Electric Poling and Relaxation Studies of PMMA Thin Films Containing Diaminopyrazole Derivatives as Dipolar Chromophores

Sanjiv Arora[1] and Sushil Kumar[2,*]

[1]*Department of Chemistry, Kurukshetra University, Kurukshetra – 136 119, India*

[2]*Department of Chemistry, S.D. College, Ambala Cantt – 133 001, India*

Abstract: Vacuum-deposited thin films of polymethylmethacrylate (PMMA) doped by varying concentrations (2-10 % by weight of polymer) of some 3,5-diaminopyrazole derivatives as dipolar chromophores were prepared to study their relaxation behaviour . Poling of thin films was carried out using multi-point corona-poling technique to orient dipolar chromophores in proper aligned position. Poling and depoling behaviours of these thin films have been investigated by UV/Vis absorption spectra. For each chromophore, poling efficiency was found to increase with poling voltage as well as poling temperature up to a certain limit retaining the properties of thin films. Maximum value of concentration dependent order parameter was obtained at temperature slightly lower than glass transition temperatures of corresponding guest-host matrices. After 300 hrs. of poling under the conditions (5 kV, near T_g, 30 min.), the decayed amounts of order parameters at room temperature were within the range 25-38 % of the initial value for various guest-host systems. Relaxation behaviour of poling-induced chromophore alignment has also been studied at elevated temperature.

Keywords: Dipolar chromophore, electric poling, order parameter, thermal properties, relaxation behavior.

1. INTRODUCTION

Poled polymeric materials [1-8] containing dipolar chromophores have been studied extensively because of their potential applications in efficient, ultrafast and low-voltage integrated electro-optical devices. Dipolar chromophores can be incorporated into macroscopic environment in a variety of ways. However, the most common and widely used approach is to incorporate dipolar chromophore into suitable polymer host by simply dissolving the chromophore in a polymeric matrix i.e. guest-host (GH) system [9-18]. GH-systems offer several advantages including use of wide variety of dipolar chromophores and polymeric matrices, ease of processing into thin films, wide range of operating frequencies, etc. Since the orientational distribution of dipolar chromophores in the unpoled polymer film is isotropic, the corona poling at elevated temperatures is often used for producing noncentrosymmetric alignment of these chromophores. However, the poling induced orientations in most of GH-systems are not stable even at room temperature. Therefore, the elements for this research comprise not only the preparation of these polymeric materials possessing dipolar chromophores but also the study of experimental parameters affecting the poling efficiency and orientational stability of aligned dipoles.

In this paper, we have reported the preparation and physico-chemical studies of the guest-host systems with varying concentrations (2-10 % by weight of polymer) of dipolar chromophores based on 3,5-diaminopyrazole derivatives as guest doped in polymethylmethacrylate (PMMA) as host. The vacuum-deposited thin films of GH systems were poled using corona-poling technique under different poling conditions to orient dipolar chromophores in proper direction. Relaxation behaviour of aligned dipoles in vacuum-deposited corona-poled polymeric-thin films has also been investigated with time at room temperature as well as at elevated temperature.

2. EXPERIMENTAL

The synthetic scheme for the chromophores **C1-C5** is shown in Figure **1** but the detailed procedure has been described in our earlier paper [19].

