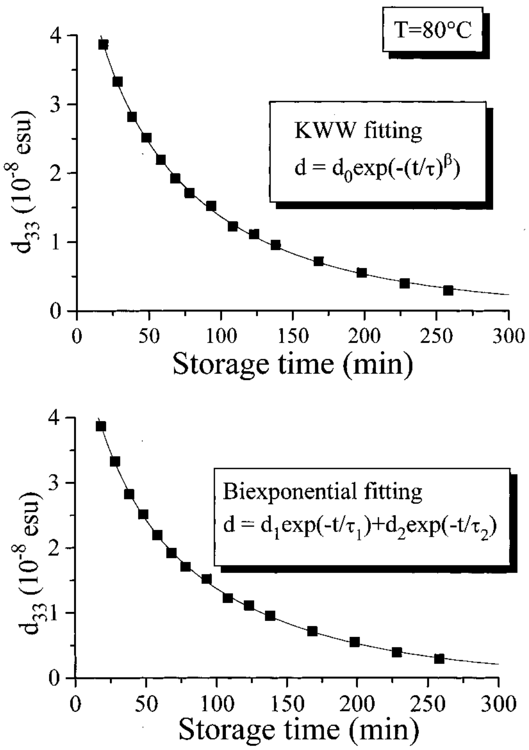

Figure 4. Relaxation decay profiles of d_{33} in T-polymer at 80 °C fitted by the KWW and two exponential functions. The sample was poled at 94 °C. $d_0 = 6.0 \times 10^{-8}$ esu, $\tau = 3.40 \times 10^3$ s, and $\beta = 0.71$ for KWW fitting; $d_1 = 2.07 \times 10^{-8}$ esu, $\tau_1 = 1.63 \times 10^3$ s, $d_2 = 3.33 \times 10^{-8}$ esu, $\tau_2 = 6.53 \times 10^3$ s for two exponential fitting.

fitting parameters for each temperatures. Table 1 summarizes the obtained τ and β values for both samples.

Thermally Stimulated Discharge Current. The thermally stimulated discharge current (TSC) technique is a useful tool for probing the depolarization profile, due to the reorientation of aligned dipole moments, the release of mobile space charge created in the polymeric matrix, and the release of the charges injected. When the NLO dipole moment and the segmental dipole moment randomize at favorable temperatures, the specific discharge current peak can be obtained in the TSC curve. Figure 6 shows the TSC curves for the T-polymer film poled at 94 °C (a) and at 80 °C (b). T-polymer poled at 94 °C shows a broad shoulder peak between 40 and 60 °C and a distinct peak at 92 °C, which are shown in (a), whereas T-polymer poled at 80 °C has a single peak around 60 °C which is shown in (b). In both figures, the TSC curves after depolarization (dashed curve in the figures) are illustrated. After depolarization for both cases, no significant TSC peak can be detected. Thus the TSC peak for the sample polarized by corona-poling can be related to the relaxation of the oriented dipole moments and the molecular motion of the polymer matrix. Broad peak between 40 and 60 °C in Figure 6a is ascribed to the release of the segmental molecular motion which is related to the glass transition temperature around 57 °C determined by DSC. The sharp peak around 92 °C in Figure 6a is attributed to the randomization of aligned NLO dipole moments which is related to the significant SHG activity loss at the temperature around 85 °C as shown in Figure 3. As for the sample films poled at 80 °C, the relaxation of the aligned NLO dipole moments is overlapped by the release of the segmental molecular motion, and both appeared as the broad peak around 60 °C.

