Synthesis and Nonlinear Optical Properties of Novel Y-Type Polyurethanes Containing Different Concentrations of Chromophore

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ABSTRACT: A new series of Y-type polyurethanes containing different concentrations of nonlinear optical (NLO) chromophore with aniline donor and tricyanofurane (TCF) acceptor have been successfully prepared, and characterized by FTIR, UV-Vis, and ^{1}H-NMR spectra. New polyurethanes were synthesized with different chromophore contents by introducing diol *N*, *N*-dihydroxyethylaniline or 4-[*N*, *N*-(dihydroxyethyl)amino]benzaldehyde. These NLO polyurethanes exhibit good film forming property and high thermal stability up to 281°C. The highest electro-optic coefficient (r_{33}) of polymers is up to 39 pm V^{-1} measured by simple reflection technique at 1310 nm, and the temporal stability of the poling-induced order at elevated temperature of 80°C was much improved through the introducing of hydrogen bonding interaction in this system. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2012

INTRODUCTION

Nonlinear optical (NLO) materials have been extensively studied over the past decade[1,2] and NLO polymers have many advantages such as low cost, ultrafast response, wide response wave band, high optical damage threshold, and good processability.[3,4] For the practical applications, organic polymeric materials should mainly meet four requirements: large optical nonlinearity, high alignment stability of chromophores, good device processability, and low optical loss.[5] One of the major challenges in this research is to achieve the reasonable tradeoff among all these properties in one sample.

In the developments of NLO polymers for electro-optic (EO) device applications, stabilization of electrically induced dipole alignment is one of important considerations. Generally, there are two approaches to solve this problem.[6–8] One is to employ chemical crosslinking method[9–13] and the other is to utilize high glass transition temperature (T_g) polymers as matrix such as polyimides.[14–18] But there are disadvantages in the two methods. For the chemical crosslinking method, the crosslinking temperature (T_c) has to be higher than T_g to ensure an efficient poling of the chromophores before the crosslinking reaction starts.[19] Actually, only a relatively small number of chemical crosslinking systems have been reported, because it's difficult to

find a suitable system which fulfils the above condition. And that for the utilization of high T_g polymers, the chromophores can be prone to decomposition when the materials are subjected to the high temperatures during the poling process. Since polyurethane matrix with extensive hydrogen bonding between urethane linkages can form physical crosslinking system,[20–24] we choose this physical crosslinking system as polymer matrix to investigate the alignment stability of materials. This kind of system formed physical crosslinking network around the NLO chromophores and built special environment to restrain the movement of chromophores, which directly optimized the EO activity stability.[25] Furthermore, hydrogen bonding interaction could also improve the homogeneity and processability in polymer relative to chemically crosslinked systems.[26,27] However, there were still some problems to be solved when polyurethane matrix was used for investigating EO activity stability. For example, as the T_g of main chain polyurethane was too high, the chromophores would be destroyed in the poling process, and its solubility and processability did not meet the application requirements because of the strong rigid chain of polyurethane.

In order to solve these problems, a novel series of Y-type polymers containing NLO chromophores with aniline donor and tricyanofurane (TCF) acceptor were prepared in this article.

These Y-type polymers have the advantages of both main-chain and side-chain NLO polymers, and improve the processability of main chain polymers and enhance the alignment stability of side chain polymers, which help to study the influence of the physical crosslinking system on EO properties.[28–30] In order to adjust the T_g of the polyurethane and reduce the electrostatic interactions between the chromophores and furthermore improve the solubility and processability, the concentrations of chromophores in polyurethane matrix were changed by adding another diol parts, such as N, N-dihydroxyethylaniline or 4-[N, N-(dihydroxyethyl)amino]benzaldehyde.[31] Meanwhile, the introduced aldehyde group of 4-[N, N-(dihydroxyethyl)amino]benzaldehyde could form more hydrogen bonds with the urethane linkages and it was propitious to make the physically crosslinked network denser. Hereby, in this polyurethane system the polymer network could restrain the movement of chromophores more efficiently and the temporal stability of EO activity could be improved.[32]