2.1. Preparation of Guest-Host Systems

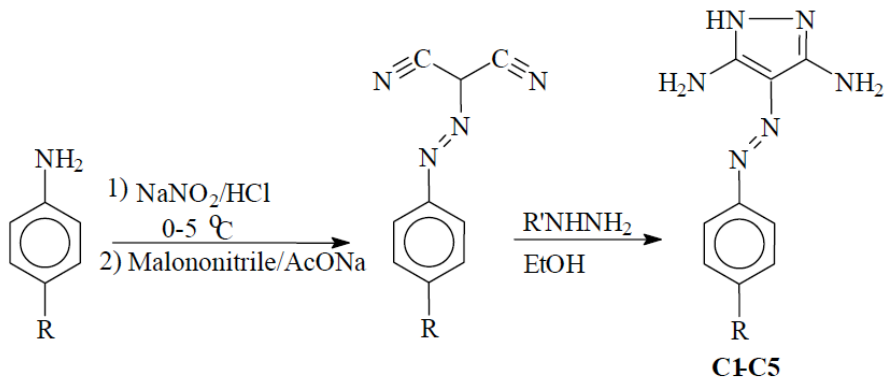
To prepare guest-host systems, the homogeneous solutions of different amounts of dipolar chromophores **C1**-**C5** in distilled dichloromethane were mixed in PMMA solution. The chromophores were present in these concentrations: 2, 4, 6, 8, and 10 % by weight of PMMA. After evaporating the solvent at room temperature, the resulting blends were further dried on water bath for about 12 hr. to yield 2-10 % guest-host systems.

2.2. Measurements

Differential scanning calorimetery (DSC) and thermogravimetric analysis (TGA) were performed by Perkin Elmer (Pyris Diamond) thermal analyzer at the

*Address correspondence to this author at the Department of Chemistry, S.D. College, Ambala Cantt – 133 001, Haryana, India; Tel: +91-9416990024; Fax: 0171-2640283; E-mail: drsushilgoswami@yahoo.com

E-ISSN: 1929-5995/13



	R	
C1	F	3,5-diamino-4- (4'-fluorophenyldiazo) pyrazole
C2	Cl	3,5-diamino-4- (4'-chlorophenyldiazo) pyrazole
C3	Br	3,5-diamino-4- (4'-bromophenyldiazo) pyrazole
C4	NO_2	3,5-diamino-4- (4'-nitrophenyldiazo) pyrazole
C5	CN	3,5-diamino-4- (4'-cyanophenyldiazo) pyrazole

Figure 1: Synthetic scheme for chromophores.

heating rate of 10°C/min under nitrogen atmosphere. Alumina was used as the reference material. Thin films of these guest-host systems 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 kept about 1000 Å with the help of thickness monitor. The vacuum deposited thin films of different GH systems were poled under different poling conditions using optimized high potential multi-point corona poling technique to orient dipolar chromophores in proper direction. UV/Vis absorption spectra of thin films of these polymeric materials were recorded with the help of Shimadzu UV-2500 PC spectrophotometer attached to integrated sphere assembly (ISR-240 A). The relaxation behaviour of aligned dipoles in corona poled polymeric thin films was studied by monitoring UV/Vis absorption spectra at different time intervals after poling.

3. RESULTS AND DISCUSSION

3.1. Thermal Properties

Thermograms of guest-host systems with **C1-C5** as dipolar chromophores are shown in Figures **2-5** (as an illustration, some thermograms are shown only).

Figure **2**, showing DSC thermograms, indicates that GH-systems with **C2** as dipolar chromophore exhibit glass transition temperatures (T_g's) 87-104 °C. Similarly; DSC traces for GH-systems with chromophores **C1**, **C3**, **C4** and **C5** possess glass transition temperatures 84-106 °C, 82-111 °C, 84-107 °C and 83-112 °C respectively (Table **1**).

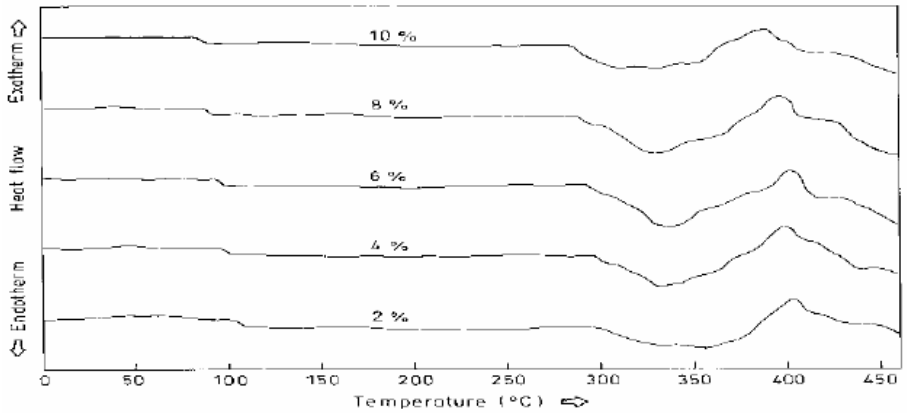


Figure 2: DSC thermograms of chromophore **C2**/PMMA guest-host polymeric systems.

