

Vacuum-deposited poled polyimide thin films with high poling stability of dipolar chromophores

S. ARORA, S. KUMAR^{a,*}

Department of Chemistry, Kurukshetra University, Kurukshetra - 136 119, India

^aDepartment of Chemistry, S.D. College, Ambala Cantt - 133 001, India

Polyimides with high glass transition temperatures were prepared by reaction of various diaminopyrazole derivatives with 4, 4'-(hexafluoroisopropylidene)diphthalic anhydride and characterized by spectral and thermal techniques. Glass transition temperatures of resulting polyimides in the range of 193-216 °C were obtained. Vacuum-deposited thin films of polyimides were corona poled under different poling conditions and analyzed for poling stability of aligned dipolar chromophore. At room temperature, polar order remained stable for all the polymers with only 1-2 % decay even after 30 days of poling under the conditions (5 kV, 185 °C, 30 min.). It was further observed that after 200 h, poled order stabilized in the range 81-92 % and 69-85 % of initial value when polymeric thin films were heated at 80 °C and 90 °C respectively.

(Received October 15, 2010; accepted November 29, 2010)

Keywords: Polyimide, Thin film, Corona poling, Poling stability, Dipolar Chromophore

1. Introduction

Poled polymeric thin films [1-10] with dipolar chromophore have been identified as strong candidates for use in electro-optic devices. However, fabrication of efficient electro-optic devices is a challenging task because such devices need to meet stringent requirements. Although, extensive efforts have been focused on this field, problems, such as relaxation of dipole orientation induced by electrical field and optical losses still exist. For practical application of poled polymeric materials, high thermal stability of both polymer and dipolar chromophore as well as the induced polar order are required. Different design strategies have been proposed by the researchers to synthesize the polymers with enhanced aligned dipoles. A common method to suppress reorientation is to synthesize polymers with rigid polymer backbone exhibiting high glass transition temperature (T_g) such as polyimides [11-18]. Polyimides with high glass transition temperatures are expected to show excellent poling stability of induced dipoles. Another attractive feature of polyimides is their high thermal stability which enables them to survive at elevated temperatures during fabrication of, and operation in, integrated optoelectronic devices.

In view of this, we have synthesized some novel polyimides using chemical imidization of diaminopyrazole derivatives with 4, 4'-(hexafluoroisopropylidene)diphthalic anhydride. Vacuum-deposited thin films of resulting polyimides were poled using corona poling technique to study poling stability of induced dipoles.

2. Experimental

2.1 Chemicals

N-Methylpyrrolidine (NMP), acetic anhydride and pyridine were purified by distillation. 4-chloroaniline, 4-fluoroaniline, 4-bromoaniline, 4-cyanoaniline and 4-

nitroaniline were purchased from Across Organics Co.; malonodinitrile, hydrazine hydrate and sodium acetate were purchased from Rankem and 4, 4'-(hexafluoroisopropylidene) diphthalic anhydride was purchased from Aldrich Chemical Co. All the chemicals were used as received unless otherwise stated.

2.2 Measurements

I.R. spectra were recorded with the help of BUCK SCIENTIFIC M 500 spectrometer. ¹H NMR spectra were recorded on BRUKER DRX 300 MHz NMR spectrometer using TMS (tetramethylsilane) as the internal reference. UV/Vis absorption spectra of the polymers were recorded with the help of Shimadzu UV-2500 PC spectrophotometer attached to integrated sphere assembly (ISR-240 A). Molecular weights of these polyimides were calculated by GPC technique against polystyrene standard using THF as the solvent. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were performed by Perkin Elmer (Pyris Diamond) thermal analyzer at the heating rate of 10 °C/min under nitrogen atmosphere using alumina as the reference material. Thin films (thickness ~1000 Å) of these polyimides were grown on the cleaned quartz glass slides at a vacuum of 10⁻⁶ mm/Hg with the help of high vacuum coating system (NIRVAT EU-300) attached with thickness monitor. Poling of these vacuum deposited thin films was carried out under different poling conditions using optimized high potential multi-point corona poling technique.

