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Activation Energy Determination of Polyimide Film From Its Thermal Behaviour

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This study deals the determination of activation energy of azo group containing polyimide film. Presence of azo group in the polymer enchances the reaction rate. The activation energy can be easily determined from the thermal degradation behaviour of polyimide film by four different method (a) Murray and White (b) Coats and Redfern (c) Doyles and (d) Freemans and Carrols method. The activation energy determined by different methods were compared.

Key Words: Azo polyimide film, Thermal imidization method, Thermal behaviour, Activation energy.

INTRODUCTION

Polyimides are high performance polymer with a range of properties including high thermal stability, resistance to chemical attack and lower dielectric constant. The synthesis of polyimide film [ABTD-DAP] based on 3,3',4,4'-azo benzene tetra carboxylic dianhydride and 1,3-propanediamine by classical thermal imidization method is reported. The synthesis and characterzation were reported by earlier[1]. TGA experiments were performed to elucidate the thermal behaviour and supplied the data that characterize the degradation. From the study of thermal degradation the activation enrgy was calclulated by four different methods.

EXPERIMENTAL

Synthesis of polyimide film: The polyimide film ABTD-DAP was synthesized by two step classical thermal imidization method. The first step involves the condensation between the dianhydride and diamine to give polyamic acid precursor which is subsequently cyclized to form the imide linkage in presence of (NMP) N-methyl-2-pyrrolidone. In the second step removal of water can be achieved by heating polyamic acid as a cast film.

Test methods

Thermal analyses: Thermal analyses (TGA) were recorded in nitrogen for the film NET Z SCH STA-409 C/CD model simultaneous TGA apparatus. About 26 mg of the sample was heated at the heating rate of 10 °C/min for the film. Thermocouple was used to measure the temperature.

RESULTS AND DISCUSSION

Thermal analysis of the polyimide film were carried out in a nitrogen atmosphere to evaluate their thermal stability shows in Fig. 1. From the primary thermograms obtained for the polyimide film by plotting the per cent weight loss against temperature, activation energy can be calculated.

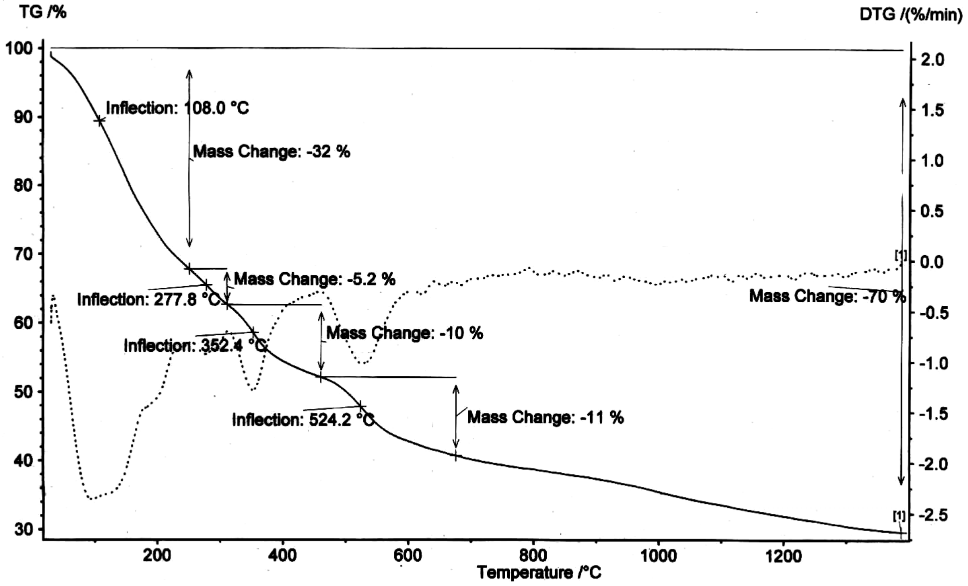

Fig. 1. TGA of polyimide film ABTD-DAP

Arrhenius equation can be given as:

$$\frac{dc}{dt} = A.e^{-E^*/RT}(1-c)^n \qquad (1)$$

Or the form that includes the linear rate of temperature rise β.