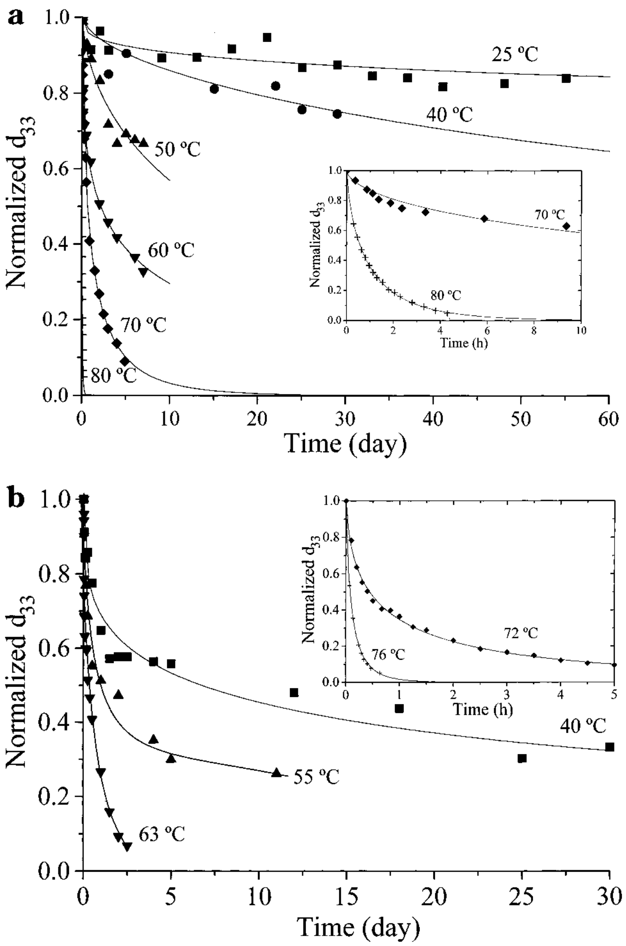

Figure 5. KWW fittings of relaxation decay curves at various temperatures for T-polymer poled at 94 °C (a) and 80 °C (b).

Discussion

Results of the relaxation time exhibit that T-polymer poled at 94 °C has long-term thermal stability over 50 years at room temperature. The dependence of the inverse of the relaxation time on the inverse of temperature for T-polymer is described well by an single energy-activated Arrhenius expression as shown in Figure 7. This result is contrast to the fact that the guest–host system does not obey the single energy-activated Arrhenius plot.[12,13] It is noted that the relaxation time of T-polymer poled at 94 °C is 3 orders of magnitude larger than that poled at 80 °C as listed in Table 1. The slope of the Arrhenius relation of the inverse of the relaxation time with the inverse of temperature gives the activation energy for the reorientation of the aligned NLO dipole moments. The activation energy is related to the potential barrier that NLO dipole moments meet when they thermally orient with the assistance of corona-poling. From the Arrhenius plot in Figure 7, both relaxation processes have the same activation energy of 195 kJ/mol. Then the question arising is why the orientation of NLO dipole moments for the sample poled at 94 °C is more stable than that for the sample poled at 80 °C.

Let us think of the effect of glass transition temperature on SHG activity. The DSC profile shows that T-polymer has T_g at 57 °C. It is noted that SHG activity for T-polymer poled at 94 °C is stable at temperatures beyond T_g and that poled at 80 °C is remarkably

Table 1. Relaxation Time τ (s) and β Values Obtained from the Appropriate Fitting of KWW Stretched Exponential Function

(a) Sample Poled at 94 °C

	25 °C	40 °C	50 °C	60 °C	70 °C	80 °C	87 °C	90 °C
τ value	1.62×10^9	2.11×10^7	2.23×10^6	5.04×10^5	1.04×10^5	3.40×10^3	2.70×10^3	6.60×10^2
β value	0.31	0.59	0.60	0.37	0.58	0.71	0.65	0.65

(b) Sample Poled at 80 °C

	40 °C	45 °C	55 °C	63 °C	72 °C	76 °C
τ value	3.00×10^4	3.70×10^3	5.10×10^3	6.90×10^2	3.80×10^1	5.10×10^0
β value	0.33	0.37	0.34	0.52	0.44	0.61