2.3 Synthesis [19] of 3, 5-diamino-4- (4'-fluorophenyldiazo) pyrazole C1 (Scheme-1)

The suspension of 2.2 g (20 mmol) of 4-fluoroaniline in a mixture of 50 ml of water and 7 ml of HCl was cooled to 0 °C. The cooled solution of 1.3 g (20 mmol) of NaNO₂

in 10 ml of distilled water was added dropwise with continuous stirring to the suspension of 4-fluoroaniline. The temperature was not allowed to rise above 2 °C. The suspension was further stirred for about 30 minutes to get clear solution. The solution was added portion wise to a stirred mixture obtained by dissolving 1.4 g (20 mmol) of malonodinitrile and 2.0 g (25 mmol) of CH₃COONa in 50 ml ice cooled water. The resulting compound was filtered off, washed with water and dried. The suspension of 1.4 g (10 mmol) of the above hydrazone, 1.0 ml (20 mmol) of hydrazine hydrate in 40 ml of ethanol was heated for 30 minutes. After that, the reaction mixture was allowed to cool down at room temperature and acidified with acetic acid. The solvent was evaporated at reduced temperature and the resulting solid was mixed with 100 ml water,

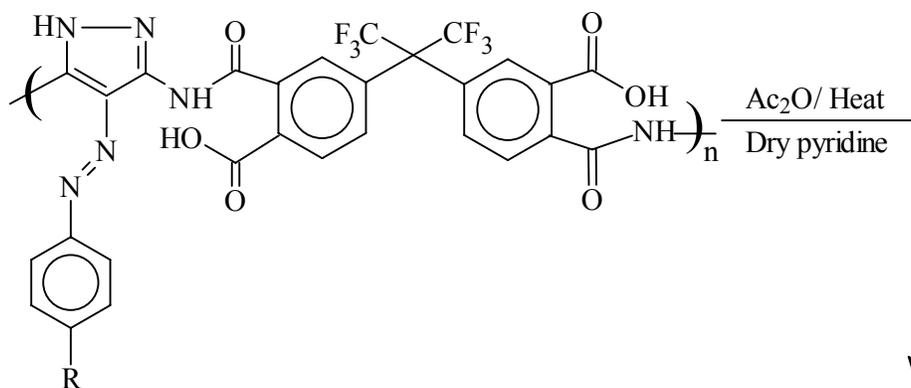
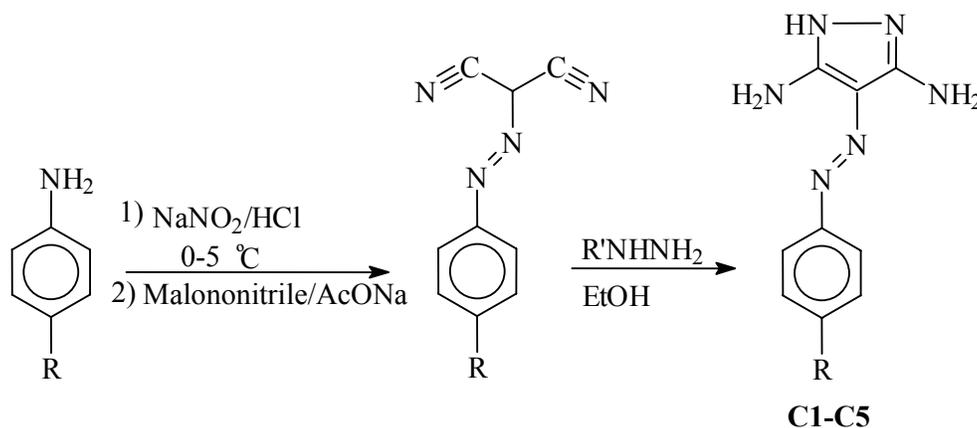
filtered off, and dried. The resulting crude product **C1** was further purified by recrystallization from ethanol.