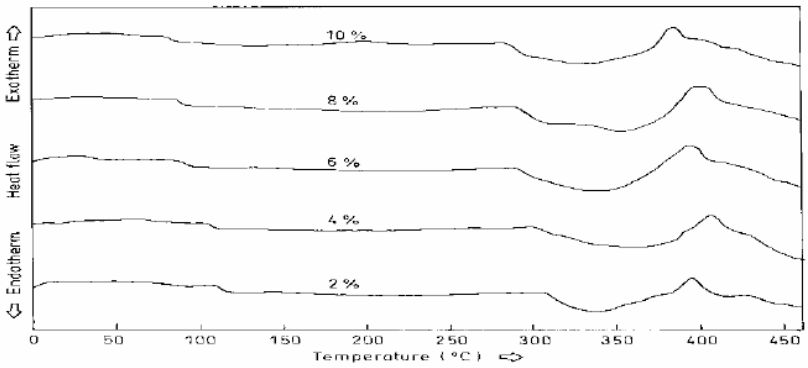


Figure 3: DSC thermograms of chromophore **C5**/PMMA guest-host polymeric systems.

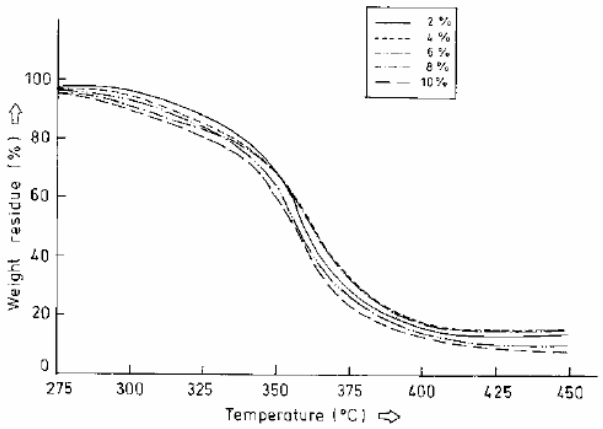


Figure 4: TG thermograms of chromophore **C1**/PMMA guest-host polymeric systems.

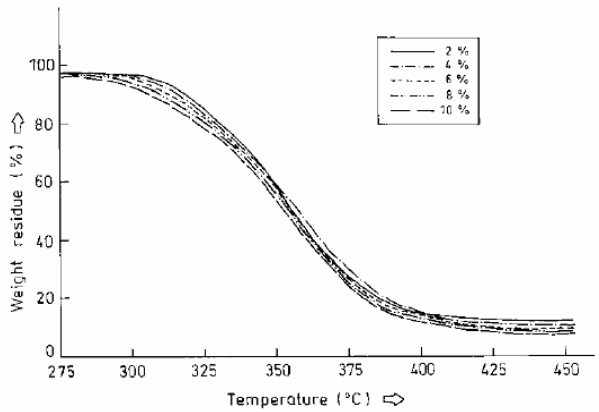


Figure 5: TG thermograms of chromophore **C4**/PMMA guest-host polymeric systems.

For all these chromophores, the glass transition temperatures were observed to decrease with increase in concentration of chromophore. When the concentration of chromophores increased from 2 % to 10 %, T_g value decreased by 22 °C, 17 °C, 29 °C, 23 °C and 29 °C for chromophores **C1**, **C2**, **C3**, **C4** and **C5** respectively. TG thermograms of GH-blends with chromophores **C1** and **C4** are shown in Figures **4** and **5**. The decomposition temperatures (T_d's) of these guest-host blends lie in the range 280-305 °C, 282-300 °C, 290-310 °C, 286-309 °C and 282-308 °C; respectively, for chromophore **C1**, **C2**, **C3**, **C4** and **C5** (Table **1**).