$$\frac{dc}{dt} = \frac{A}{\beta} e^{-E^*/RT}(1-c)^n \qquad (2)$$

The integral form of the above equation may be written as:

$$\int_{C_o}^{C} \frac{dc}{(1-c)^n} = \frac{A}{\beta} \int_{T_0}^{T} e^{-E^*/RT} dT \qquad (3)$$

where T_o = initial absolute temperature, Integration of the left hand side gives

$$\int_{C_0}^{C} \frac{dc}{(1-c)^n} = \frac{(1-c)^n - 1}{1-n} \text{ for n not equal to 1} \qquad (4)$$

$$= \text{In}\,(1\text{-}c) \qquad (5)$$

For the right handside of eqn. 3 the most complete integral are so cumbersome to use, that various authors have sought and found approximate integrals that permitted more convenient and reasonable accurate evaluation of kinetic parameters. Some of these will be discussed below.

Murray and White[2]:

$$\int_{To}^{T} e^{-E^{*}/RT} \approx (RT^{2}/E)e^{-E^{*}/RT}$$

Plots:

In [In (1-c)] -21nT *vs.* 1/T for (n = 1)

$$\text{In}\left[\frac{(1-c)^{1-n}-1}{1-n}\right]-2\ \text{In T}\ \textit{vs.}\ 1/\text{T for (n not equal to 1)}$$

Coats and Redfern[3]:

$$\int_{To}^{T} e^{-E^{*}/RT}dT \approx (RT^{2}/E)[1-2RT/E]e^{-E^{*}/RT}$$

Plots:

$$\log\left[\frac{\ln(1-c)}{T^{2}}\right]\ \text{vs.}\ \frac{1}{T}(\text{for } n=1)$$

$$\log\left[\frac{(1-c)^{1\text{-}n}-1}{T^{2}(1-n)}\right]\ \text{vs.}\ \frac{1}{T}(\text{for } n=1)$$

Doyle[4]:

$$\text{Log}\,{}^{R}\!/_{E}\int_{T_0}^{T} e^{-E^{*}/RT}.dT=-2.315-0.4567({}^{E}\!/_{RT})$$

$$\text{for} 20 \geq E/RT \geq 60$$

Plots:

log [In (1-c)] *vs.* 1/T (for n =1)

$$\log\left[\frac{(1-c)^{1-n}-1}{(1-n)}\right]\text{vs.}\ \frac{1}{T}\ \ (\text{for n not equal to 1})$$

The activation energies were calculated graphically from equation after introducing the appropriate approximations assuming the correct order of the reaction which is determined by Freeman and Carroll's difference differential method.

Freeman and Carroll's Method[5]: Equation is derived for non-reversing reactions so that rate dependant parameters such as energy of activation and order of reaction may be calculated from the single experimental curve. For this purpose, a relationship between specific rate and temperature is assumed Arrhenius equation $k = A\ e^{-E^{*}/RT}$. A general derivation is presented and applied to thermogravimetry.

For a reaction in the liquid or solid state where one of the products β is volatile, all other substances being in the condensed state.

$$aA = bB_{(g)} + cC$$

The rate expression for the disappearance of reactant A from the mixture is

$$\frac{-dx}{dt} = KX^{x}$$

where, X = concentration, mole fraction or amount of reactant, A; K = specific rate; x = order of reaction with respect to A; substituting for k in (6) as $k = A\,e^{-E^{*}RT}$ gives

$$\frac{-(dx/dt)}{X^{x}} = Ae^{-E^{*}RT} \tag{7}$$

The logarithmic form of eqn. 7 is differentiated with respect to dX/dt, X and T, resulting in eqn. 8.

$$\frac{E^{0}}{RT^{2}}dt = d\ln(-dX/dt) - x\,d\ln X \tag{8}$$

Integrating the eqn. 8 gives

$$\frac{-E^{*}}{R}\Delta\left[\frac{1}{T}\right] = \Delta\ln(-dX/dt) - x\Delta \mathrm{In} X \tag{9}$$