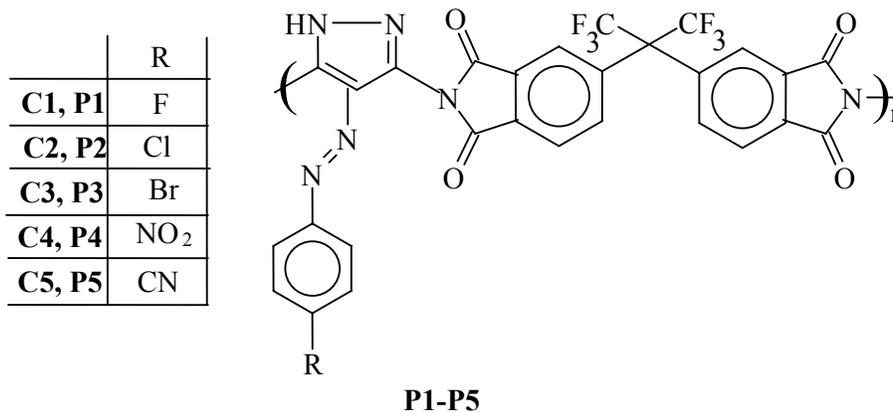
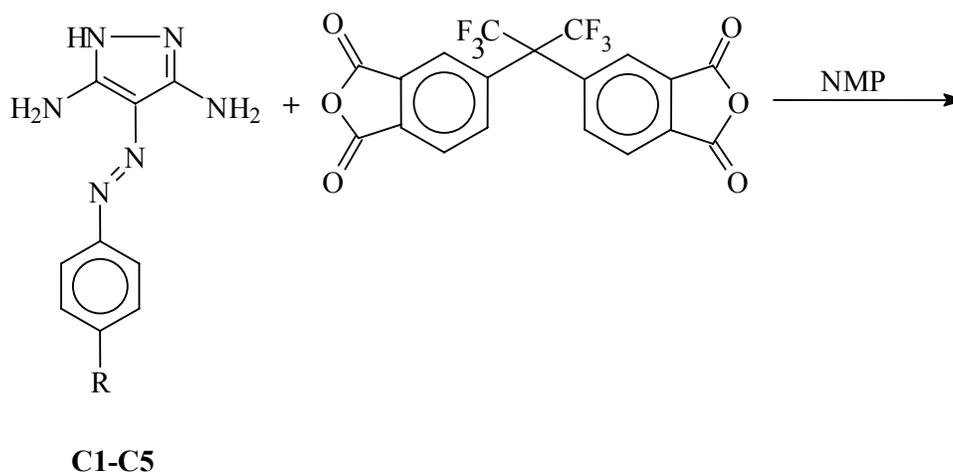
Yield: 2.01 g (68 %), Melting point: 271-273 °C, Literature melting point [19]: 272-275 °C

¹H NMR (CDCl₃): δ (ppm)= 3.48 (s, 1H, NH), 6.25 (bs, 4H, NH₂), 7.38 (d, 2H, Ar H), 7.98 (d, 2H, Ar H).

IR (KBr, cm⁻¹): 3420, 3315 & 3190 (NH₂ & NH str.), 1608 (C=C str.).

On the same lines, other chromophores 3,5-diamino-4-(4'-chlorophenyldiazo) pyrazole **C2**, 3,5-diamino-4-(4'-bromophenyldiazo) pyrazole **C3**, 3,5-diamino-4-(4'-nitrophenyldiazo) pyrazole **C4** and 3,5-diamino-4-(4'-cyanophenyldiazo) pyrazole **C5** were prepared by treating 4-chloroaniline, 4-bromoaniline, 4-nitroaniline and 4-aminobenzonitrile respectively in place of 4-fluoroaniline with other reagents.





Scheme 1. Synthesis of Polyimides.

3,5-diamino-4-(4'-chlorophenyldiazo) pyrazole C2

Yield: 2.03 g (65 %), Melting point: 282-284 °C,
Literature melting point [20,21]: 283-285 °C

¹H NMR (CDCl₃): δ (ppm)= 3.52 (s, 1H, NH), 6.35 (bs, 4H, NH₂), 7.40-7.53 (m, 4H, Ar H).

IR (KBr, cm⁻¹): 3430, 3328 & 3196 (NH₂ & NH str.), 1604 (C=C str.).

3,5-diamino-4-(4'-bromophenyldiazo) pyrazole C3

Yield: 2.28 g (64 %), Melting point: 293-295 °C,
Literature melting point [22] : 294-295 °C

¹H NMR (CDCl₃): δ (ppm)= 3.45 (s, 1H, NH), 6.29 (bs, 4H, NH₂), 7.36-7.50 (m, 4H, Ar H).

IR (KBr, cm⁻¹): 3405, 3313 & 3208 (NH₂ & NH str.), 1610 (C=C str.).

3,5-diamino-4-(4'-nitrophenyldiazo) pyrazole C4

Yield: 2.26 g (70 %), Melting point: 262-263 °C,
Literature melting point [23]: 263-264 °C

¹H NMR (CDCl₃): δ (ppm)= 3.58 (s, 1H, NH), 6.45 (bs, 4H, NH₂), 7.42 (d, 2H, Ar H), 8.12 (d, 2H, Ar H).

