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Kinetic Study of Thermal Degradation of Polyurethanes with Nonlinear Optical Chromophore

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ABSTRACT

In this work, thermal degradation of polyurethanes containing different feed concentration of 4-[bis(2-hydroxyethyl)amino]-4′-nitroazobenzene as nonlinear optical chromophore (NLO) is presented, using dynamic thermogravimetric analyzer (TGA) in air atmosphere at different heating rates viz. 5, 10 and 20°C min^{-1}. Polyurethanes were synthesized by copolymerization of 4-[bis(2-hydroxyethyl)amino]-4′-nitroazobenzene and N-phenyldiethanolamine with 2,4-tolyenediisocyanate. Degradation activation energies are calculated using model free multiple-heating rate methods i.e. Kissinger, Friedman and Ozawa-Flynn-Wall. The values of activation energy thus obtained are directly proportional to the feed concentration of chromophore.The lower value of activation energy for polyurethane containing 100% chromophore feed concentration suggests its lower resistance to heat during its use in electro optic device applications.

Key Words: Activation Energy, Copolymerization, Polyurethanes, TGA, Thermal degradation.

INTRODUCTION

In recent years, poled polymers [1-7] with nonlinear optical (NLO) chromophores have attracted a great deal of attention owing to their tremendous potential for ultra fast electro optic devices. However, fabrication of efficient photonic devices is a challenging task as such systems place additional demands on poled polymeric materials including exceptional thermal stability of both polymer and chromophore, high density of NLO chromophore, good temporal stability of poling-induced polar order, etc. Generally, polymers possessing high glass transition temperatures (T_g) can lock the chromophore in their acentric order after poling and hence show good temporal stability of aligned chromophores [8, 9]. Recently, we have reported [10] novel high T_g polyurethanes with NLO chromophore synthesized using copolymerization approach. Moreover, the resulting polymeric materials were found to possess good temporal stability of poling induced aligned chromophores and hence they seemed to be promising materials for NLO applications. Therefore, it is essential to study thermal degradation kinetics of these polyurethanes to further enhance their performance for NLO applications.

The kinetic study of thermal degradation provides useful information to determine optimum conditions for integration and packing process of NLO devices. Thermal degradation may cause serious problems to these polymeric materials during their use at elevated temperatures. Therefore, an accurate control of the processing and working conditions of these NLO polymeric materials is very important to design the devices with desired electro optic properties without damage of any sort.

Thermogravimetric analysis (TGA) is often used to examine the behavior of polymeric materials during thermal degradation [11-16]. One of its main advantages is the high reproducibility of results in dynamic mode that assures the calculation of precise kinetic parameters. The kinetic equations describing the material weight loss at different temperatures and atmospheres can be applied to optimize the operating conditions for device applications.

The aim of the work undertaken is to investigate the thermal degradation kinetics of polyurethanes with NLO chromophore under flowing air conditions. Dynamic thermogravimetric runs were carried out to examine the behavior of materials at different heating rates. It is now recognised that kinetic analysis based on single heating rate methods is very unreliable and problematic [17, 18]. Therefore, the use of multiple-heating rate methods, e.g., Kissinger [19], Friedman [20] and Ozawa-Flynn-Wall (O-F-W) [21, 22] etc. is preferred. Therefore, in the present study kinetic parameters of thermal degradation of polyurethanes were determined by using Friedman, O-F-W and Kissinger methods. This paper also reports the effect of feed concentration of NLO chromophore on activation energies of polyurethane degradation stages.