EXPERIMENTAL

Materials and Measurement

All the reagents were purchased from Beijing Chemical Reagent Company and used as received unless stated. Toluene 2,4-diisocyanate (TDI) was distilled under reduced pressure before use. DMF were freshly distilled prior to use. Chromophore d-TCF was prepared according to previous literature.[33] ^{1}H-NMR spectra were determined by Varian Gemini 300 (300 MHz) NMR spectrometer (tetramethylsilane as internal reference). FTIR spectra were recorded on BIO-RAD FTS-165 spectrometer; UV–Vis spectra were performed on Hitachi U2001 spectrophotometer. The number-average molecular weight (M_n) and weight-average molecular weight (M_w) values of the polyurethanes were estimated by gel permeation chromatography (GPC). Tetrahydrofuran (THF) was used as the eluent and polystyrene (PS) standards were used for the molecular weight calibration. Thermogravimetric analysis (TGA) was determined by TA5000-2950TGA (TA co) with a heating rate of $10°C$ min^{-1} under the protection of nitrogen; differential scanning calorimetry (DSC) measurements were performed on a TA5000, 2910MDSC with a heating rate of $10°C$ min^{-1} under the protection of nitrogen. Atomic Force Microscope (AFM) was characterized by multimode 8 bruker. The thickness of the films was measured with an Ambios Technology XP-1 profilometer.

Synthesis

General Procedure for the Synthesis of Polyurethanes. Common polyurethane (P0)[34] was synthesized by chromophore d-TCF, TDI, and the catalyst dibutyltion dilaurate in appropriate anhydrous DMF solution at room temperature for 48 h in an atmosphere of dry nitrogen. P-10 and P-40 were synthesized by chromophore d-TCF, N, N-dihydroxyethylaniline (compound 1) and TDI under the similar condition. P-10-A and P-40-A were synthesized by chromophore d-TCF, 4-[N, N-(dihydroxyethyl)amino]benzaldehyde (compound 2) and TDI under the similar condition. The resulting solution was poured into cold water and filtered, and than the precipitate was dissolved in a minimum quantity of DMSO and reprecipitated by pouring into a large quantity of water. The polymer

was further purified by extraction in a Soxhlet extractor with ethanol and dried under vacuum.

P0: chromophore d-TCF (1.513 g, 3.879 mmol), TDI (0.675 g, 3.879 mmol). P0 was obtained as deep purple powder (1.7 g, 78%). M_w = 3098 g mol^{-1}. IR (KBr pellet), v (cm^{-1}): 1720 (C=O), 2222 (-CN). ^{1}H-NMR (DMSO-d_6) δ (ppm): 2.11 (Ph-CH$_3$, s, 3H), 3.86 (Ph-N-CH$_2$-, t, 4H), 4.31 (-CH$_2$-OCO-, t, 4H), 6.91-6.95 (vinylic, d, 1H), 7.04–7.18 (aromatic, m, 3H), 7.52 (aromatic, d, 2H), 7.80 (aromatic, d, 2H), 7.91–7.95 (vinylic, d, 1H), 8.91-9.00 (N-H, d, 1H), 9.63 (N-H, s, 1H). UV–vis (THF): λ_{max} (nm) = 544.

P-10: chromophore d-TCF (0.201 g, 0.515 mmol), compound 1 (0.873 g, 4.823 mmol), TDI (0.929 g, 5.339 mmol). P-10 was obtained as deep purple powder (1.7 g, 85%). M_w = 16,345 g mol^{-1}. IR (KBr pellet), v (cm^{-1}): 1720 (C=O), 2222 (-CN). ^{1}H-NMR (DMSO-d_6) δ (ppm): 2.13 (Ph-CH$_3$, s, 30H), 3.67 (Ph-N-CH$_2$-, t, 40H), 4.24 (-CH$_2$-OCO-, t, 40H), 6.84–6.85 (vinylic, d, 1H), 7.08–7.19 (aromatic, m, 30H), 7.52 (aromatic, d, 20H), 7.79 (aromatic, d, 20H), 7.91–7.95 (vinylic, d, 1H), 8.89–8.98 (N-H, d, 10H), 9.62 (N-H, s, 10H). UV–vis (THF): λ_{max} (nm) = 547.