IR (KBr, cm⁻¹): 3416, 3308 & 3190 (NH₂ & NH str.), 1600 (C=C str.), 1535 & 1358 (N=O str.).

3,5-diamino-4-(4'-cyanophenyldiazo) pyrazole C5

Yield: 2.18 g (72 %), Melting point: 266-268 °C,
Literature melting point [20, 21]: 268-270 °C

¹H NMR (CDCl₃): δ (ppm)= 3.48 (s, 1H, NH), 6.48 (bs, 4H, NH₂), 7.45 (d, 2H, Ar H), 8.23 (d, 2H, Ar H).

IR (KBr, cm⁻¹): 3422, 3310 & 3195 (NH₂ & NH str.), 2225 (C≡N str.), 1597 (C=C str.).

2.4 Synthesis of Polyimide P1 (Scheme-1)

1.1 g (5 mmol) of **C1** was dissolved in 25 ml of anhydrous NMP followed by the addition of 2.3 g (5 mmol) of 4, 4'-(hexafluoroisopropylidene) diphthalic anhydride at 0 °C under nitrogen atmosphere. After stirring for 1 hr. at 0 °C and then at room temperature for 24 hr., resulting highly viscous poly (amic acid) was imidized by adding a mixture of 10 ml of acetic anhydride and 5 ml of dry pyridine. The mixture was stirred for 10 hr. at room temperature and finally at 60-70 °C for additional 5 hr. The resulting polyimide solution was then precipitated into deionized water with vigorous stirring

and filtered to give polymer **P1**. The polymer **P1** was further purified by repeated dissolution in NMP and precipitation into water.

On the same lines, polymers **P2-P5** were prepared using the same procedure by treating **C2-C5** in place of **C1** with other reagents.

Polyimide	P1	P2	P3	P4	P5
Yield	1.95 g (62 %)	1.86 g (58 %)	2.24 g (65 %)	2.06 g (63 %)	1.93 g (60 %)

3. Results and discussion

Polyimides **P1-P5** have been synthesized using chemical imidization according to scheme-1. We have chosen 4, 4'-(hexafluoroisopropylidene)diphthalic anhydride as the starting material since the resulting fully imidized polymeric materials are expected to be soluble in a number of common organic solvents.

Table 1. Molecular weights and description of UV/Vis Data.

Polymer	Weight-Average Molecular Wt. (M _w)	Polydispersity index (PDI)	λ_{\max} (nm) Thin Films
P1	15700	1.64	380
P2	16090	1.62	376
P3	16180	1.63	370
P4	18200	1.52	390
P5	18780	1.50	396

All the polyimides, we synthesized, have good solubility in many common organic solvents, such as THF, DMF, DMAc and NMP, due to flexible $-\text{CF}_3$ groups in these polymers. It indicates that incorporation of fluorinated group into the polyimide backbone enhances its solubility. Because of the good solubility of the polyimides in THF, the molecular weight can be measured by using gel permeation chromatography. The weight-average molecular weights, M_w of these polyimides **P1-P5** as determined by GPC using THF as the eluent are presented in Table 1.

IR and ^1H NMR studies: The structures of polyimides were confirmed by IR and ^1H NMR spectroscopy. The supporting IR and ^1H NMR data of polyimides **P1-P5** are shown in Table 2. IR spectrum of polyimide **P1** showed the characteristic absorption peaks around 1780 and 1725 cm^{-1} indicating carbonyl groups in the imide linkages [24]. The absorption bands due to C-F

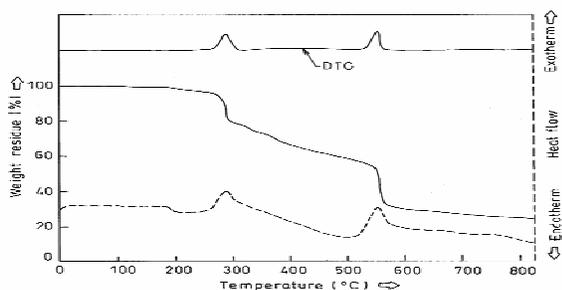
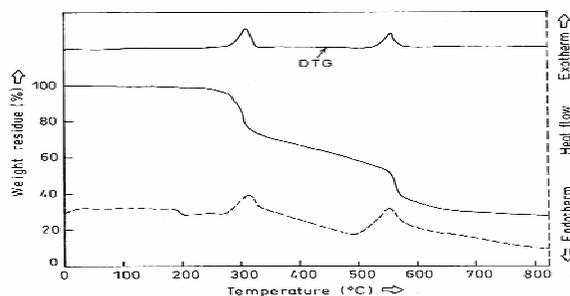
str. appeared at 1265 and 1218 cm^{-1} . The broad band appeared at 3280 cm^{-1} is ascribed to N-H str. of pyrazole ring. All other polymers **P2-P5** also showed similar peaks due to imide linkages and C-F str. In addition, IR spectrum of polymer **P4** shows absorption bands at 1528 and 1338 cm^{-1} due to nitro group and polymer **P5** exhibits absorption band at 2215 cm^{-1} suggesting cyano group. ^1H NMR spectra of various polymers show peaks around 3.42-3.62 ppm, which correspond to the proton of pyrazole ring. All the polymers possess peaks within the range 6.92-7.73 ppm due to aromatic protons.