MATERIALS AND METHODS

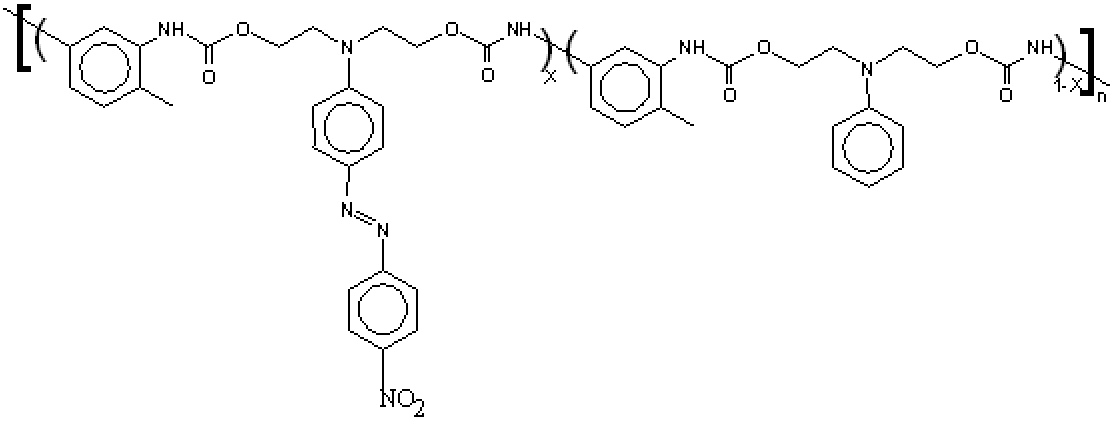

Fig. 1. Structure of polyurethanes with different chromophore concentration

Polyurethane	X
P1	1
P2	1/2
P3	1/3
P4	1/4

Sample Preparation

The synthesis of polyurethanes with different feed concentrations of 4-[bis(2-hydroxyethyl)amino]-4′-nitroazobenzene as NLO chromophore has been described in our earlier paper [10] (Figure 1). The synthesized polyurethanes were characterized using different techniques including IR, NMR, gel permeation chromatographic (GPC) technique, UV/Visible absorption spectroscopic technique and thermal techniques. Molecular weights of the polymers determined by GPC were found in the range M_W = 4910-5880 (M_W/M_n = 1.88-1.98). The glass transition temperatures of these polyurethanes with different feed concentrations of NLO chromophore have been found in the range 231-245 ˚C (except for polyurethane with 100 % feed concentration of NLO chromophore, which show absence of T_g). The prepared samples were dried in a vacuum desiccator before taking the thermograms.

Methods

Thermal degradation measurements were carried out using Perkin Elmer, thermogravimetric/differential thermal analyzer (TG/DTA) in flowing air atmosphere (50 mL min^{-1}). The TG/DTA analyzer was calibrated before recording thermograms. Dried alumina powder was used as reference material and ceramic sample holder was used for taking thermograms. The samples were heated from ambient temperature to 700 ˚C at various heating rates (β) of 5, 10 and 20 ˚C min^{-1} on each sample. Heating rates were kept to a maximum of 20 in order to avoid the onset of mass and heat transfer limitations, which would invalidate a kinetic analysis. Samples were accurately weighed (between 6 and 7 mg) in a standard ceramic pan to record the thermograms.

RESULTS AND DISCUSSION

Thermal studies

TGA data for all the samples were obtained in the standard form of %mass loss as function of temperature at three heating rates (5, 10 and 20 ˚C min^{-1}) is shown in Figures 2a-2d. All polymers showed an initial weight loss in the range of 150-250 °C, suggesting that degradation starts at the urethane bond [23]. Decomposition of the urethane bond leads to the formation of primary amine and olefin or to the formation of secondary amine and carbon dioxide [23]. As expected, the shapes of TGA curves are quite similar shifting towards higher temperatures at higher heating rates. The resulting TGA thermograms showed a very sharp degradation stage at lower temperature, followed by another broad and irregular stage at higher temperature associated with comparatively small mass loss.