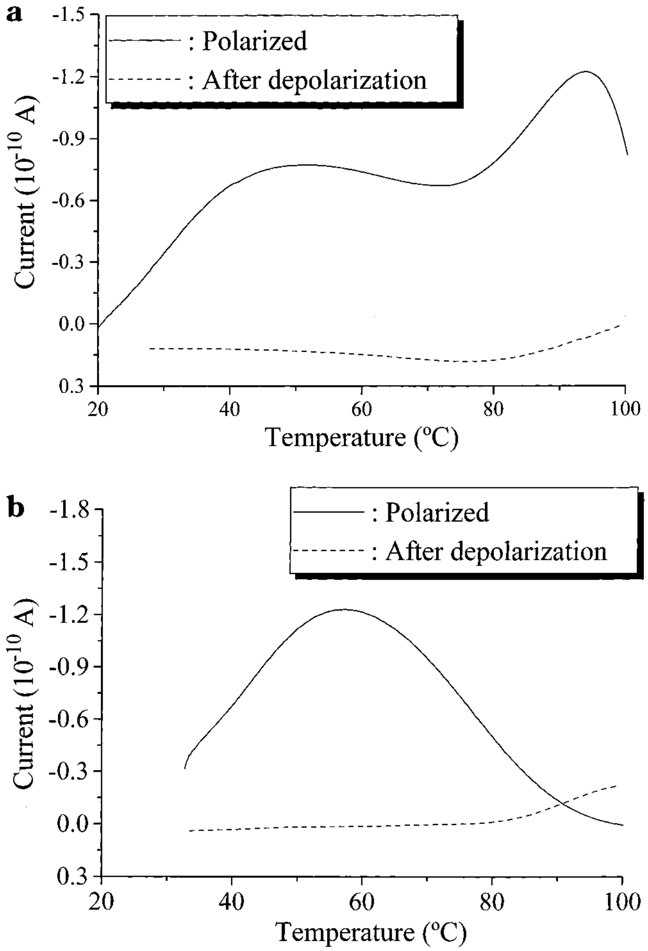

Figure 6. TSC profiles of T-polymer poled at 94 °C (a) and 80 °C (b). Dashed TSC curves in both figures are those for the depolarized samples.

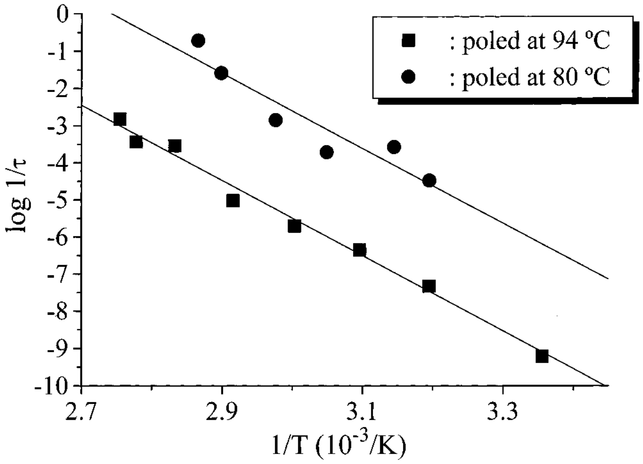

Figure 7. Arrhenius plots of the relaxation time for T-polymer poled at 94 and 80 °C.

depressed at temperature above T_g as shown in Figure 3. To our common knowledge, the glass transition temperature is the temperature when the oriented amorphous NLO dipole moments are usually randomized and the resultant SHG activity is largely depressed. However the present results suggest that the T_g value determined by DSC is not necessarily a measure for determining the thermal stability of NLO dipole moments. Therefore, the effective transition temperature, T_0, for SHG activity must be introduced to understand the difference of the orientational relaxation between samples poled at 80 and 94 °C. As shown in Figure 6a, the TSC curve for the sample poled at 94 °C gives a sharp and distinct peak at 92 °C, and the SHG measurement on annealing as shown in Figure 3 shows that SHG activity is significantly depressed around 85 °C. Thus the effective transition temperature T_0 for the sample poled at 94 °C is 85 °C. As for the sample poled at 80 °C, T_0 is 60 °C from the result of TSC curve as shown in Figure 6b and the thermal stability of SHG on annealing shown in Figure 3. The effective transition temperature for SHG activity is the useful measure for comparing orientation-relaxation of NLO chromophores. In order to compare the orientation-relaxation of NLO chromophore in polymers with different transition temperatures, the scaling relation of

$$\tau(T) = A' \exp\left(\frac{T_0 - T}{T}\right) \tag{2}$$

is proposed, where A' is a constant and T_0 is the transition temperature of polymers.[6,14] Another same type plot of

$$\tau = \tau_0 \exp\left(\frac{B}{T_0' - T}\right) \tag{3}$$

is also proposed, where B and τ_0 are the fitting parameters[12] and T_0' is the effective temperature ($=T_g + 50$ °C). Both scaling plots are related to the Williams–Landel–Ferry (WLF) or the Vogel–Tamann–Fulcher (VTF) expressions frequently used to describe in the field of viscoelastic properties of polymers above T_g. Figure 8 shows the scaling plot of the relaxation time in the present system using eq 2 with $T_0 = 85$ °C for the sample poled at 94 °C and $T_0 = 60$ °C for the sample poled at 80 °C. The logarithmic τ value for the relaxation of NLO chromophore in the present polyurethane is linearly dependent on the $(T_g - T)/T$. One can understand that the remarkable difference of the relaxation time for the samples poled at different temperatures is ascribed to the difference of effective transition temperature for SHG activity between both samples. The next question is what is the origin for the difference of effective transition temperature between both conditions. One possible explanation is the free