Table **1** dictates that decomposition temperatures of GH-blends are sufficiently higher than their glass transition temperatures. Therefore, these polymeric materials can be poled near glass transition temperature without damaging the polymeric systems.

3.2. Optical Studies

The electronic spectral maxima for these guest-host systems occurs at 340, 355, 348, 354 and 358 nm due to the dipolar chromophore **C1, C2, C3, C4** and **C5** respectively. To characterize poling efficiency, order parameter (ϕ) was determined using the equation

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

Table 1: T_g and T_d Values of Guest-Host Systems

GH-system	T_g (°C)					T_d (°C)				
	C1	C2	C3	C4	C5	C1	C2	C3	C4	C5
2 %	106	104	111	107	112	305	300	310	309	308
4 %	98	100	105	102	106	296	295	302	305	300
6 %	95	96	93	95	93	290	290	298	302	294
8 %	88	90	88	88	88	285	286	295	296	290
10 %	84	87	82	84	83	280	282	290	286	282

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

To optimize the poling conditions corresponding to maximum poling efficiency, order parameters were determined under different conditions of poling voltages and temperatures. Figures **6-9** indicate the order parameter values for different poling temperatures and poling electric fields.

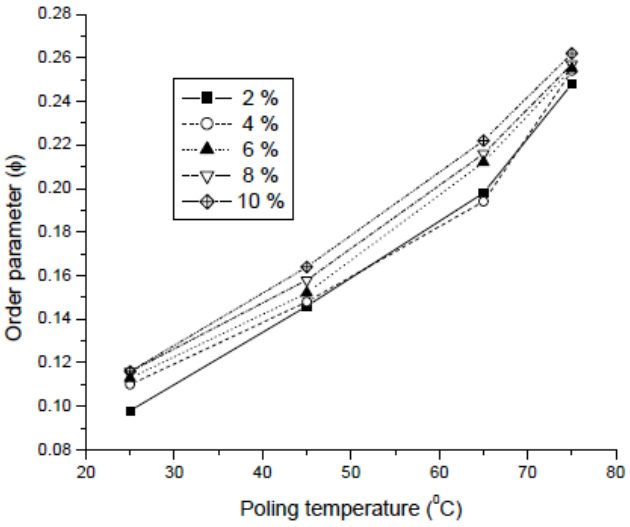


Figure 6: Variation of order parameter of chromophore **C1**/PMMA guest-host polymeric thin films with poling temperature under poling conditions (5 kV, 30 min).

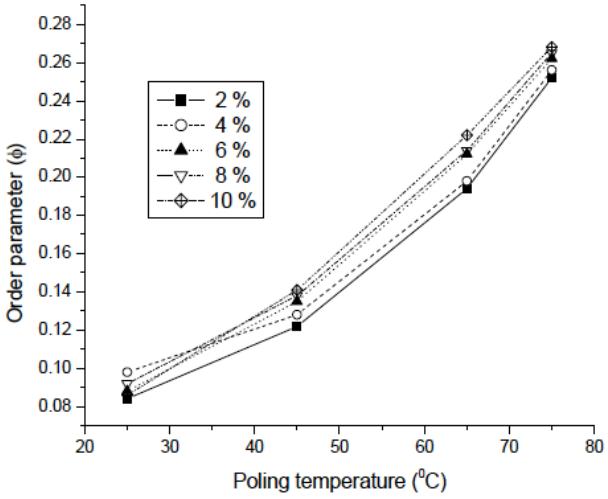


Figure 7: Variation of order parameter of chromophore **C5**/PMMA guest-host polymeric thin films with poling temperature under poling conditions (5 kV, 30 min).