P-40: chromophore d-TCF (0.802 g, 2.056 mmol), compound 1 (0.434 g, 2.398 mmol), TDI (0.776 g, 4.460 mmol). P-40 was obtained as deep purple powder (1.8 g, 89.5%). M_w = 8706 g mol^{-1}. IR (KBr pellet), v (cm^{-1}): 1720 (C=O), 2224 (-CN). ^{1}H-NMR (DMSO-d_6) δ (ppm): 2.13 (Ph-CH$_3$, s, 5.7H), 3.67–3.86 (Ph-N-CH$_2$-, t, 7.6H), 4.24–4.31 (-CH$_2$-OCO-, t, 7.6H), 6.84–6.86 (vinylic, d, 1H), 6.91–7.19 (aromatic, m, 5.7H), 7.52 (aromatic, d, 3.8H), 7.80 (aromatic, d, 3.8H), 7.92–7.96 (vinylic, d, 1H), 8.89–8.98 (N-H, d, 1.9H), 9.63 (N-H, s, 1.9H). UV–vis (THF): λ_{max} (nm) = 549.

P-10-A: chromophore d-TCF (0.200 g, 0.513 mmol), compound 2 (0.934 g, 4.469 mmol), TDI (0.874 g, 5.023 mmol). P-10-A was obtained as deep purple powder (1.7 g, 85%). M_w = 3970 g mol^{-1}. IR (KBr pellet), v (cm^{-1}): 1716 (C=O), 2220 (-CN), 2853 (-CHO). ^{1}H-NMR (DMSO-d_6) δ (ppm): 2.10 (Ph-CH$_3$, s, 24H), 3.81 (Ph-N-CH$_2$-, t, 32H), 4.30 (-CH$_2$-OCO-, t, 32H), 6.91-6.93 (vinylic, d, 1H), 7.00–7.28 (aromatic, m, 24H), 7.50 (aromatic, d, 16H), 7.72 (aromatic, d, 16H), 7.91–7.95 (vinylic, d, 1H), 8.90–8.99 (N-H, d, 8H), 9.63 (N-H, s, 8H), 9.70 (Ph-CHO, s, 7H). UV–vis (THF): λ_{max} (nm) = 547.

P-40-A: chromophore d-TCF (0.386 g, 0.990 mmol), compound 2 (0.222 g, 1.062 mmol), TDI (0.362 g, 2.080 mmol). P-40-A was obtained as deep purple powder (0.9 g, 93%). M_w = 5161 g mol^{-1}. IR (KBr pellet), v (cm^{-1}): 1716 (C=O), 2222 (-CN), 2854 (-CHO). ^{1}H-NMR (DMSO-d_6) δ (ppm): 2.11 (Ph-CH$_3$, s, 5.4H), 3.66 (Ph-N-CH$_2$-, t, 7.2H), 4.39 (-CH$_2$-OCO-, t, 7.2H), 6.91–6.94 (vinylic, d, 1H), 6.99–7.11 (aromatic, m, 5.4H), 7.51 (aromatic, d, 3.6H), 7.80 (aromatic, d, 3.6H), 7.92–7.96 (vinylic, d, 1H), 8.91–9.00 (N-H, d, 1.8), 9.62 (N-H, s, 1.8), 9.70 (Ph-CHO, s, 0.8H). UV–vis (THF): λ_{max} (nm) = 541.

