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Relaxation behavior of dipolar chromophore in corona-poled vacuum-deposited polyurethane thin films

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Polyurethanes with different feed concentrations of 4-[bis (2-hydroxyethyl) amino]-$4^{4'}$-formylazobenzene as dipolar chromophore have been synthesized and characterized using GPC, IR, ^{1}H NMR, UV/Vis absorption spectroscopic technique, DSC and TGA techniques. The resulting polymeric materials possess good solubility in polar aprotic solvents, high T_g and high thermal stability. The vacuum-deposited thin films of synthesized polyurethanes were corona-poled to orient the dipolar chromophores in proper direction. To investigate the potential of these materials for practical applications, the temporal stability of aligned dipoles has been studied at room temperature as well as at elevated temperatures. The results suggest only 4.5-6 % decay of polar order at room temperature even after 2 months of poling under the conditions (5 kV, 210 °C, 30 min.). The temporal stability of dipole orientation was found to increase on decreasing the feed concentration of dipolar chromophore.

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1. Introduction

Poled polymers [1-8] with dipolar chromophore have attracted considerable interest in recent years as promising candidates for applications in high-performance elecrtooptical devices. However, additional requirements such as good thermal and temporal stability, low optical loss, etc, must be satisfied before these polymeric systems can demonstrate their potential as actual device materials. The electronic structure of polar groups in the material must allow for rectification in the polarization induced by incident electromagnetic fields and this microscopic characteristic must be carried over into the bulk properties. These polar groups responsible for the nonlinearity may be included in the materials as doped guests [9-13] or by covalent bonding [14-17] to the polymeric structure. Insufficient temporal stability of the induced polar ordering of dipolar chromophores at elevated temperatures is a major hindrance to further progress in developing polymeric electrooptical devices. The common method to suppress this reorientation is to synthesize rigid polymer backbones exhibiting high glass transition temperatures. Generally, polymer systems with increased glass transition temperatures show improved temporal stability, although the efficacy varies depending on how the dipolar chromophore is incorporated into the polymeric matrix. Since there are a number of requirements to obtain optimal properties, it is difficult to combine these in single polymeric system. On the chemical basis, this requires a very variable system that allows modifications with respect to chromophore or glass transition temperature (T_g), in a simple manner.

Keeping in view these factors, the approach that we describe here is to incorporate dipolar chromophore, namely 4-[bis (2-hydroxyethyl) amino]-$4^{4'}$-formylazobenzene, possessing high second order molecular hyperpolarizability into polyurethane backbone through covalent bonding. The synthesized polymers were characterized using gel permeation chromatographic (GPC) technique, IR, ^{1}H NMR, UV/Vis absorption spectroscopic techniques, differential scanning calorimetery (DSC) and thermogravimetric analysis (TGA) techniques. The relaxation behaviour of dipolar chromophore in vacuum-deposited corona-poled polyurethane thin films was studied using UV/Vis absorption spectroscopic technique. Attempts were then made to relate temporal stability of poling induced dipolar alignment with feed concentrations of chromophore since these relationships are important to further enhance the performance of these materials.

2. Experimental

Chromophore 4-[bis (2-hydroxyethyl) amino]-$4^{4'}$-formylazobenzene was synthesized according to the procedure reported in the literature [18]. Polyurethanes with different feed concentrations of chromophore were synthesized using the procedure given elsewhere [17]. Molecular weights of the polymers were calculated with the help of GPC technique against polystyrene standard using tetrahydrofuran (THF) as the solvent. I.R. and ^{1}H NMR spectra were recorded on BUCK SCIENTIFIC M 500 spectrometer and BRUKER DRX 300 MHz NMR spectrometer (using $CDCl_3$ solvent with tetramethylsilane as the internal reference) respectively. UV/Vis absorption spectra of these polyurethanes were recorded with the help of Shimadzu UV-2500 PC spectrophotometer attached to integrated sphere assembly (ISR-240 A). Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) of polyurethanes were performed under nitrogen atmosphere at a heating rate of 10 °C/min. on Perkin Elmer (Pyris Diamond) thermal analyzer from ambient temperature to 800 ºC. Thin films of these polymeric materials were grown on the cleaned quartz glass slides by vacuum deposition technique at a vacuum of 10^{-6} mm/Hg with the help of high vacuum coating system (NIRVAT EU-300). The thickness of these polymeric thin films was controlled with the help of thickness monitor and kept about 1000 Å. Optical band gaps for polymeric materials have been measured [7] using UV/Vis absorption spectroscopic technique.