Figures **6** and **7** showing variation of order parameter with poling voltage, indicate that poling efficiency increases with increase of electric field. To understand the effect of poling temperature on poling efficiency, thin films of GH-systems were corona-poled

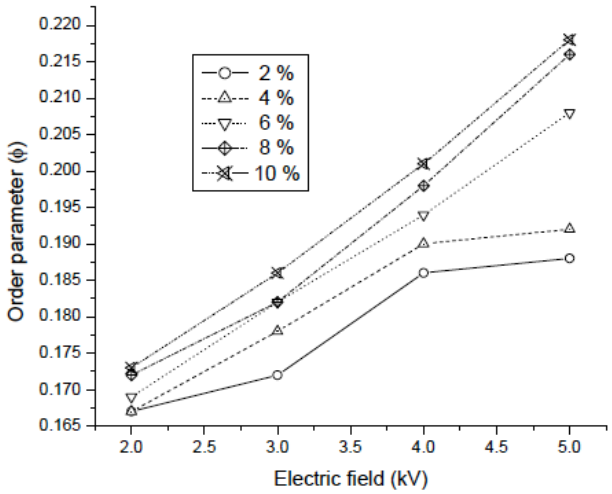


Figure 8: Variation of order parameter of chromophore **C2**/PMMA guest-host polymeric thin films with poling voltage under poling conditions (45 °C, 30 min).

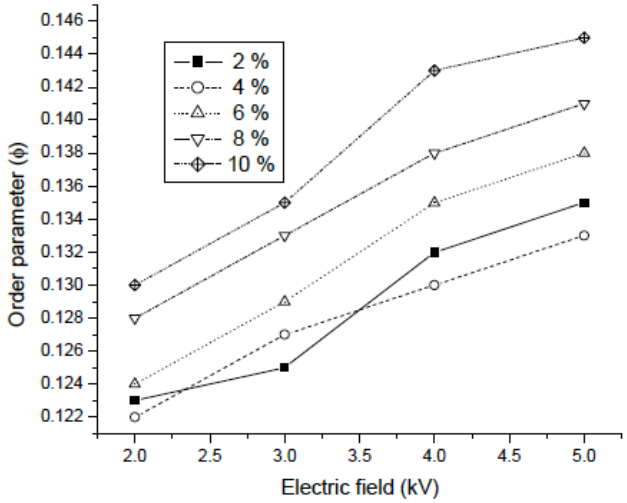


Figure 9: Variation of order parameter of chromophore **C4**/PMMA guest-host polymeric thin films with poling voltage under poling conditions (45 °C, 30 min).

under different poling temperatures at 5 kV for 30 min. For each chromophore, order parameters were found to increase with increase of poling temperature having maximum value near glass transition temperature (Figures **8** and **9** corresponding to chromophore **C1** and **C5** for illustration). Order parameters for these guest-host systems poled under optimum poling conditions (5 kV, near T_g, 30 min.) are shown in Table **2**.

The practical applications of these poled polymeric thin films depend on the stability of aligned dipoles. The orientational stability depends on the number of factors including nature of chromophore and host polymer, size and concentration of dopant chromophores, etc.

Table 2: Order Parameters of Guest-Host Systems under the Poling Conditions (5 kV, near T_g, 30 min)

GH-system	Order parameter				
	C1	C2	C3	C4	C5
2 %	0.278	0.253	0.249	0.260	0.262
4 %	0.263	0.261	0.252	0.264	0.263
6 %	0.262	0.252	0.244	0.256	0.267
8 %	0.258	0.249	0.245	0.258	0.265
10 %	0.262	0.250	0.243	0.259	0.268

Therefore, relaxation behaviour of aligned dipoles must be studied for guest-host systems to determine the optimum concentration of dipolar chromophore suitable for practical applications, which can provide maximum orientational stability. The relaxation behaviour of these dipolar chromophores at room temperature is shown in Figures **10** and **11**. After 300 hrs. of poling under the conditions (5 kV, near T_g, 30 min.), the decayed amounts of order parameters at room temperature were 32-38 %, 29-35 %, 25-30 %, 27-34 %, and 30-37 % of the initial value for the guest-host systems with dipolar chromophores **C1**, **C2**, **C3**, **C4** and **C5** respectively.