Preparation of the NLO Films

The polymers were dissolved in cyclopentanone (concentration 20 wt %), and the solutions were filtered through 0.22-μm syringe filters. The filtrate was spin-coated onto indium-tin oxide
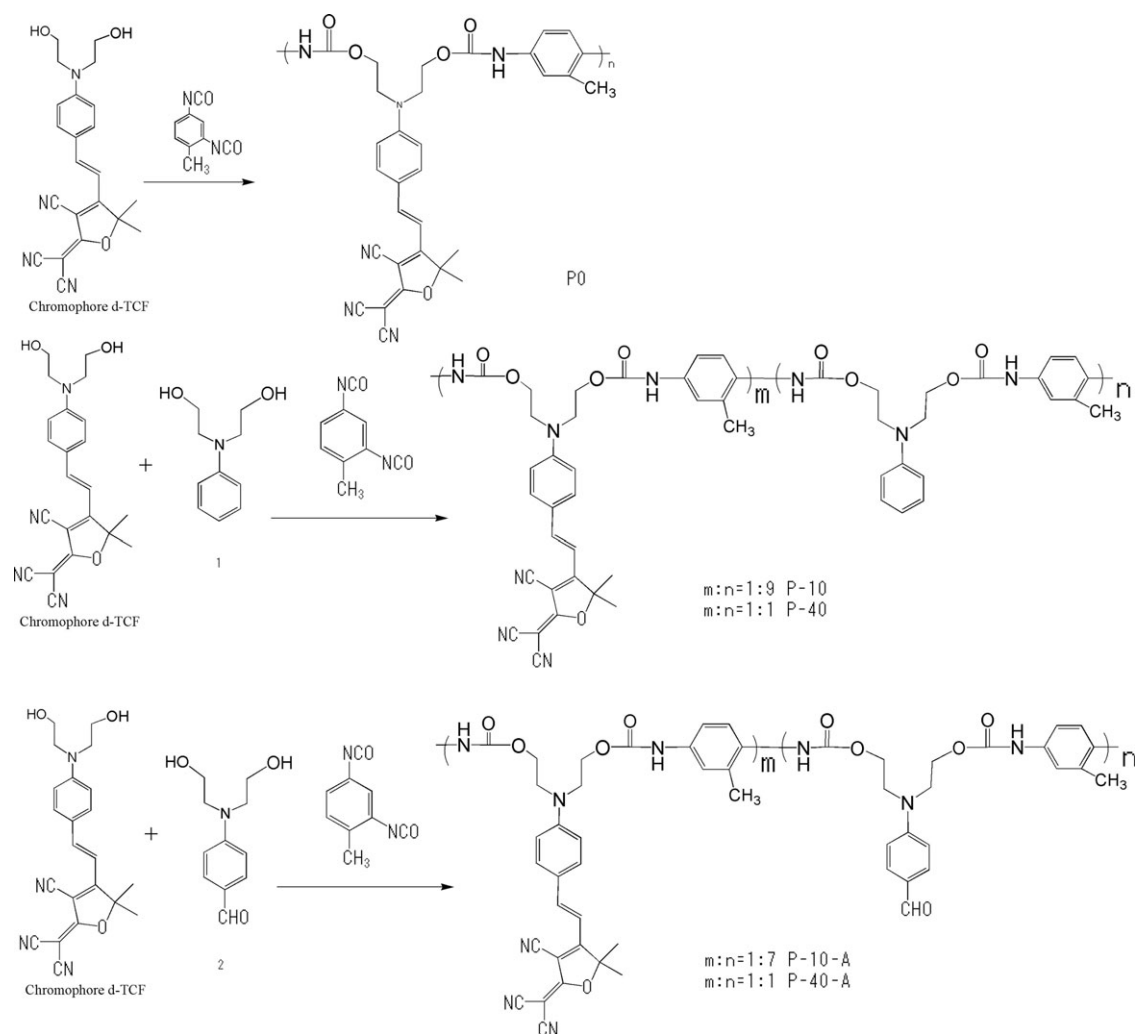
Scheme 1. The synthesis of the polyurethanes.

(ITO)-coated glass substrates, which were cleaned by distilled water, acetone, and ethanol sequentially in an ultrasonic bath before use. Residual solvent was removed by heating the films at 40°C in a vacuum oven.

RESULTS AND DISCUSSION

Synthesis and Characterization of the Polyurethane

As shown in Scheme 1, polyurethane P0 was prepared by the polymerization between diol chromophore d-TCF and TDI. To adjust the concentration of the chromophore, compound 1 or compound 2 was introduced to obtain polyurethane P-10, P-40, P-10-A, and P-40-A. The chromophore concentrations of P-10 and P-10-A were about 10 wt %, and those of P-40 and P-40-A were about 40 wt %.

The structures of the obtained polyurethanes were confirmed by FTIR, ^{1}H-NMR, and GPC. In the ^{1}H-NMR spectrum of the polyurethanes the chemical shifts was consistent with the proposed polymer structure. The singlet at 9.62 ppm and doublet at 8.89–9.00 ppm assigned to the amine proton indicate the formation of urethane linkage. The singlet at 9.70 ppm assigned to

the benzaldehyde proton indicates the introduction of another monomer to reduce the content of chromophore. The composition of the copolymer was determined by the ratio of the integrated peak areas of the peaks at 8.89–9.70 ppm, 9.62 ppm (amine protons) and 7.91–7.96 ppm (vinylic protons of chromophore). The calculated mass fraction of chromophore in P-10, P-40, P-10-A, and P-40-A are 10.8 wt %, 44.3 wt %, 12.4 wt %, and 44.4 wt %, respectively. All the results were summarized in Table I.