The vacuum deposited thin films of these polyurethanes were poled under different poling conditions using optimized high potential multi-point corona poling technique to orient nonlinear optical chromophores in proper direction. Fig. 1 shows our arrangement for corona poling.

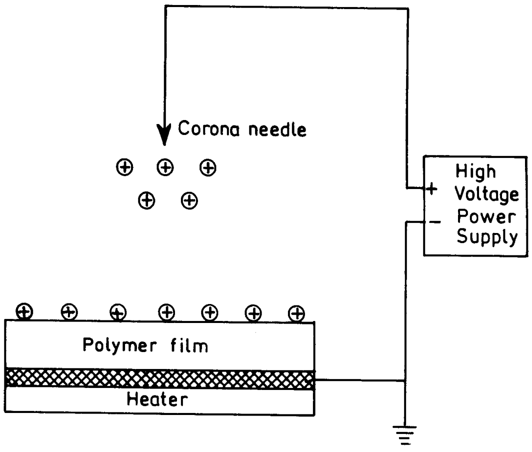
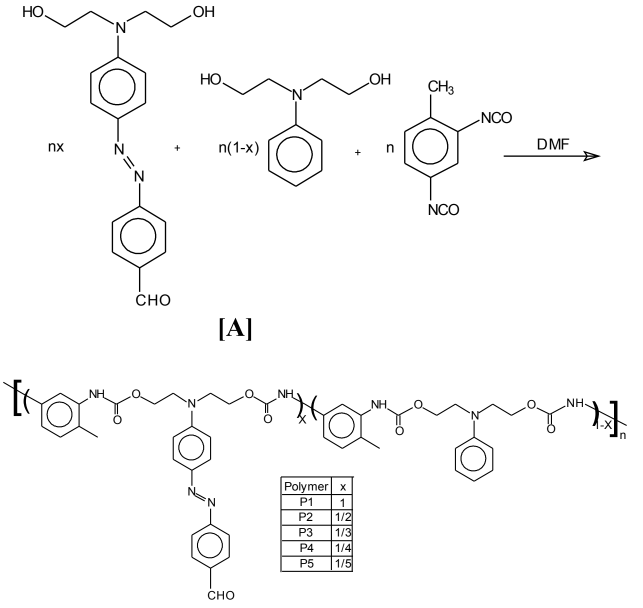


Fig. 1. Corona poling set up. + sign indicates the ionization of gas.

The polymeric thin films were heated at various temperatures depending on glass transition temperatures of these polyurethanes and then a high voltage (2-5 kV) was applied to corona needle, positioned at a short distance (1 cm) above the film surface. An electrode placed below the film was connected to earth. Corona poling creates an electric field by generating a discharge from metallic point source. As shown in Fig. 3.1, the intense field generated at the needle tip creates ions with the same polarity as the needle. These gas ions are accelerated toward the film surface and get deposited creating a uniform, high magnitude field across the thin film capable of producing the desired orientation of the dipoles within the film. The thin films were then cooled down to room temperature under the application of electric field resulting into poled polymers with noncentrosymmetric alignment of dipolar chromophores.

3. Results and discussion

Polyurethanes with different feed concentrations of 4-[bis (2-hydroxyethyl) amino]-4'-formylazobenzene **[A]** as dipolar chromophore have been synthesized according to scheme-1.



Polymer	x
P1	1
P2	1/2
P3	1/3
P4	1/4
P5	1/5

Scheme 1: Synthesis of Polyurethanes

All the polymers **P1-P5** were obtained with very high yield (80-88 %) possessing solubility in polar aprotic solvents like N, N-dimethylformamide, tetrahydrofuran, etc. The resulting polymers **P1-P5** were characterized with the help of GPC, spectral and thermal techniques.

The formation of urethane linkage due to polymerization has been indicated by IR spectra of these polymers. All these polymers **P1-P5** show characteristics intense absorption peak around 1725-1729 cm^{-1} due to carbonyl group of urethane linkage. The chemical shifts are also in agreement with the proposed polymer structures. The supporting IR and ^1H NMR data of the polymers are shown in Table 1.

Table 1. IR and ^1H NMR ($CDCl_3$) data of polyurethanes.