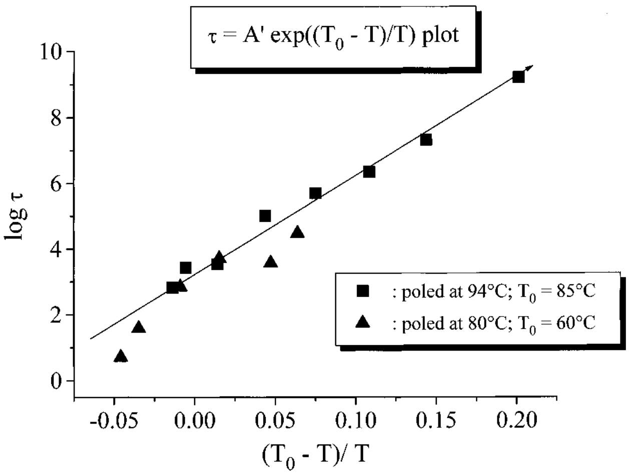

Figure 8. Plots of logarithmic τ vs $(T - T_0)/T$ for both samples.

Table 2. Dependence of Density and Free Volume (V_f) on Poling Temperature

sample	density (g/cm^3)	V_t (cm^3/g)	V_0 (cm^3/g)	V_f (cm^3/g)
as-cast film	1.246	0.803	0.632	0.171
film annealed at 80 °C	1.248	0.801	0.632	0.169
film annealed at 94 °C	1.261	0.793	0.632	0.161

volume of the matrix which provides the free space where the aligned dipole moments can be thermally reoriented. The density of the sample annealed at 94 °C is larger than that at 80 °C as listed in Table 2. The larger density leads to the smaller free volume. The free volume V_f can be estimated from the experimentally obtained specific volume V_t (the reciprocal value of measured density) and the zero point molar volume V_0

$$V_f = V_t - V_0 \tag{4}$$

where V_0 can be calculated from the van der Waals volume V_w of the polymer, $V_0 = 1.3V_w$.[15] V_w of polymers was determined by the summation of the van der Waals volumes of group contributions.[16] Free volumes estimated by using eq 4 are listed in Table 2. The smaller free volume for the samples poled at 94 °C contributes to the restriction of molecular motion of NLO moiety in the matrix and thus the increase of the effective transition temperature. The absorption due to the hydrogen bonded N−H stretching vibration can be observed at 3380 cm^{-1} in the Fourier transform infrared (FT-IR) spectra for both samples. Also the small absorption due to the free N−H stretching vibration can be observed at 3540 cm^{-1}. The absorption intensity ratio between 3380 and 3540 cm^{-1} was not affected by the annealing temperature. Therefore, the quantity of hydrogen bonding measured from the FT-IR spectra does not provide a direct explanation for the difference in relaxation time. However, one can say that the hydrogen bonding might be related to the orientational stability of NLO chromophore.

Another possibility for retaining the macroscopic orientation of the NLO chromophore in the matrix may be due to the nanocrystalline or crystalline regions which is induced by annealing at 94 °C. However, there is no direct evidence of the crystalline state. Space charges formed by the injected charge also contribute to the orientational retaining of the aligned NLO chromophores unless they come out from the sample film. Thus, if the charges were injected in the process of poling at 94 °C to form the space charges in the matrix, they assist to stabilize the orientation of aligned NLO chromophore. In the case of space charge effects, a higher TSC peak around 92 °C for the sample corona-poled at 94 °C shown in Figure 6a can be interpreted as the loss of the space charges from the sample film and the subsequent significant depression of SHG activity.