Figure 1(a) shows the FTIR spectra of polymers. The absorption peak around 2220 cm^{-1} was assigned to the cyano group of the chromophore. A new absorption peak appearing at 1720 cm^{-1} was characterized as the vibration of the carbonyl group in a urethane group, indicating the success of polymerization. The FTIR spectra of P-10-A, P-40-A, and N, N-diethyl-4-amino benzaldehyde (as reference) in the range 1450–1800 cm^{-1} were shown in Figure 1(b). In N, N-diethyl-4-amino benzaldehyde the absorption peak of benzaldehyde was at 1682 and 1666 cm^{-1}, while in P-10-A, that shifted to 1655 cm^{-1}. This shift indicated the existence of the hydrogen bonds between

Table I. Characteristics and r$_{33}$ Values of Various Kinds of the Polymers

Polymer	Chromophore : 1 or 2 feed ratio	Chromophore : 1 or 2 measured ratio	Chromophore content[a] (wt %)	Thickness of the films (μm)	M_w[b] (g mol^{-1})	M_w/M_n[b]	λ$_{max}$ (THF) (nm)	T_g[c] (°C)	T_d[d] (°C)	r$_{33}$[e] (pm V^{-1})
P0	–	–	69.1	1.6	3098	1.357	544	172	281	35
P-10	1 : 9.4	1 : 8.6	10.8	2.6	16345	2.580	547	105	256	13
P-40	1 : 1.2	1 : 0.95	44.3	1.8	8706	2.113	549	132	263	38
P-10-A	1 : 8.7	1 : 7.3	12.4	2.5	3970	1.612	547	134	260	10
P-40-A	1 : 1.1	1 : 0.82	44.4	1.9	5161	1.907	541	150	259	39

[a]This is calculated by ^{1}H-NMR spectra.
[b]Determined by GPC in THF on the basis of a polystyrene calibration.
[c]T_g values were performed at a heating rate of 10°C min^{-1} under nitrogen atmosphere by DSC.
[d]T_d values were defined as weight loss at 5 wt %, which were performed at a heating rate of 10°C min^{-1} under nitrogen atmosphere by TGA.
[e]EO coefficients were measured by simple reflection technique at 1310 nm.

benzaldehyde and urethane bond.[27,35] Because the formation of hydrogen bonds increased the dipole moment, the wavenumber of bonding benzaldehyde increased.

All the polymers are soluble in common polar organic solvents, such as THF, DMF, and DMSO. In the UV-Vis absorption spectra, the maximum absorption wavelengths of all the polymers are listed in the Experimental Section and Table I.

Thermal Properties
The thermal behavior of the polymers was summarized in Table I. Thermal decomposition temperatures (T_d) were calculated at the loss of 5 wt % from TGA thermogram. TGA thermogram (Figure 2) showed that the T_d values of the polyurethanes were in the range of 256–281°C. The results showed that all the polyurethanes had good thermal stability. The T_g values of the polymers were obtained from DSC curves as shown in Figure 3. It was observed that the T_gs of the polyurethanes ranged from 105 to 172°C depending on the contents of the NLO chromophores attached to the polyurethane backbone and the amount of hydrogen bond. In the similar polyurethane backbone, the T_g values increased with the content of the chromophore because of the steric effect. Compared P-10-A to P-10 and P-40-A to

P-40, it was found that polyurethanes containing the benzaldehyde moiety exhibited higher T_g values than the ones without benzaldehyde, which even had larger molecular weights. This was because in P-10-A and P-40-A more hydrogen bonds between the benzaldehyde and the urethane group were formed, and the physically crosslinked network was denser. On the other hand, P0 exhibited highest T_g values (172°C) than the other polyurethanes. This could be attributed to the enhanced chain rigidity caused by the high-content chromophore and the electronic interaction between the chromophore moieties.