Polymer	δ (ppm)	IR frequencies (cm^{-1})
P1	2.22 (br, 3H, Ph CH_3), 3.63 (br, 4H, N$\underline{CH_2}$), 4.38 (br, 4H, O$\underline{CH_2}$), 6.72-6.78 (m, 4H, Ar H), 7.64 (s, 1H, Ar H), 7.83-7.92 (m, 6H, Ar H), 8.34 (br, 2H, N$\underline{H}$COO), 10.18 (s, 1H, C$\underline{H}$O).	3346 (br, N-H str.), 1725 (ure. C=O str.), 1690 (ald.C=O str.), 1610 (Ar. C=C str.).
P2	2.24 (br, Ph CH_3), 3.66 (br, N$\underline{CH_2}$), 4.42 (br, O $\underline{CH_2}$), 6.75-6.81 (m, Ar H), 7.63 (s, Ar H), 7.78-7.89 (m, Ar H), 8.36 (br, N$\underline{H}$COO), 10.22 (s, C$\underline{H}$O).	3350 (br, N-H str.), 1728 (ure. C=O str.), 1692 (ald.C=O str.), 1615 (Ar. C=C str.).
P3	2.17 (br, Ph CH_3), 3.60 (br, N$\underline{CH_2}$), 4.43 (br, O$\underline{CH_2}$), 6.73-6.79 (m, Ar H), 7.65 (s, Ar H), 7.77-7.82 (m, Ar H), 8.35 (br, N$\underline{H}$COO), 10.15 (s, C$\underline{H}$O).	3342 (br, N-H str.), 1726 (ure. C=O str.), 1689 (ald.C=O str.), 1598 (Ar. C=C str.).
P4	2.18 (br, Ph CH_3), 3.63 (br, N$\underline{CH_2}$), 4.40 (br, O$\underline{CH_2}$), 6.76-6.80 (m, Ar H), 7.62 (s, Ar H), 7.75-7.87 (m, Ar H), 8.29 (br, N$\underline{H}$COO), 10.18 (s, C$\underline{H}$O).	3353 (br, N-H str.), 1729 (ure. C=O str.), 1690 (ald.C=O str.), 1598 (Ar. C=C str.).
P5	2.20 (br, Ph CH_3), 3.60 (br, N$\underline{CH_2}$), 4.38 (br, O$\underline{CH_2}$), 6.72-6.77 (m, Ar H), 7.67 (s, Ar H), 7.80-791 (m, Ar H), 8.32 (br, N$\underline{H}$COO), 10.20 (s, C$\underline{H}$O).	3358 (br, N-H str.), 1729 (ure. C=O str.), 1688 (ald.C=O str.), 1600 (Ar. C=C str.).

The weight-average molecular weights, M_w of the resulting polymers **P1-P5** calculated against polystyrene standard using THF as the solvent were found in the range 5180-6070 (M_w/M_n = 1.80-1.86) [Table 2].

Table 2. Physicochemical properties of polyurethanes

Polymer	X	Yield (%)	Weight-Average Molecular Wt. (M_w)	Polydispersity index (PDI)	T_g [a] (°C)	T_d [b] (°C)	λ_{max} (nm)		Band gap (eV)
							THF	Thin Films	
P1	1	83	5180	1.86	-	290	468	438	2.58
P2	1/2	84	5290	1.85	224	300	474	458	2.63
P3	1/3	80	5630	1.85	228	308	460	447	2.39
P4	1/4	88	5760	1.82	234	309	466	452	2.43
P5	1/5	80	6070	1.80	237	320	476	456	2.65

[a] Glass transition temperature determined by DSC
[b] Decomposition temperature determined by TGA