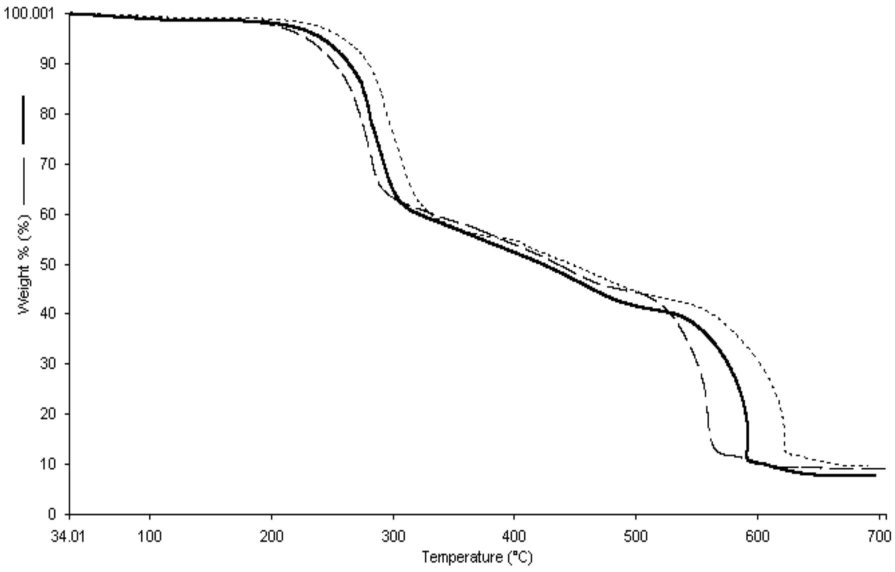

Fig. 2a. TGA curves of P1 at heating rates of (- - - -) 5, (——) 10 and (……) 20 ºC min^{-1}.

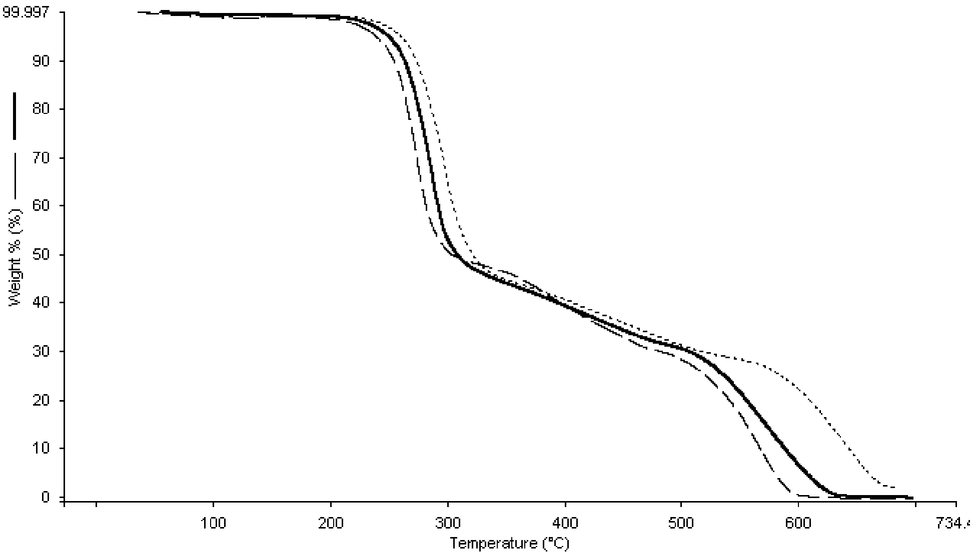

Fig. 2b. TGA curves of P2 at heating rates of (- - - -) 5, (——) 10 and (……) 20 °C min^{-1}.

Kinetic studies

TGA thermograms of samples showed three important areas of weight loss. Because of the three-step nature of thermal decomposition reactions, it was necessary to determine and use different kinetic methods to describe the thermal degradation over the entire temperature range. Therefore, the kinetic parameters of polyurethane were determined for the first, second and third stage, separately. The main equations of the kinetic methods used in this work to analyze the degradation behavior are summarized in Table 1. In these methods, β is the heating rate, T_m is the temperature at maximum rate of mass loss, n is the apparent reaction order, R is the universal gas constant, A is the pre-exponential factor, α is the degree of conversion and E is the apparent activation energy.