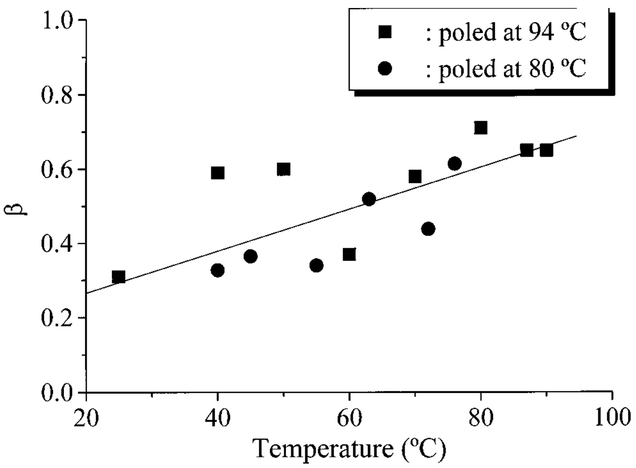

Figure 9. Plots of β values vs annealing temperature for both samples.

β values are plotted against annealing temperature in Figure 9. In both cases of T-polymer poled at 80 and 94 °C, β values increase with increasing temperature, which is consistent with the idea that the increase of temperature leads to narrowing the width of the distribution of relaxation time, i.e., approaching a single exponential decay.

Conclusion

Orientational stabilities of NLO dipole moments in linear urethane polymer, T-polymer, poled at different temperatures are studied. SHG activity losses due to the relaxation of aligned NLO dipole moments at various temperatures are fitted well by a KWW stretched exponential function. The relaxation time of T-polymer poled at 94 °C is 3 orders of magnitude larger than that poled at 80 °C, and the relaxation time results exhibit that T-polymer poled at 94 °C has long-term thermal stability, over 50 years at room temperature. The TSC curve for the T-polymer poled at 94 °C clearly shows the broad peak between 40 and 60 °C and distinct sharp peak at 92 °C which correspond well to the transition due to the segmental molecular motion and the reorientation of the NLO dipole moments, respectively, whereas the TSC curve for the sample poled at 80 °C has a single broad peak around 60 °C due to the reorientation of the NLO dipole moments, which may be overlapped by the transition due to the segmental molecular motion. Remarkable stability of SHG activity for the sample poled at 94 °C is explained by the increase of effective transition temperature for SHG activity. This higher effective transition temperature for SHG activity is related to the smaller free volume and/or the space charges retaining the macroscopic orientation of the aligned NLO chromophores.

Experimental Section

Materials. 4-[(2-Hydroxyethyl)amino]-2-(hydroxymethyl)-4′-nitroazobenzene (T-AZODIOL) was used as the NLO chromophore whose dipole moment is aligned transverse to the main chain. T-AZODIOL was synthesized via two-step reactions: First, 3-[(2-hydroxyethyl)amino]benzyl alcohol (DIOL) was prepared from *m*-aminobenzyl alcohol with 2-chloroethanol. Then the coupling reaction of DIOL with diazotized *p*-nitroaniline gave rise to T-AZODIOL. The details of synthesis procedure are shown in our previous paper.[9] Commercially available tolylene 2,4-diisocyanate (TDI) was used without further purification.

Corona Poling. Spun-cast films were both positively corona-poled at an elevated temperature to orient the NLO dipole moments in the poling direction. The distance between the sample and 0.1 ϕ tungsten wire for corona poling was kept at 1.4 cm.

SHG Measurements. The Maker fringe method[17,18] was employed to measure the SHG intensity of the poled spun-cast films. The laser source is a Continuum model Surelite-10 Q-switched Nd:YAG pulse laser with 1064 nm p-polarized fundamental beam (320 mJ maximum energy, 7 ns pulse width, and 10 Hz repeating rate). The generated second harmonic (SH) wave was detected by a Hamamatsu Model R928 photomultiplier. The SH signal averaged on a Stanford Research Systems (SRS) Model SR-250 gated integrator and boxcar averager module was transferred to a microcomputer through a SRS Model SR-245 computer interface module. The precise experimental procedure is described in refs 19 and 20.

Characterization. DSC was carried out at a heating rate of 10 °C/min in a nitrogen atmosphere, using a Perkin-Elmer DSC7 controlled by a 1020 TA workstation. TSC was measured at a heating rate of 4 °C/min, using the sandwich type cell with the positively corona-poled surface grounded. The FT-IR spectrum was recorded with a resolution of 2 cm^{-1}. The density of the polymer film was measured in potassium iodide solution at 30 °C using a sink and float test.

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