Thermal Studies: DSC, TG and DTG thermograms of polyimides **P1-P5** were obtained in nitrogen atmosphere from ambient temperature to 800 °C at a heating rate of 10 °C/min. and are shown in Figs. 1-3 (for illustration, thermograms of only **P1**, **P3** and **P5** are shown). The glass transition temperatures of the polymers **P1-P5** were measured using DSC thermograms and are presented in Table 3. All the polyimides possess high glass transition temperatures within the range 193-216 °C. No crystalline melting transitions were detected for all of the polymers indicating that polymers are all amorphous. In the DSC thermograms of these polyimides, two exothermic peaks were observed. The 1st exothermic peak was observed at different temperatures for different polyimides whereas the 2nd peak was observed at almost same temperature. The 1st exothermic peak (maxima) occurring in the range 290-330 °C in DSC scans of all these polyimides shows the decomposition of azo chromophores. The initiation, maximum and final peak temperatures for these exotherms are presented in Table 3. TGA thermograms indicate that polymers **P1-P5** possess decomposition temperatures (corresponding to 95 % weight loss) around 275-310 °C.

Table 2. IR and ^1H NMR (CDCl_3) data of polyimides.

Polymer	δ (ppm)	IR frequencies (cm^{-1})
P1	3.42 (s, 1H, NH), 7.18 (d, 2H, Ar H), 7.42 (d, 2H, Ar H), 7.51 (d, 2H, Ar H), 7.60 (d, 2H, Ar H), 7.68 (s, 1H, Ar H).	3280 (br, N-H str.), 1780 & 1725 (C=O str.), 1605 (Ar. C=C str.), 1265 & 1218 (C-F str.).
P2	3.56 (s, 1H, NH), 6.92-6.98 (m, 4H, Ar H), 7.53 (d, 2H, Ar H), 7.61 (d, 2H, Ar H), 7.72 (s, 1H, Ar H).	3285 (br, N-H str.), 1778 & 1728 (C=O str.), 1612 (Ar. C=C str.), 1260 & 1214 (C-F str.).
P3	3.48 (s, 1H, NH), 6.90-6.96 (m, 4H, Ar H), 7.50 (d, 2H, Ar H), 7.62 (d, 2H, Ar H), 7.70 (s, 1H, Ar H).	3294 (br, N-H str.), 1784 & 1722 (C=O str.), 1598 (Ar. C=C str.), 1264 & 1215 (C-F str.).
P4	3.62 (s, 1H, NH), 7.26 (d, 2H, Ar H), 7.48-7.57 (m, 4H, Ar H), 7.64 (d, 2H, Ar H), 7.73 (s, 1H, Ar H).	3282 (br, N-H str.), 1776 & 1729 (C=O str.), 1610 (Ar. C=C str.), 1528 & 1338 (N=O str.), 1262 & 1215 (C-F str.).
P5	3.46 (s, 1H, NH), 7.18 (d, 2H, Ar H), 7.50-7.58 (m, 4H, Ar H), 7.60 (d, 2H, Ar H), 7.69 (s, 1H, Ar H).	3290 (br, N-H str.), 2215 (C \equiv N str.), 1775 & 1726 (C=O str.), 1608 (Ar. C=C str.), 1265 & 1218 (C-F str.).

The peak maxima (DTG curve) corresponding to Ist maximum weight loss for these polyimides **P1-P5** occurs around 290, 295, 310, 322 and 330 $^{\circ}\text{C}$ respectively, further supporting the DSC data (Table 3). The 2nd exothermic peak around 558 $^{\circ}\text{C}$, which is almost at the same position for all the polyimides, shows decomposition of polyimide backbone. TG thermograms, showing 2nd weight loss around 558 $^{\circ}\text{C}$, again support DSC results. Table 4 shows %age weight loss for various temperature ranges.