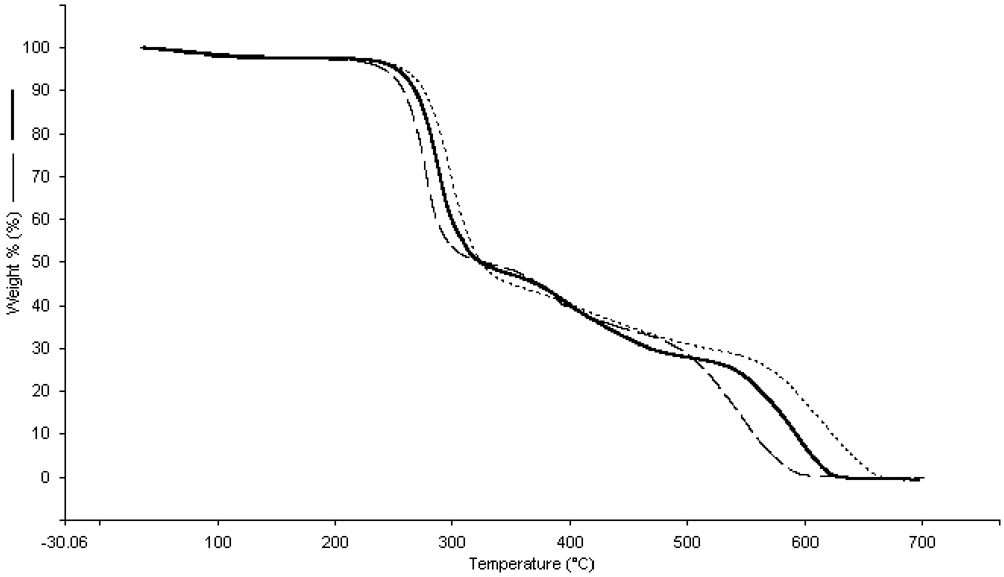

Fig. 2c. TGA curves of P3 at heating rates of (- - - -) 5, (——) 10 and (……) 20 °C min^{-1}.

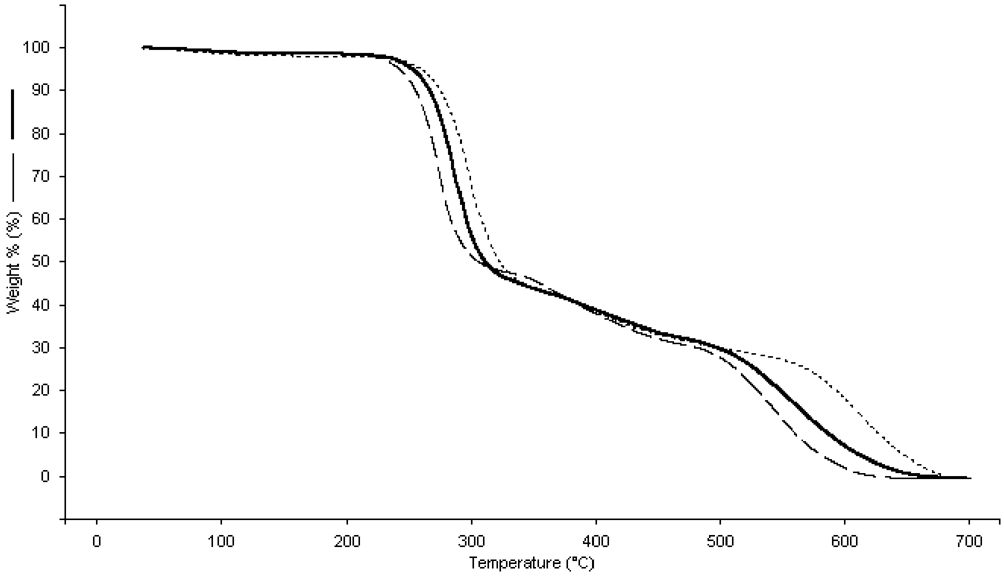

Fig. 2d. TGA curves of P4 at heating rates of (- - - -) 5, (——) 10 and (……) 20 °C min^{-1}.

The plots of application of the isoconversional Friedman method [20] to the polyurethanes with different feed concentration of chromophore are shown in Figures 3a-b (as illustration, curves for P1 is shown). For degree of conversion from 0.01 to 0.9, the plots between ln (dα/dT) vs. 1/T were found to be linear with high regression coefficient greater than 0.988. However, at some values of degree of conversion, much lower regression coefficients were obtained and thus, not included in final report for the same reason (Table 2). It is observed that there is noticeable difference of activation energy in going from polymer P1 to any of polymers P2-P4. Moreover, the value of activation energy corresponding to first stage is very important as polymer chain scission starts in this region [23]. Its value decreases when NLO chromophore feed concentration is reduced from 100% (x = 1) to 25% (x = 1/4). Therefore, polymer P4 containing 25% feed concentration (x = 1/4) of NLO chromophore possess comparably high resistance to heat. The activation energies of these polymeric systems are similar to those reported in the literature for other polyurethane systems [24].