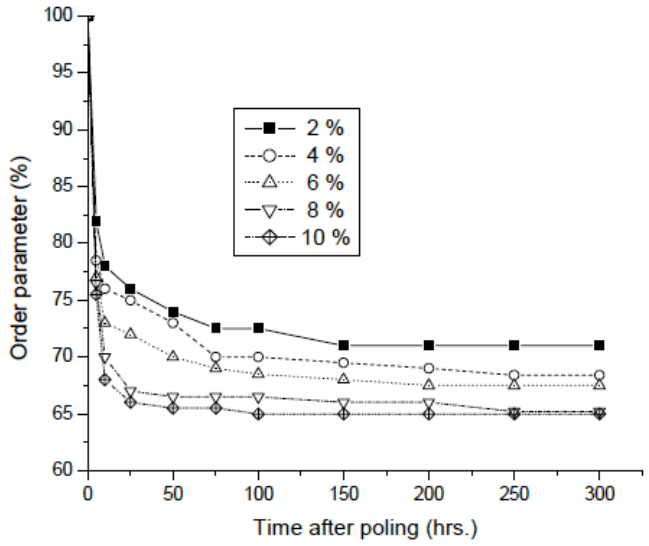


Figure 10: Relaxation behaviour of chromophore **C2**/PMMA guest-host polymeric thin films at room temperature poled at (5 kV, near T_g, 30 min).

For each chromophore, the decayed amounts increased with concentration, which can be explained on the basis of their glass transition temperatures. Moreover, it was observed that the chromophore temporal stability of these GH-blends obey the order: **C1** <**C5** <**C2** <**C4** <**C3**. The relaxation behaviours of aligned chromophores at 50 °C are shown in Figures **12** and **13**. When the poled polymeric thin films were subjected to heat treatment for 200 hours at 50 °C, the dipolar chromophores relaxed by 46-52 % for chromophore **C1**, 43-50 % for chromophore **C2**, 38-45 % for chromophore **C3**, 39-44 % for chromophore **C4** and 45-49 % for chromophore **C5**.

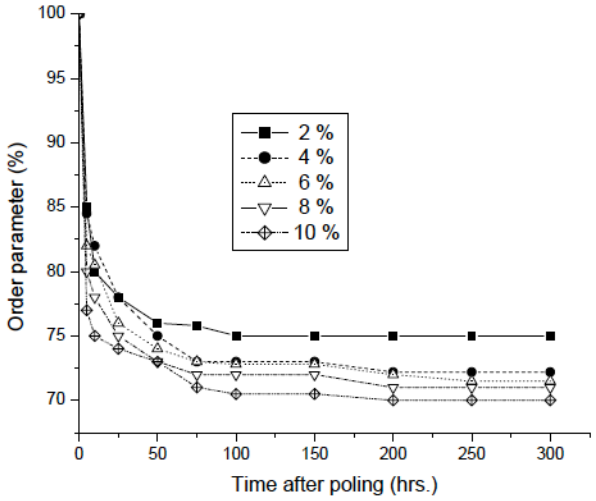


Figure 11: Relaxation behaviour of chromophore **C3**/PMMA guest-host polymeric thin films at room temperature poled at (5 kV, near T_g, 30 min).

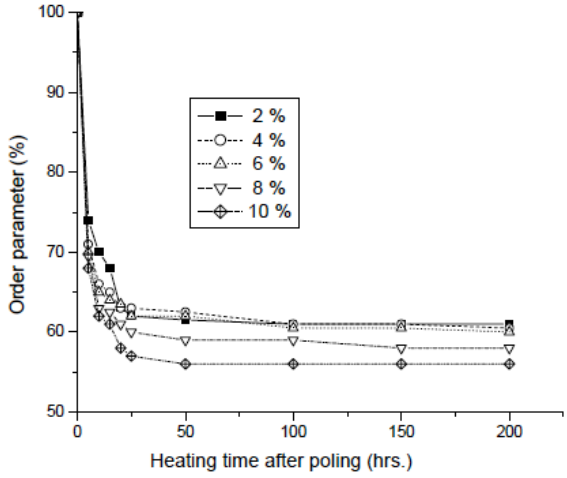


Figure 12: Relaxation behaviour of chromophore **C4**/PMMA guest-host polymeric thin films at 50 °C poled at (5 kV, near T_g, 30 min).