Fig. 1. DSC, TGA and DTG Thermograms of Polyimide **P1**.Fig. 2. DSC, TGA and DTG Thermograms of Polyimide **P3**.

Optical studies: The polymeric thin films of these polyimides **P1-P5** exhibited a typical absorption due to azo chromophore, with maxima at 380, 376, 370, 390 and 396 nm respectively (Table 1). After the molecular dipoles were aligned along the direction of the electric field by corona poling, the maximum absorbance was reduced. Poling efficiency has been determined in terms of order parameter defined by

$$\phi = 1 - A_{\perp} / A_0$$

where A_0 and A_{\perp} are the absorbances of the polymer film before and after corona poling.

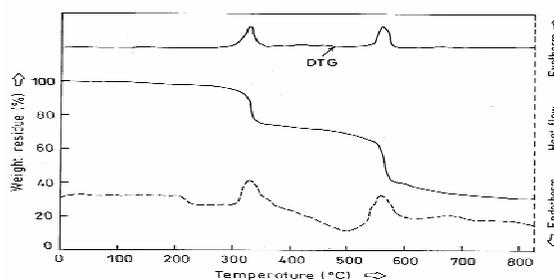
Fig. 3. DSC, TGA and DTG Thermograms of Polyimide **P5**.

Table 3. Description of DSC data.

Polymer	T _g (°C)	Description of exothermic peaks					
		1 st Peak			2 nd Peak		
		Initiation	Peak Temp. (°C)	Termination	Initiation	Peak Temp. (°C)	Termination
P1	193	260	290	335	510	555	580
P2	196	265	295	340	525	558	585
P3	198	275	310	355	500	555	615
P4	213	280	322	365	530	560	610
P5	216	305	330	365	510	560	600

The order parameters of these polymers were determined for different poling conditions. The variation of order parameters with poling temperatures and poling voltages are shown in Fig. 4 and 5 respectively. Order parameter values were found to increase with poling temperature as well as poling voltages. The maximum values of order parameter for these polyimides were estimated to be 0.198-0.217 when poled under the electric field of 5 kV applied to corona needle for 30 min. at 185 °C.

We have studied the temporal stabilities of aligned dipoles by monitoring the UV/Vis absorption spectra of poled polymeric thin films at different time intervals. At room temperature, the polar order remained stable for all the polymers with only 1-2 % decay even after 30 days of poling at (5 kV, 185 °C, 30 min.). To probe the long-term stability of the aligned chromophores in the polymeric matrix, we monitored the temporal stability of the polar order at elevated temperatures. Polyimides **P4** and **P5**, which have higher T_g, showed better stability than polymers **P1-P3**.

Table 4. Description of TG Data.

Polymer	DTG Maxima (°C)	Stage	Temp (°C)	Weight (%)	T _d (°C)
P1	290, 555	First	20-	2	275
		Second	200	32	
		Third	200-	36	
		Fourth	400	6	
			400-600 600-800		
P2	295, 558	First	20-	2	278
		Second	200	29	
		Third	200-	35	
		Fourth	400	9	
			400-600 600-800		
P3	310, 555	First	20-	1	280
		Second	200	32	

		Third Fourth	200-400 400-600 600-800	32 7	
P4	322, 560	First Second Third Fourth	20-200 200-400 400-600 600-800	2 31 29 7	300
P5	330, 560	First Second Third Fourth	20-200 200-400 400-600 600-800	2 25 33 9	310

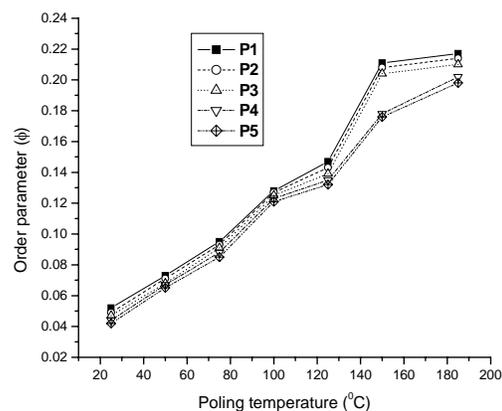


Fig. 4. Variation of order parameter of polymers with poling temperature under poling conditions (5 kV, 30 min.).