Table 1. Final equations of kinetic methods used in the study

Method	Final Equation
O-F-W	$\log(g(\alpha)) = \log(\frac{AE}{R}) - \log(\beta) - 2.315 - 0.4567\frac{E}{RT}$
Kissinger	$\frac{d(\ln(\beta/T_m^2))}{d(1/T_m)} = -\frac{E}{R}$
Friedman	$\ln(\frac{d\alpha}{dt}) = \ln(\beta(\frac{d\alpha}{dT})) = \ln A + n\ln(1-\alpha) - \frac{E}{RT}$

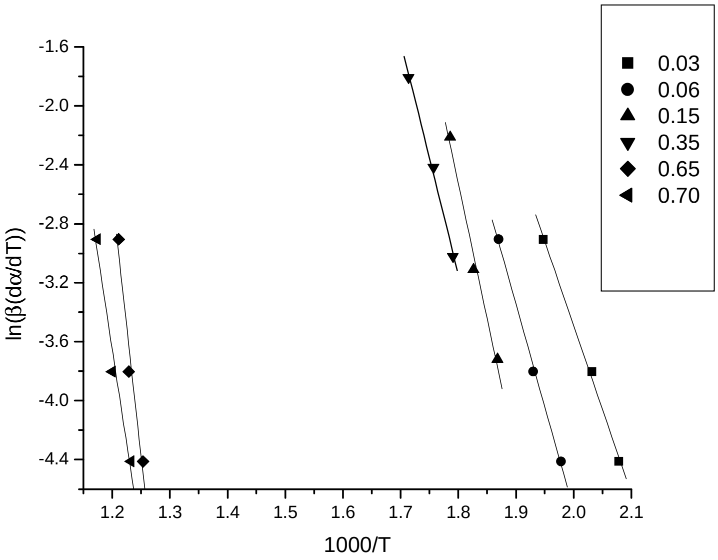

Fig. 3a. Iso-conversional plots of Friedman method for P1.

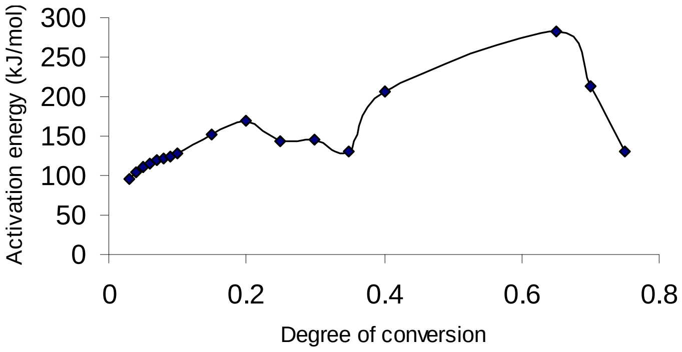

Fig. 3b. Variation of activation energy for P1, calculated by Friedman method, with degree of conversion, α.

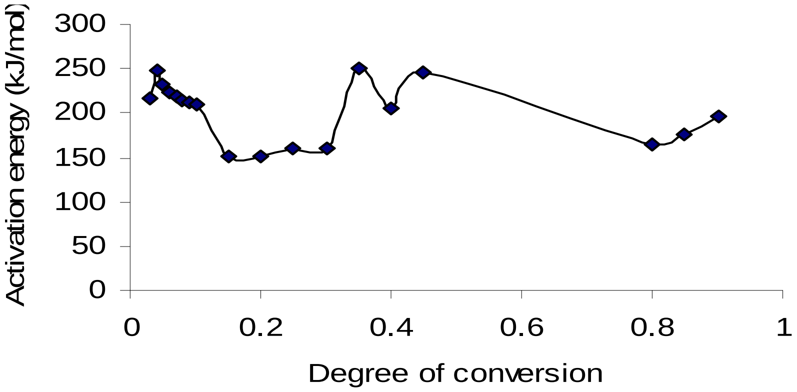

Fig. 3c. Variation of activation energy for P4, calculated by Friedman method, with degree of conversion, α.

Table 2. Activation Energies for Polyurethanes Calculated by O-F-W and Friedman Methods at Varying Degree of Conversion, α.