Dividing eqns. 8 and 9 by d ln X and Δ In X, respectively, one obtain eqns. 10 and 11.

$$\frac{E^{*}dT}{RT^{2}d\ln X} = \frac{d\ln(-dx/dt)}{d\ln X} - x \tag{10}$$

$$\frac{\frac{-E^{*}\Delta(1/T)}{R}}{\Delta\ln x} = \frac{\Delta\ln(-dx/dt)}{\Delta\ln X} - x \tag{11}$$

From eqns. 10 and 11 it is apparent that plots of

$$\frac{dT}{T^{2}\log X} \text{ vs. } \frac{d\log(-dx/dt)}{d\log X}$$

and

$$\frac{\Delta(1/T)}{\Delta\log X} \text{ vs. } \frac{\Delta\log(-dX/dt)}{\Delta\log X}$$

Should result in straight lines with slopes of + or - E*/2.303 R and intercepts of -x where x is the order of the reaction and E* is the activation energy of polyimides which are calculated from their intercept and slopes of straight lines, respectively.

Let us consider the cases where X refers to (1) mole fraction of A, (2) molar concentration and (3) amount of reactant

(1) Mole fraction of A, $X = n_a/M = NA$

where n_a = Number of moles of A at time t.

M = total number of moles in reaction mixture.

(a) Total number of moles is constant during reaction. Substituting for X in (7) results in the relationships.

$$\mathrm{In}\ k = \mathrm{In}\ M^{x-1} + \mathrm{In}\ (-dn_a/dt) - x\ \mathrm{In}\ n_a \tag{12}$$

and

$$\frac{-(E^*/R)\Delta(1/T)}{\Delta \ln n_a} = -x + \frac{\Delta\, \mathrm{In}(-dn_a/dt)}{\Delta\, \mathrm{In}\, n_a} \tag{13}$$

Eqn. 13 may also be written in a differential form as eqn. 8

(b) Total number of moles is not constant. For this case

$$\mathrm{In}\ k = (x-2)\ \mathrm{In}\ M - x \ln n_a + \ln (n_a\, dM/dt - M\, dn_a/dt) \tag{14}$$

$$\frac{\frac{E^*}{RT^2}dT}{d(\mathrm{In}M - \ln n_a)} = \frac{X + d\ln(n_a dM/dt - Mdn_a/dt) - 2d\ln M}{d(\ln M - \ln n_a)} \tag{15}$$

and

$$\frac{-E^*R\Delta(1/T)}{\Delta(\mathrm{In}M - \mathrm{Inn}_a)} = x + \frac{\Delta \mathrm{In}(n_a dM/dt - Mdn_a/dt - 2\Delta \mathrm{In}M}{\Delta(\ln M - \ln n_a)} \tag{16}$$

(2) Molar concentration $X = n_a / V$

where V = volume of reaction mixture.

The result obtained by this equation is identical to the case of mole fraction with the exception that V replaces M.

(3) $X = n_a$

For this case

$$\ln k = x \ln n_a + \ln (-dn_2/dt) \tag{17}$$

The final equation is identical to (13).

The above relationships may be applied simply to measurements of weight or volume changes by the appropriate substitutions for M and n_a. After evaluation x and E* the frequency factors may be calculated by combining equation $k = Ae^{-E^*/RT}$ and (6)

Using differential thermal analysis[5] an equation was derived from which order of a reaction and energy of activation were determined. The expression given was

$$k = \left[\frac{KAV}{n_a}\right]^{x-1} \frac{C_p d\Delta T/dt + K\Delta T}{[K(A-a) - C_p\Delta T)^x} \tag{18}$$

where, K = heat transfer coefficient; A = area under curve; ΔT = differential temperature at a particular time; dΔT/dt = rate of change of differential temperature at the point where ΔT is measured; V = volume of solution; n_a = initial number of moles of reactants; C_p = Total heat capacity of reactant solution or liquid; a = area under curve upto time where ΔT and dΔT/dt is taken; x = order of reaction with respect to one components.