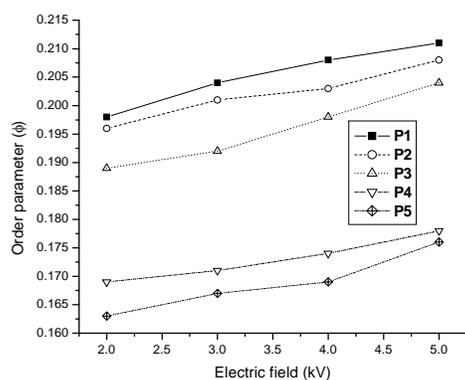


Fig. 5. Variation of order parameter of polymers with voltage under poling conditions (150 °C, 30 min.).

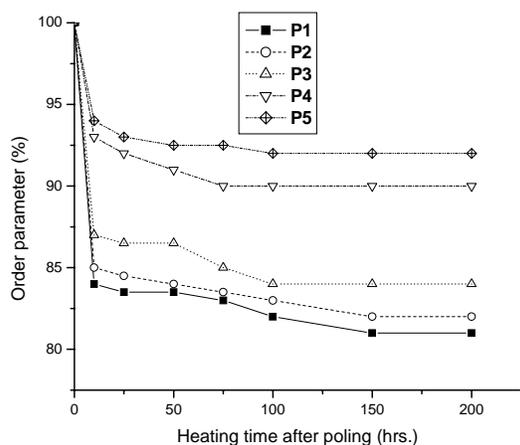


Fig. 6. Relaxation behaviour of aligned dipoles in polymeric thin films at 80 °C after poling at (5 kV, 185 °C, 30 min.).

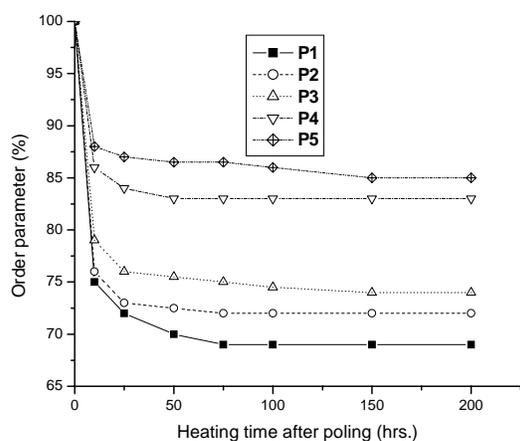


Fig. 7. Relaxation behaviour of aligned dipoles in polymeric thin films at 90 °C after poling at (5 kV, 185 °C, 30 min.).

Under the same poling conditions; when the polar order of **P5** was monitored at 80 °C for 200 h, the decay was noticeable at the initial stages and then stabilized at 92 % of its initial value (Fig. 6). Polymer **P4** also retained 90 % of the initial polar order when treated for the same conditions. Polymers **P3**, **P2** and **P1** showed similar relaxation behaviour, since these polymers possess close glass transition temperatures. Their polar order stabilized at 84 %, 82 % and 81 % of their initial value, respectively, after 200 hrs. Yu *et al.* [25] reported functionalized aromatic polyimide with a pendent nonlinear optical chromophore, which retained 60 % of the initial nonlinearity after 170 hrs. at 150 °C. Jeon *et al.* [26] have reported polyimides retaining 67-89 % of the NLO response after 24 hrs. at 80 °C. We have also investigated the temporal stabilities of aligned chromophores at 90 °C (Fig. 7). The relaxation rate of the poled NLO chromophores was found to increase in the order of **P5**<**P4**<**P3**<**P2**<**P1**. After 200 h at 90 °C, polyimides **P1-P5** retained 69 %, 72 %, 74 %, 83 % and 85 % of their original order parameter values respectively. The glass transition values (Table 3) of these polyimides explain the observed order of temporal stabilities. These results indicate that these materials are stable enough to withstand the working temperature for long periods.

4. Conclusions

Polyimides with diamino pyrazole derivatives as dipolar chromophore have been synthesized and characterized by thermal and spectral techniques. Polymers exhibit high thermal stability as well as high glass transition temperatures (193-216 °C). The resulting polymers have been found to possess good poling stability of aligned dipoles at room temperature as well as at elevated temperatures. Therefore, these polymers may be promising candidates for the construction of electro-optic devices.