Morphology Study
To justify the alignments of NLO chromophores along the direction of field poling, domain structure of NLO polymer films were obtained using atomic force microscopy. Figure 4 illustrates the AFM scans of spin-coated film of P-40-A before and after poling. Before poling, the AFM image [Figure 4(a)] shows that surface of the film was somewhat flat and clean. However, when it was subjected to poling, the good quality film was dramatically changed, resulting to numerous hills and valleys in the surface structure as shown in Figure 4(b). This clearly justifies that after the poling, molecules were effectively aligned along the direction of the field poling.
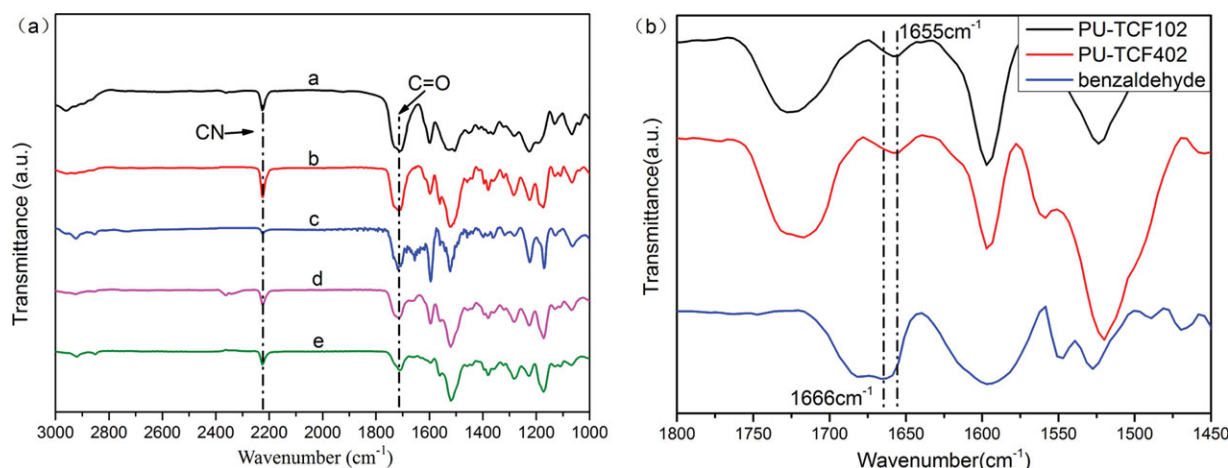

Figure 1. (a) FTIR spectra of the polymer films. a: P-10, b: P-40, c: P-10-A, d: P-40-A, d: P0. (b) FTIR spectra of P-10-A, P-40-A, and *N, N*-Diethyl-4-amino benzaldehyde in the range 1450–1800 cm^{-1}. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 2. TGA curves of the polymers. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
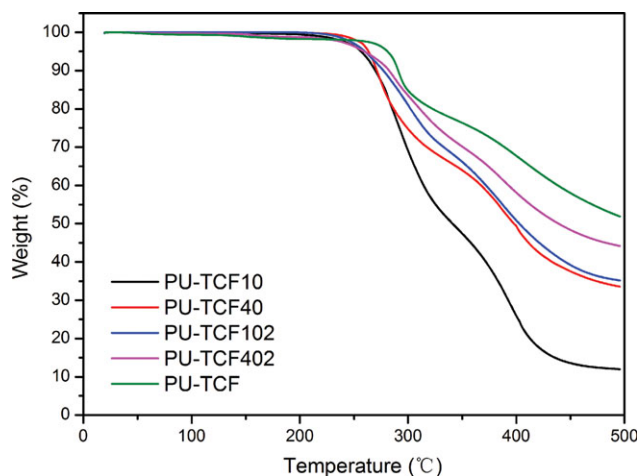

Figure 3. DSC curves of the polymers. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

NLO Properties

To evaluate the EO activity of the polymers, films with the thickness of about 2 μm were poled at 115–177°C for 5 min under the electric field of 10.5–11.5 kV using corona poling method. After the films were cooled to room temperature, the electric field was removed.