The method used to determine x and E* is as follows. A value of x is chosen and used to calculate k over the entire temperature range using eqn. 18. A graph of log k *vs.* 1/T was plotted. If a linear relationship was obtained, it was assumed that the value of x was valid and the energy of activation could then be calculated from the slope of the line.

A method of evaluating x and E* which eliminates this trial and error procedure becomes apparent if $k = Ae^{-E^*/RT}$ is substituted in eqn. 18. The resulting expression written in logarithmic form is

$$\text{In } Z\text{-}E^*/RT = (x-1) \text{ In } KAV/n_0 - x \text{ In } [K(A-a) - C_p\Delta T] + \text{In } [C_p d\Delta T/dt + K\Delta T \quad (19)$$

Differentiating and integrating (19) gives equation (20) and (21).

$$\frac{\dfrac{E^* dT}{RT^2}}{d\ln[K(A-a)-Cp\Delta T]} = -x + \frac{d\ln(C_p d\Delta T/dt + K\Delta T)}{d\ln[K(A-a)-C_p\Delta T]} \qquad (20)$$

$$\frac{\dfrac{-E^*}{R}\Delta(1/T)}{\Delta\ln[K(A-a)-Cp\Delta T]} = -x + \frac{\Delta\ln(C_p d\Delta T/dt + K\Delta T)}{d\ln[K(A-a)-C_p\Delta T]} \qquad (21)$$

From the above, it is clear that plots of

$$\frac{\dfrac{dT}{T^2}}{d\log[K(A-a)-Cp\Delta T]} \text{Vs} \frac{d\log(d\Delta T/dt + K\Delta T)}{d\log[K(A-a)-C_p\Delta T]}$$

and

$$\frac{\Delta(1/T)}{\Delta\log[K(A-a)-C_p\Delta T)} \text{Vs} \frac{\Delta\log(d\Delta T/dt + K\Delta T)}{\Delta\log[K(A-a)-C_p\Delta T]}$$

should result in straight lines with intercepts at -x and slopes of + or - E*/2.303 R for any physical or chemical reaction. It should be noted however, that eqn. 18 and subsequent one are valid only where the volume of the reaction mixture does not change appreciably.

Figures indicate a continuous tracing of change in sample weight as a function of time and temperature where the polymers were heated from 25 to 500 ºC. Since the reactions under consideration involve solid state decomposition, it was assumed that the rate expression might be given in terms of the amount of reactants where eqns. 22 and 23 apply.

$$\frac{(E^*/R)\Delta(1/T)}{\Delta\ln n_a} = \frac{-x + \Delta\ln(-dn_a/dt)}{\Delta\ln n_a} \qquad (22)$$

$$\text{In } k = -x \ln n_a + \ln(-dn_a/dt) \qquad (23)$$

where n_a = number of moles A at time t.

The following relationships might be used to relate number of moles of reactant to weight.

$$\frac{-dn_a}{dt} = \frac{n_0}{\varpi_c} - \frac{d\varpi}{dt} \tag{24}$$

$$\text{and} \qquad Wr = \omega_c - \omega$$

where n_0 = initial number of moles of A; ω_c = weight loss at completion of reaction; ω = total weight loss upto time t.

Combing eqns. 24 and 25 with eqn. 22, eqn. 26 was obtained which was used to evaluate the energy of activation.

$$\frac{\frac{E^*}{2.303R}\Delta(1/T)}{\Delta \log Wr} = -x + \frac{\Delta \log dw/dt}{\Delta \log Wr} \tag{25}$$

Freeman and Carroll's method is the plot of

$$\frac{\Delta \log dw/dt}{\Delta \log Wr} \text{VS} \frac{\Delta(1/T)}{\Delta \log Wr} \tag{26}$$