References

- [1] C. Weder, P. Neuenchwander, U.W. Suter, P. Pretre, P. Kaatz, P. Gunter, *Macromolecules*. **28**, 2377 (1995).
- [2] N. Nemoto, F. Miyata, Y. Nagase, J. Abe, M. Hasegawa, Y. Shirai, *Macromolecules*. **29**, 2365 (1996).
- [3] O. Ahumada, C. Weder, P. Neuenchwander, U. W. Suter, S. Herminghaus, *Macromolecules*. **30**, 3256 (1997).
- [4] R. Dworezak, W.M.F. Fabian, D. Kieslinger, H. Junek, *Dyes and Pigments*. **34**, 13 (1997).
- [5] D. W. Kim, S. I. Hong, S.Y. Park, N. Kim, *Bull. Kor. Chem. Soc.* **18**, 198 (1997).
- [6] Y. H. Hwang, J. L. Kim, S.Y. Park, S. I. Hong, *Polymer Bulletin*. **42**, 175 (1999).
- [7] M. Li, E. Zhou, X. Zhao, J. Xu, *Polymer Bulletin*. **42**, 575 (1999).
- [8] N. Kalra, F. Chand, S. C. Mishra, D. R. Vij, D. K.

- Chaturvedi, S. Kumar, S. Arora, S. C. K. Misra, *Journal of Nonlinear Optical Physics & Materials*. **13**, 65 (2004).
- [9] S. Arora, S. Kumar, *Optoelectron. Adv. Mater. – Rapid Commu.* **2**, 360 (2008).
- [10] S. Arora, S. Kumar, *Optoelectron. Adv. Mater. – Rapid Commu.* **3**, 1359 (2009).
- [11] E. Gubbelmans, T. Verbiest, M. Van Beylen, A. Persoons, C. Samyn, *Polymer*. **43**, 1581 (2002).
- [12] S. Li, Z. Yang, P. Wang, H. Kang, W. Wu, C. Ye, M. Yang, Y. Yang, *Macromolecules*. **35**, 4314 (2002).
- [13] Y. Suzuki, K. Komatsu, T. Kaino, Y. Honda, *Optical Materials*. **21**, 521 (2003).
- [14] J. Luo, M. Haller, H. Li, H.-Z. Tang, A. K.-Y. Jen, K. Jakka, C.-H. Chou, C.-F. Shu, *Macromolecules*. **37**, 248 (2004).
- [15] J. Y. Do, S. K. Park, J.-J. Ju, S. Park, M.-H. Lee, *Optical Materials*. **26**, 223 (2004).
- [16] J. Y. Lee, C. S. Baek, E. J. Park, *European Polymer Journal*. **41**, 2107 (2005).
- [17] F. Qiu, Y. Cao, H. Xu, Y. Jiang, Y. Zhou, J. Liu, *Dyes and Pigments*. **75**, 454 (2007).
- [18] F. Qiu, H. Xu, Y. Cao, Y. Jiang, Y. Zhou, J. Liu, X. Zhang, *Materials Characterization*. **58**, 275 (2007).
- [19] V. Krystof, P. Cankar, I. Frysova, J. Slouka, G. Kontopidis, P. Dzubak, M. Hajduch, J. Srovnal, W. F. de Azevedo Jr., M. Orsag, M. Paprskarvo, J. Rolcik, A. Latr, P.M. Fischer, M. Strnad, *J. Med. Chem.* **49**, 6500 (2006).
- [20] J. Wrubel, R. Mayer, *Z. Chem.* **24**, 256 (1984).
- [21] H.A. Elfahham, G. E. H. Elgemeie, Y. R. Ibraheim, M. H. Elnagdi, *Liebigs Ann. Chem.* 819 (1988).
- [22] Z. Kandeel, T. Fuchigami, T. Nonaka, *J. Chem. Soc. Perkin Trans.* **1**, 1379 (1986).
- [23] G. H. Elgemeie, S. A. Sood, *J. Chem. Res. Synop.* **10**, 439 (2001).
- [24] H. Y. Woo, H.-K. Shim, K.-S. Lee, M.-Y. Jeong, T.-K. Lim, *Chem. Mater.* **11**, 218 (1999).
- [25] D. Yu, L. Yu, *Macromolecules*. **27**, 6718 (1994).
- [26] B.-J. Jeon, S. W. Cha, M.-Y. Jeong, T. K. Limand, J.-II Jin, *J. Mater. Chem.* **12**, 546 (2002).

*Corresponding author: drsushilgoswami@yahoo.com