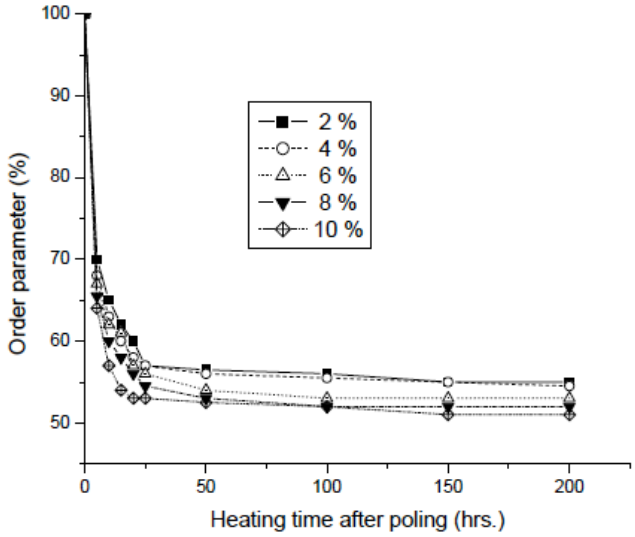


Figure 13: Relaxation behaviour of chromophore **C5**/PMMA guest-host polymeric thin films at 50 °C poled at (5 kV, near T_g, 30 min).

4. CONCLUSIONS

Thin films of guest-host systems obtained by PMMA doped with different concentrations of 3,5-diaminopyrazole derivatives as dipolar chromophores have been prepared. Optimum poling temperature for various polymeric matrices was found to be slightly lower than glass transition temperature of the corresponding doped polymeric system. Under the optimum poling conditions (5 kV, near T_g, 30 min.), order parameters of guest-host systems were found in the range 0.243-0.278. At room temperature, the decayed amounts of order parameters for these guest-host systems were 25-38 % of the initial value after 300 hrs. of poling. Dipolar chromophore relaxed by 38-52 % when polymeric thin films were subjected to heat treatment for 200 hrs. at 50 °C. The results suggested that chromophore alignment stability of these GH-systems obey the order: **C1** < **C5** < **C2** < **C4** < **C3**.

REFERENCES

[1] Arora S, Kumar S. Relaxation behaviour of dipolar chromophore in corona-poled vacuum-deposited polyurethane thin films. Optoelectron Adv Mater-Rapid Comm 2008; 2: 360-65.

[2] Arora S, Kumar S. Synthesis and characterization of styrene/maleimide copolymers with high poling stability of dipolar chromophore. Optoelectron Adv Mater-Rapid Comm 2009; 3: 1359-64.

[3] Chen JI, Marturunkabul S, Chen YM, Jeng RJ, Kumar J, Tripathy SK. A relaxation study of poled nonlinear optical polymers by infrared reflection-absorption spectroscopy. Eur Polym J 1994; 30: 1357-62. http://dx.doi.org/10.1016/0014-3057(94)90263-1

[4] Shi W, Xu Z, Fang C, *et al.* Investigation of the polyetherketone guest–host DR1/PEK-c polymer films by real-time monitoring of the second-harmonic generation. Opt Lasers Eng 1999; 32: 139-45. http://dx.doi.org/10.1016/S0143-8166(99)00061-5

[5] Xu C, Wu B, Todorova O, *et al*. Stabilization of the dipole alignment of poled nonlinear optical polymers by ultrastructure synthesis. Macromolecules 1993; 26: 5303-309. http://dx.doi.org/10.1021/ma00072a005

[6] Jing X, Yang C, Wang H, Wang F. Synthesis and characterisation of crosslinked second order nonlinear optical polymer. Synth Met 1995; 71: 1727-28. http://dx.doi.org/10.1016/0379-6779(94)03024-Z

[7] Arora S, Kumar S. Physico-chemical studies of polyurethanes with dipolar chromophore. Pol J Chem 2007; 81: 225-35.