For the purpose of this plot, dw and Wr can be determined directly from the thermogram in terms of the number of divisions. The activation energy calculation from TG curves of the film are given in Tables 1 and 2. From Figs. 2-5 shows the activation energy curve of polyimide film by different method. The activation energy of this polyimide film by Murray and White is 3.270 k cal/mol, by Coats and Redfern method is 3.407 k cal/mol, by Dolyes method 3.702 k cal/mol and by Freemans and Carrols method is 10.738 k cal/mol. The activation energies obtained from Murray and White, Coats and Redfern and Doyles method are all in good agreement with each other with in the experimental error. The large difference in the Freeman

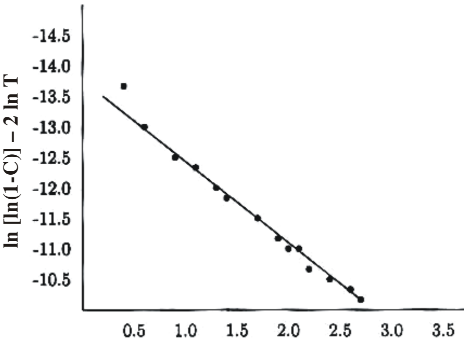

Fig. 2. Activation energy curve (by Murray and white method) of ABTD-DAP

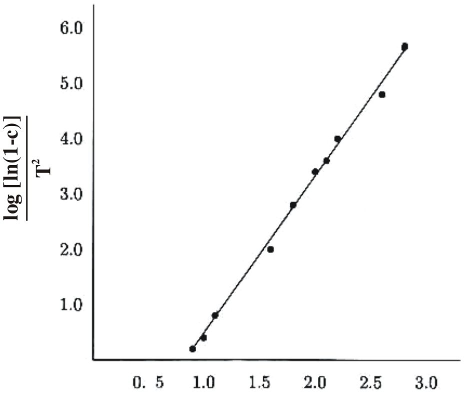

Fig. 3. Activation energy curve (by Coats and Redfern method) of ABTD-DAP

TABLE-1
CALCULATION OF ACTIVATION ENERGY FROM TG CURVE OF ABTD-DAP

Decomposition (%)	Temp. (t) (ºC)	T = t + 273 K	T^2	$1/T \times 10^{-3}$	1-C	ln T	2 ln T	ln (ln (1-C)] – 2 ln T Murray & White	$\frac{\log [\ln (1-C)]}{T^2}$ Coats & Redfern	log (ln (1-C)] Doyle's Method
5	70	343	117649	2.900	95	5.8370	121.6750	-10.15902	5.59×10^{-6}	0.6580
10	108	381	145161	2.600	90	5.9420	11.8850	-10.3809	4.49×10^{-6}	0.6530
15	138	411	168921	2.400	85	6.0185	12.0370	-10.5457	3.83×10^{-6}	-/647
20	180	455	207025	2.190	80	6.1202	12.2405	-10.7628	3.09×10^{-6}	0.6416
25	193	466	217156	2.140	75	6.1441	12.2880	-10.8253	2.92×10^{-6}	0.6352
30	220	493	243049	2.020	70	6.2005	12.4010	-10.9544	2.58×10^{-6}	0.6282
35	310	583	339889	1.780	65	6.3681	12.7363	-11.3073	1.82×10^{-6}	0.6280
40	350	623	388129	1.600	60	6.4345	12.6690	-11.4593	1.57×10^{-6}	0.6120
45	420	693	4800249	1.440	55	6.5410	13.0800	-11.6918	1.25×10^{-6}	0.6020
50	525	798	636804	1.250	50	6.6.821	13.3640	-11.999	0.93×10^{-6}	0.5920
55	570	843	710649	1.180	45	6.7369	13.4730	-12.1676	0.81×10^{-6}	0.5805
60	750	1023	10467529	0.097	40	6.93049	13.8609	-12.5557	0.54×10^{-6}	0.5660
65	1090	1363	1857769	0.070	35	7.21744	14.4340	-13.1655	0.29×10^{-6}	0.5508
70	1400	1673	2798929	0.050	30	7.4223	14.8440	-13.6198	0.18×10^{-6}	0.5316