A reflective EO polymer light modulator was fabricated using this kind of EO materials. The EO characterization of the EO film in this modulator was conducted by simple reflection technique at the wave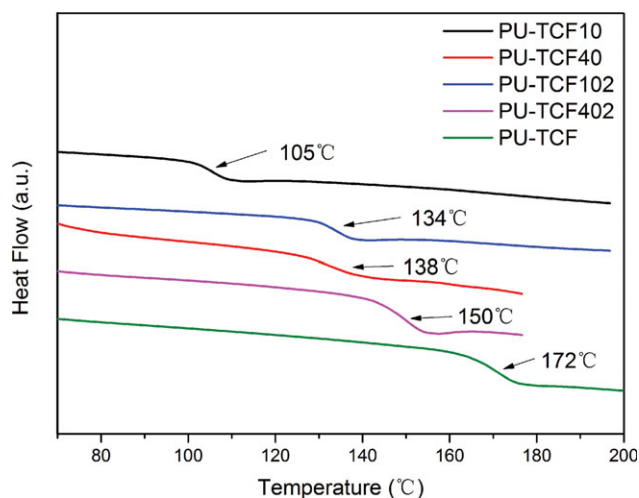length of 1310 nm.[36] The EO coefficient of active polymer layer in the EO modulator can be determined according to the following equation:

$$r_{33} = \frac{3\lambda I_m}{4\pi V_m I_c n^2} \frac{(n^2 - \sin^2 \theta)^{3/2}}{(n^2 - 2 \sin^2 \theta)} \frac{1}{\sin^2 \theta} \quad (1)$$

where r_{33} is the EO coefficient of the poled polymer layer; n is the refractive indices of the polymer film; I_m is the amplitude of the modulation; I_c is half the maximum intensity; θ is the angle
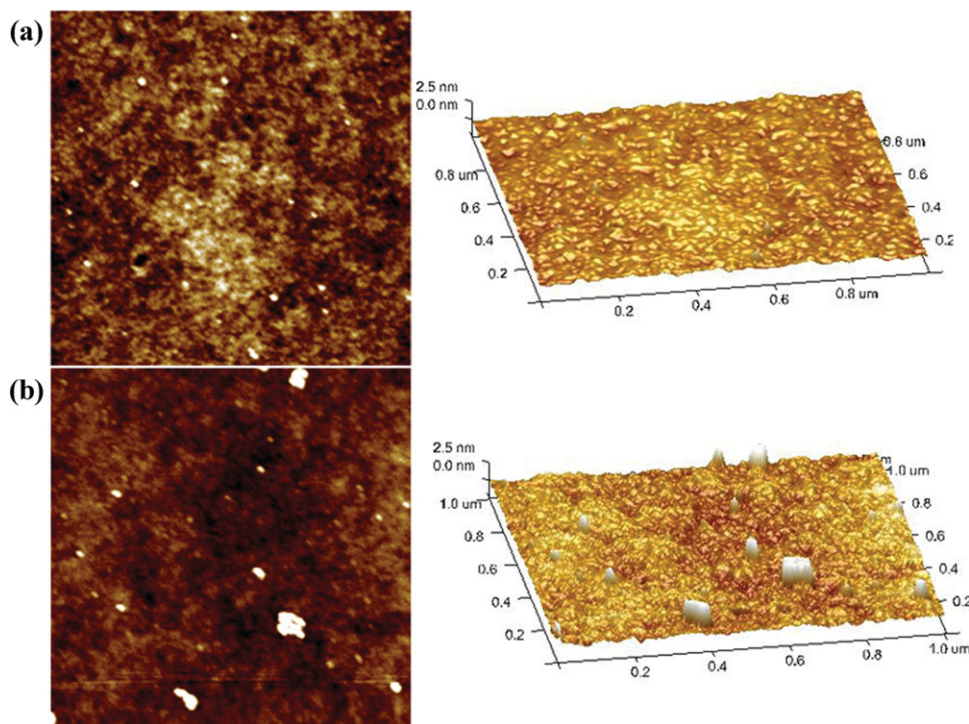