[8] Park KH, Kwak MG, Jahng WS, Lee CJ, Kim N. Nonlinear optical polymers with novel benzoxazole chromophores: III. Synthesis and characterization of self- crosslinkable glycidyl methacrylate copolymers. React Funct Polym 1999; 40: 41-49. http://dx.doi.org/10.1016/S1381-5148(98)00015-7

[9] Strutz SJ, Brower SC, Hayden LM. Temperature dependence of the activation volume in a nonlinear optical polymer: Evidence for chromophore reorientation induced by sub-T_g relaxations. J Polym Sci Part B: Polym Phys 1998; 36: 901-11. http://dx.doi.org/10.1002/(SICI)1099-0488(19980415)36:5<901::AID-POLB16>3.0.CO;2-D

[10] Strutz SJ, Hayden LM. Effect of pressure and temperature on chromophore reorientation in a side-chain nonlinear optical polymer. J Polym Sci Part B: Polym Phys 1998; 36: 2793-803. http://dx.doi.org/10.1002/(SICI)1099-0488(19981115)36:15<2793::AID-POLB13>3.0.CO;2-O

[11] Lee R-H, Hsiue G-H, Jeng RJ. A novel second-order nonlinear optical guest-host polymeric material exhibiting optical transparency down to 400 nm. Polymer 1999; 40: 13-19. http://dx.doi.org/10.1016/S0032-3861(98)00229-8

[12] Kim W-K, Hayden L-M. Effect of pressure during poling on the relaxation of a guest−host NLO polymer. Macromolecules 2000; 33: 5747-50. http://dx.doi.org/10.1021/ma0004209

[13] Shi W, Fang C, Pan Q, *et al*. Poling optimization and optical loss measurement of the polyetherketone polymer films. Solid State Commun 2000; 116: 67-71. http://dx.doi.org/10.1016/S0038-1098(00)00286-6

[14] Arora S, Kumar S. Corona poling of 4-BPMA/PMMA guest-host polymeric thin films. Optoelectron Adv Mater-Rapid Comm 2007; 1: 410-14.

[15] Qin Z, Fang C, Pan Q, *et al*. Optical properties of NAEC-PMMA nonlinear polymeric thin film. J Mater Sci 2002; 37: 4849-52. http://dx.doi.org/10.1023/A:1020889508567

[16] Barto RR, Frank CW, Bedworth PV, Ermer S, Taylor RE. Near-infrared optical absorption behavior in high-β nonlinear optical chromophore-polymer guest-host materials. 1. Continuum dielectric effects in polycarbonate host. J Phys Chem B 2004; 108: 8702-15. http://dx.doi.org/10.1021/jp037239x

[17] Arora S, Kumar S. Optical and electrical studies of thermally stable guest-host polymeric thin films. J Indian Chem Soc 2007; 84: 759-63.

[18] Shettigar S, Chandrasekharan K, Umesh G, Sarojini BK, Narayana B. Studies on nonlinear optical parameters of bis-

chalcone derivatives doped polymer. Polymer 2006; 47: 3565-67. http://dx.doi.org/10.1016/j.polymer.2006.03.062

[19] Arora S, Kumar S. Vacuum-deposited poled polyimide thin films with high poling stability of dipolar chromophores. Optoelectron Adv Mater-Rapid Comm 2010; 4: 2140-47.

Received on 27-05-2013 Accepted on 06-06-2013 Published on 26-06-2013

DOI: http://dx.doi.org/10.6000/1929-5995.2013.02.02.5