TABLE-2
CALCULATION OF ACTIVATION ENERGY (BY FREEMAN AND CARROL METHOD) FROM TG CURVES OF ABTD-DAP

Time, t (min)	Temp. t (ºC)	T = t+273 K	$1/T \times 10^3$ K	$1/\Delta T$	ω_r (mg)	$\log \omega_r$	$\Delta \log \omega_r$	log dw/dt	Δ log dw/dt	$\frac{1/\Delta T \times 10^3}{\Delta \log Wr}$ (k^{-1})	$\frac{\Delta \log dw/dt}{\Delta \log Wr}$
7.0	70	343	2.915	0.291	18.164	1.2592	0.0242	-0.599	-0.1027	12.024	-4.243
10.8	108	381	2.624	0.191	17.208	1.235	0.0241	-0.496	-0.1461	7.925	6.06
13.8	138	411	2.433	0.236	16.252	1.2109	0.0264	-0.642	-0.5093	8.939	-19.29
18.0	180	455	2.197	0.052	15.296	1.1845	0.028	-0.1334	0.3175	1.857	11.339
19.3	193	466	2.145	0.117	14.34	1.1565	0.03	-0.450	0.5228	3.9	17.42
22.0	220	493	2.028	0.313	13.384	1.1265	0.0321	-0.973	-0.3521	9.75	-10.968
31.0	310	573	1.715	0.136	12.428	1.0942	0.0348	-0.6216	0.243	3.90	6.982
35.0	350	623	1.605	0.162	11.472	1.0596	0.078	-0.864	0.1761	2.076	2.2576
42.0	420	693	1.443	0.19	10.516	1.0218	0.95	-1.0407	-0.368	0.2	-0.387
52.5	525	798	1.253	0.0668	9.56	0.9804	0.0414	-0.672	0.6021	1.613	14.543
57.0	570	843	1.1862	0.2092	8.604	0.9347	0.0457	-1.274	0.2762	4.57	6.043
75.0	750	1023	0.977	0.244	7.648	0.8835	0.058	-1.551	-0.04012	4.206	-0.6917
109.0	1090	1363	0.733	0.1353	6.692	0.8255	0.0669	-1.5109	–	2.022	–
140.0	1400	1673	0.5977	–	5.736	0.7586	–	–	–	–	–

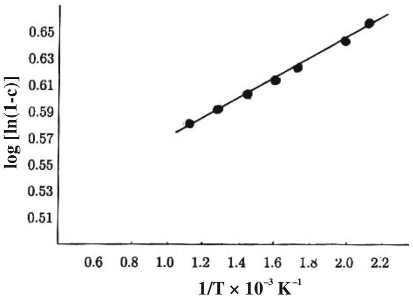

Fig. 4. Activation energy curve (by Doyle's method) of ABTD-DAP

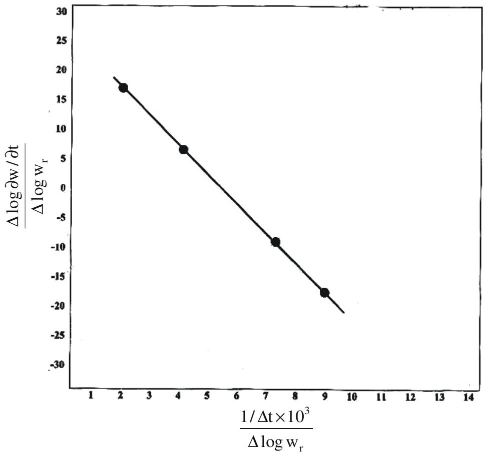

Fig. 5. Activation energy curve (by Freeman and Carrol method) of ABTD-DAP

and Carrols method is found to be the determination of the difference differential functions over short temperature intervals[6,7]. One of these is the tangent dw/dt. Therefore, any inaccuracy in determining a single value for dw/dt effects the position of the two points in the plots which are needed to determine the activation energy. Hence freeman and carrolls method shows less satisfactory and of limited applicability[8].

Conclusion

The energy of activation for the major decomposition reaction steps was calculated by various methods. The activation analysis obtained from these methods are all in good agreement with each other within the experimental error.

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