Figure 4. AFM images of the spin-coated film of P-40-A: (a) before poling; (b) after poling. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
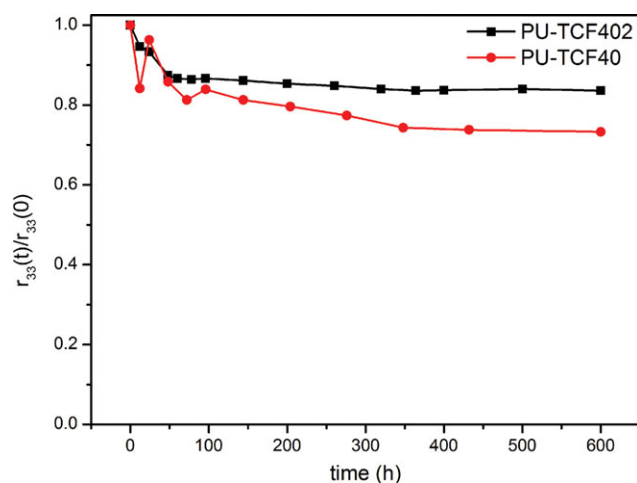
Figure 5. Temporal stability of the EO coefficient for poled polymer films at 80°C for 600 h. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

of input laser beam, and is set at 45°; V is the modulating voltage, $V_m = 40$ V; λ is the optical wavelength, $\lambda = 1310$ nm.

The EO coefficients (r_{33}) of the films were also summarized in Table I. Their refractive indices ranged from 1.60 to 1.74, and the EO coefficients were in the range of 10–39 pm V^{-1}. The r_{33} values were proportional to the chromophore contents when the concentration was less than 40 wt %, and the largest r_{33} values (38 and 39 pm V^{-1}) were achieved by P-40 and P-40-A at the chromophore concentration of 44.4 wt %. Generally, in the guest-host polymers and side-chain polymers when the r_{33} reached maximum the chromophore contents were about 20–30 wt %. However, in this polyurethanes system the number was up to 44.4 wt %. This phenomenon indicated that this kind of Y-type NLO polymers had the advantages of both main chain and side chain NLO polymers: the NLO chromophore parts could be evenly dispersed in the main chain; the intermolecular electrostatic interactions could be reduced greatly; the pendant NLO chromophores had good mobility in the process of poling. From the r_{33} value (35 pm V^{-1}) of the common polyurethane P0 with 69 wt % chromophore concentration, we can see that though the intermolecular electrostatic interactions could be reduced, with the chromophore concentration increased more, this interactions would be also enlarged.

The temporal stability of NLO activity in the poled polyurethane film was investigated by monitoring EO coefficient variation at the room temperature and elevated temperature. At the room temperature, the EO coefficients were maintained more than 95% of their initial values, which is due to their high T_g and hydrogen-bond interaction between the polymer chains. Long-term alignment stability of P-40 and P-40-A at 80°C was also recorded by heating the poled samples and measuring the r_{33} values at various point of extended time as shown in Figure 5. It can be seen that, after an initial decrease, the r_{33} values of P-40 and P-40-A tended to be stable. Totally, 73 and 84% of the initial values still remained respectively at 80°C for 600 h. These characteristics were an indication that the thermosetting

polyurethane material exhibits a long-term stability of NLO property even at elevated temperature, which may be attributed to polyurethane's physically crosslinked network limiting the relaxation of the orientated chromophore dipoles. Figure 4 shows that the temporal stability of P-40-A was better than P-40. That was because the introduced monomer with phenylaldehyde was assumed to form more hydrogen-bonds with urea groups and make the original physically crosslinked network denser. This crosslinking network restricted the mobility of NLO-groups more effectively, so even at elevated temperature (80°C), there still left some hydrogen bonds which played a role in maintaining the EO coefficients.

CONCLUSIONS

A series of novel Y-type polyurethanes containing different concentrations of chromophores were synthesized and the structures of the polymers were confirmed by FTIR, UV-Vis, ^{1}H-NMR spectra. These Y-type NLO polyurethanes exhibited good solubility in common organic solvents which enabled the fabrication of high quality thin films, and showed high thermal stability up to 281°C with relatively high T_g values. The EO coefficient of corona-poled polymer film was up to 39 pm V^{-1} at the wavelength of 1310 nm. In P-40-A, not only high EO coefficient could be obtained, but temporal stability at 80°C for 600 h was also achieved, which indicates that the structure of the Y-type polyurethane backbone and the hydrogen-bond between introduced phenylaldehyde and urea groups could restrict the mobility of NLO-groups more effectively.

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