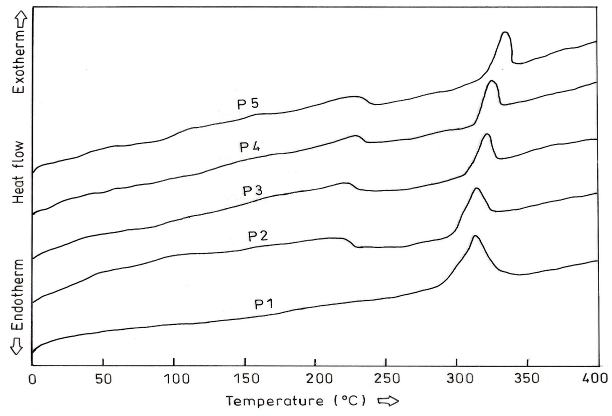


Fig. 2. DSC curves of polyurethanes P1-P5

DSC traces of the polymers **P1**-**P5** do not show any indication of the melting process (Fig. 2), suggesting non-crystalline nature of these materials. These polymers have been found to possess their glass transition temperatures in the range 224-237 °C (Table 2). Generally, polyurethanes possess moderate value of glass transition temperatures. However, using copolymerization, high T_g polyurethanes with dipolar chromophores have been reported in the literature [16, 17]. The glass transition temperature of **P2** is 224 °C and increased to 237 °C for **P5** with decrease of chromophore feed concentration. TGA thermograms of these polyurethanes **P1**-**P5** with **[A]** as dipolar chromophore are shown in Fig. 3. It was observed that for a particular temperature range, percentage weight loss goes on increasing from **P1** to **P5** with decrease of chromophore feed concentration. Comparisons of DSC and TG results suggest that the decomposition temperatures of these polyurethanes are higher than corresponding T_g values (Table 2).

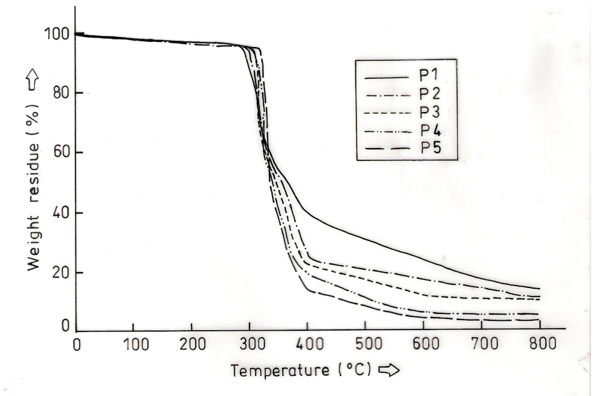


*Fig. 3. TGA curves of polyurethanes **P1-P5.***

The UV/Vis absorption maxima of polymers in THF as well as thin films are shown in Table 2. The direct optical band gaps of polyurethanes were found in the range 2.39-2.65 eV (Table 2). Thin flims of polyurethanes were poled under different poling voltages as well as poling temperatures. Fig. 4, showing temperature dependence of order parameter, indicates that order parameter increases with temperatures with maximum value near T_g. Variation of order parameter with voltage is shown in Fig. 5.

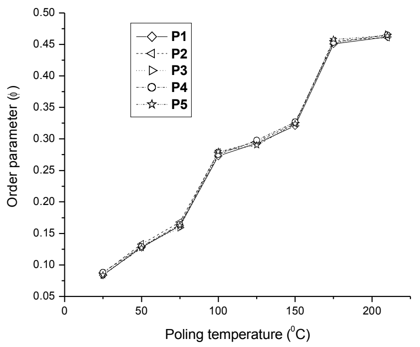


Fig. 4. Variation of order parameter of polyurethanes with temperature under poling conditions (5 kV, 30 min.)

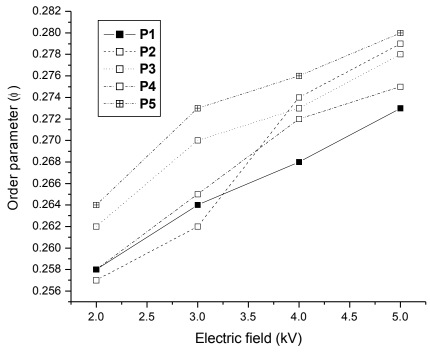


Fig. 5. Variation of order parameter of polyurethanes with voltage under poling conditions (100 °C, 30 min.)

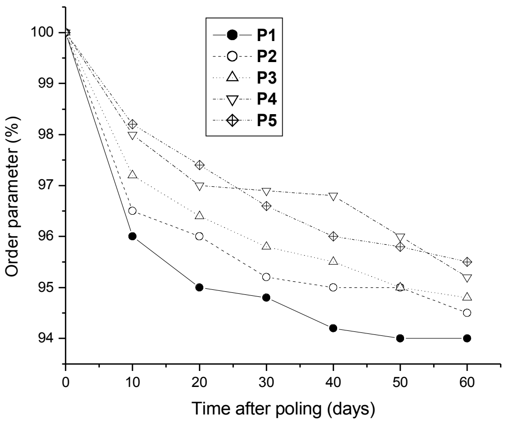


Fig. 6. Relaxation behaviour of aligned dipoles in polyurethane thin films at room temperature after poling at (5 kV, 210 °C, 30 min.)