α (degree of conversion)	Activation Energy (kJ mol^{-1})							
	P1		P2		P3		P4	
	O-F-W	Friedman	O-F-W	Friedman	O-F-W	Friedman	O-F-W	Friedman
0.03	81.6	94.7	133.1	189.6	146.8	207.8	172.5	217.1
0.04	89.4	103.3	142.8	203.4	166.9	234.9	196.7	248.0
0.05	95.8	110.4	149.6	213.0	172.5	243.5	183.7	231.7
0.06	100.6	115.8	154.2	219.6	175.0	246.0	177.6	224.0
0.07	104.7	120.5	158.5	225.7	176.7	248.2	173.1	218.5
0.08	106.6	122.6	159.7	225.6	180.5	253.4	170.6	215.3
0.09	108.5	124.8	167.3	238.4	179.9	252.7	167.8	211.8
0.1	111.2	127.8	169.9	242.1	179.0	251.2	166.1	209.8
0.15	133.4	152.3	172.8	192.4	176.6	247.9	159.7	151.1
0.2	145.7	169.8	163.5	232.8	171.6	190.5	155.2	151.0
0.25	150.0	143.5	159.9	192.5	164.1	163.5	154.3	160.3
0.3	147.5	145.9	161.2	162.6	158.9	161.7	153.6	161.1
0.35	142.3	131.1	158.2	141.8	157.7	160.6	157.7	249.4
0.4	176.4	205.5	157.0	189.2	156.3	167.6	164.1	205.9
0.45	-----	-----	168.3	238.4	176.8	249.4	193.5	246.8
0.65	240.0	283.3	-----	-----	-----	-----	-----	-----
0.7	186.9	212.4	-----	-----	-----	-----	-----	-----
0.75	154.0	131.5	133.5	188.0	123.3	172.2	-----	-----
0.8	147.8	-----	119.2	167.4	118.9	166.5	128.6	165.1
0.85	132.2	-----	115.8	162.8	118.1	165.6	136.4	174.8
0.9	124.8	-----	115.8	163.2	118.9	166.6	152.5	195.7

The activation energy increases slowly with degree of conversion for each polyurethane (except P4), then increases significantly at moderate value of α and starts decreasing thereafter at high values of α (Figure 3b). For P4, the activation energy decreases at low α, vary irregularly at moderate α and then increases at high value of α (Figure 3c).

Secondly, we used O-F-W method [21, 22] to calculate the activation energy for different conversion degrees by fitting the plots of lnβ vs 1/T. for illustration, O-F-W plots for polyurethanes P1 is shown in Fig. 4a and activation energies calculated thereof are shown in Table 2. The resulting fitting straight lines (regression coefficient > 0.998) show the applicability of O-F-W method to these polyurethanes for the mentioned degrees of conversion. Moreover, the results observed with this method follow almost similar trend as obtained with Friedman method [20], again showing the validity of this approach for these materials (Figures 4b-c). Comparing the data (Table 2), we observed that for almost all the degree of conversion investigated, the activation energies obtained by Friedman method are slightly higher as compared to those obtained with O-F-W method.

The value of the temperatures of maximum weight loss at different rates was used to evaluate the apparent activation energy by Kissinger method [19]. In this method, a straight line graph was obtained between ln (β/T_m^2) vs. $1/T_m$ with slope Ea /R, where T_m is the temperature of maximum degradation.

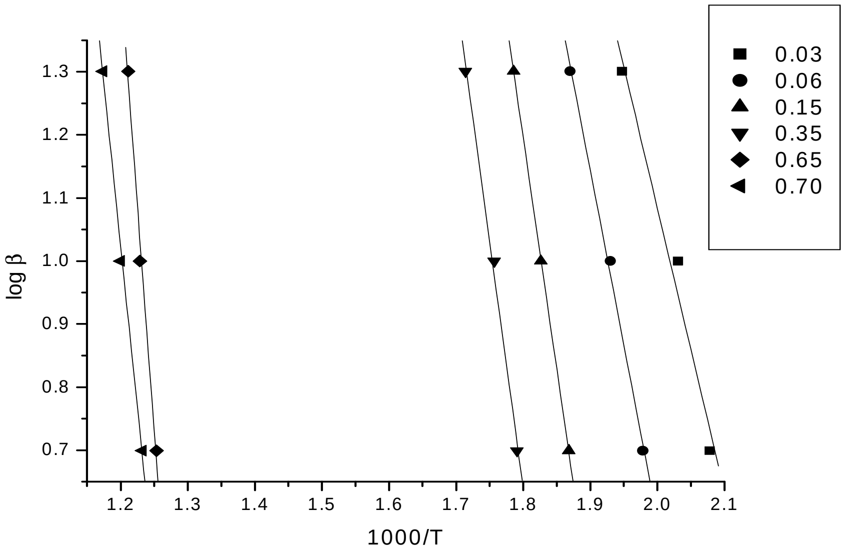

Fig. 4a. Iso-conversional plots of O-F-W for P1.