UV/Vis measurement is also one of the techniques capable of evaluating the stability of aligned dipoles. The motivation to prepare these polyurethanes was the expectation that these may exhibit a high temporal stability of dipole orientation, which is one of the most important requirements for the polymeric materials to possess practical applications in electro optic devices. Relaxation behaviour of the aligned dipoles at room temperature as well as at high temperatures has been investigated by monitoring UV/Vis absorption spectra at different time-intervals. Fig. 6 dictates relaxation behaviour of dipoles at room temperature after poling under the conditions (5 kV, 210 °C, 30 min.). The results suggest only 4.5-6 % decay of polar order at room temperature even after 2 months of poling.

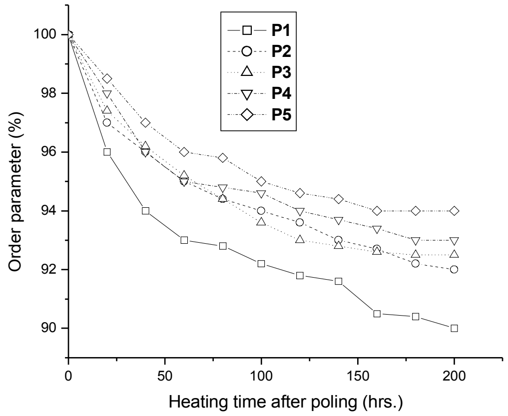


Fig. 7. Relaxation behaviour of aligned dipoles in polyurethane thin films at 50 °C after poling at (5 kV, 210 °C, 30 min.)

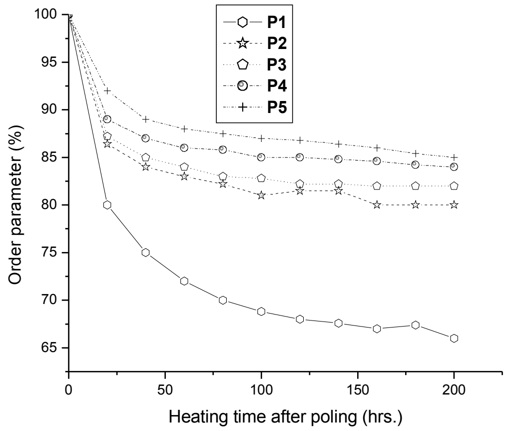


Fig. 8. Relaxation behaviour of aligned dipoles in polyurethane thin films at 100 °C after poling at (5 kV, 210 °C, 30 min.)

To probe the temporal stability of dipole orientation at high temperatures, the relaxation behaviour of dipole orientation was studied at 50 °C as well as 100 °C. At 50 °C, the polar order decayed by 1.5-4 % when subjected to heat treatment for 20 hr. and decayed by 6-10 % after heat treatment for 200 hr. (Fig. 7). Moreover, the percentage-decayed amount for the polymer **P5** was found to be comparatively small, suggesting more temporal stability of dipole orientation. At 100 °C, the polymeric thin films retained 66-85 % of order parameter when the poled samples were subjected to heat treatment for over 200 hr. (Fig. 8). The decayed amount of polar order was found to decrease from polyurethane **P1** to **P5**, which is obvious. The decayed amounts of order parameter at 100 °C are more as compared to 50 °C because at high temperature these aligned chromophores get more freedom to move in their original random orientation. The temporal stability of aligned dipoles increased on decreasing the feed concentrations of chromophore. However, the nonlinear optical properties are expected to decrease with decreasing dipolar chromophore concentration. Therefore, these polyurethane systems provide variable system that allows modifications with respect to chromophore feed concentration to obtain optimal properties.

4. Conclusions

The synthesized polyurethanes were obtained with very high yield possessing good solubility in polar aprotic solvents, high glass transition temperatures and good thermal stabilities. The resulting poled polyurethane thin films show negligible decay of polar order at room temperature. Even at elevated temperatures, these polyurethane films possess good temporal stability of aligned dipoles suggesting their potential for electrooptical devices operating at high temperatures. It was observed that stability of dipolar alignment increased on decreasing feed concentration of chromophore.

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