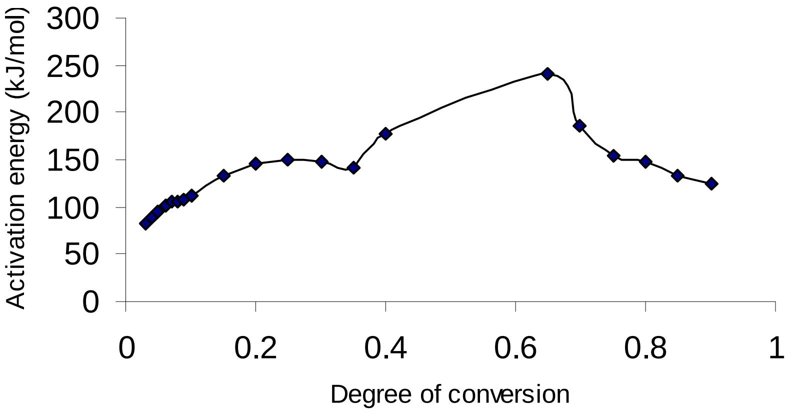

Fig. 4b. Variation of activation energy for P1, calculated by O-F-W method, with degree of conversion, α.

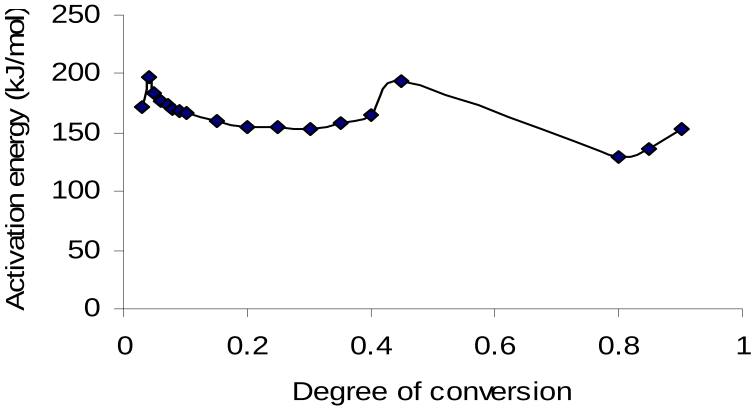

Fig. 4c. Variation of activation energy for P4, calculated by O-F-W method, with degree of conversion, α.

For effective comparison of data obtained using three methods, the mean values of activation energy for each stage were calculated as given in Table 3. Activation energy for the first stage, calculated using Kissinger method, increases as the feed concentration decreases, indicating the trend to be same as in the case of Friedman and O-F-W methods. Therefore, it can be said that the heat resistance of these polymeric systems can be increased by decreasing chromophore loading level as the beginning of structurally important urethane bond took place during the first stage [23]. However, practical utility of these polymers for NLO applications depends on the thermal stability as well as density of NLO chromophore. Therefore, the optimum conditions can be set for these polyurethane systems by suitably adjusting the chromophore loading level. However, for the second and third stage, uniform trend is absent.

Table 3. Mean Degradation Activation Energy Values of Polyurethane Samples

Degradation stage	Method	Activation Energy (kJmol^{-1})			
		P1	P2	P3	P4
I	O-F-W	99.8	154.4	172.1	176.0
	Kissinger	130.0	180.4	192.5	195.0
	Friedman	114.9	219.6	242.2	222.1
II	O-F-W	149.2	162.9	166.0	162.5
	Kissinger	-	-	-	-
	Friedman	158	192.8	191.6	189.3
III	O-F-W	164.2	121.0	119.8	139.1
	Kissinger	143.5	80.0	98.1	120.0
	Friedman	209.0	170.3	167.7	178.5

CONCLUSION

Thermal degradation of polyurethanes with 4-[bis(2-hydroxyethyl)amino]-4'-nitroazobenzene as NLO chromophore can be kinetically described by O-F-W, Friedman and Kissinger methods. Activation energy corresponding to a particular degradation stage vary with chromophore feed concentration. Activation energy for first degradation stage obtained using Kissinger, Friedman and O-F-W methods follow the order P1<P2<P3<P4. Polyurethane P1 has lower activation energy as compared to other polymeric systems P2-P4 indicating that activation energy increases with decrease of chromophore loading level. Therefore, polyurethane P1 will show lower resistance to heat during its use in electro optic device applications and its resistance towards heat can be increased by adjusting chromophore feed concentration.

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