A Study on the Thermal Imidization of Polyimide

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Polyimide is a polymer material with outstanding electrical property, thermal stability and distinguished synthetical properties. It is widely applied in semiconductive devices for surface protection, interlayer insulation and alignment film for LCD. Polyimide is most commonly applied by coating a polyamic acid solution followed by a thermal imidization. The imidization process possesses great influence upon the property of the coating. To optimize the process and to assure the property of the coating, the imidization of several types of polyimide was studied and the kinetic parameters of the imidization process were calculated using a macroscopic statistical treatment. Because polyamic acid obtained from polar solvents (such as DMA) usually contains large amount of residue solvent. The solvent, which bonded with polyamic acid through hydrogen bond, is difficult to remove even at a raised temperature. Therefore, the kinetic parameters obtained in the analysis represent the apparent process containing imidization and evaporation. Because in an actual application precedure, thermal imidization process does contain evaporation of the solvent and the imidization of polyamic acid, the study on the apparent process has theoretical significance.

1. Experimentation

0.01mol 4,4'-diamino-3,3'-dimethyldiphenylmethane was dissolved in 35ml DMF and cooled to 0 ℃. To it, 0.01mol benzophenone-3,3',4,4'-tetracarboxylic acid dianhydride was added. The reaction was maintained for 4 hours with the efficient agitation. The resultant polyamic acid was then poured into anhydrous ethanol, filtered and dried in a vacuum oven at 45 ℃ for 3 hours.

The isothermal TGA curves of the polyamic acid samples were carried out on a Perkin Elmer TGA7 Thermal Analyzer.

2. Results and Discussion

(1). TGA Curve Using Linear Temperature Scan

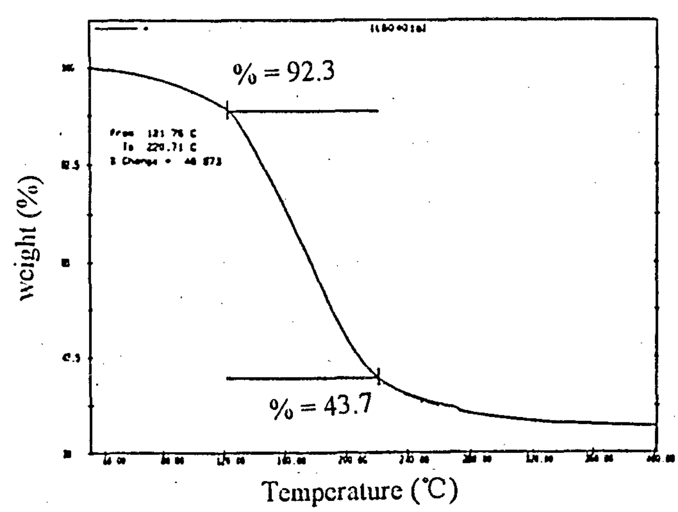

Figure 1 TGA Curve of PSPI-1 Under Linear Temperature Rise

Figure 1 is the TGA curve of PI-1 with a scan rate of 20 ℃/min. The curve may be divided into three parts. The weight loss during the part 1 (room temperature ~ 120 ℃) was observed to be 7.7%; During the part 2 (120 ~ 250 ℃), the system lost 48.6% of its weight. The curve became flatted in part 3 (250 ~ 400 ℃). It could be suggested that the weight loss in part 1 was due to remaining solvent and moisture absorbed; The weight loss in part 2 was resulted from the evaporation of the small molecules formed in the imidization process. Therefore, part 2 represents the main part in which the imidization reaction happens. The appearance of the platform in part 3 means that the imidization reaction is close to finish.

(2). Dynamic Study of the Imidization Reaction

The isothermal TGA curves of PSPI-1 were recorded at 120 ℃, 170 ℃, 180 ℃, 190 ℃ and 200 ℃. It was observed that with the increase of imidization time, the weight increased and the speed of the weight loss decreased. The imidization was finished within 15 minutes at all temperature except 120 ℃. From the isothermal TGA curves, the weight loss and the speed of the weight loss at a certain time can be obtained. The results were listed in Table 1.

Table 1. Isothermal Weight Loss of PI-1 at Various Temperatures

T (℃)	170 ℃		180 ℃		190 ℃		200 ℃		120 ℃	
t (min)	Gt (%)	dGt/dt (%/min)	Gt (%)	dGt/dt (%/min)	Gt (%)	dGt/dt (%/min)	Gt (%)	dGt/dt (%/min)	Gt (%)	dGt/dt (%/min)
1.25			14.31	18.67	15.85	23.5				
1.50	15.23	19.50	19.33	19.00	23.12	26	42.02	18.67	10.74	5.40
1.75			23.38	10.50	28.51	18.00	46.72	12		
2.00	22.73	16.3	27.36	15.50	32.34	16.33	48.94	6.5	13.56	6.00
2.26					36.24	11.5	50.16	4.5		
2.50	27.68	8.5					51.01	3	15.7	4.80
2.75							51.72	2.5		
3.00	31.39	6.5	37.47	6.00	41.85	5.5	52.24	1.33	17.66	3.5
3.27							52.73	1.67		
3.50	34.23	5	40.06	6.00	44.11	4.00			19.31	3.8
4.00	36.46	2.67	41.86	3.5	45.72	2.00	53.66	1.00	20.85	2.2
4.50	38.3	2.33	43.28	1.67	47.00	1.33	54.13	0.667	22.19	3.2
5.00	39.68	2.5	44.46	2.00	48.00	2.00				
5.51	40.93	2					54.85	1.00	24.67	2.00
6.5	42.78	1.5	46.82	1.5	50.18	1.5			26.52	1.4
7.50	44.24	1.5	47.98	1.00	51.24	1.00			28.32	1.5
9.00	45.94.	1	49.30	0.33	52.47	0.5			30.6	1.00
10.0	47.58	1	50.64	0.5	53.63	0.5			31.95	1.2
13.0	48.83	0.5	51.64	0.5					35.18	0.6
15.0	49.79	0.5							36.93	0.6

If the degree of the imidization reaction (P) at time t equals to the ratio of the weight loss (at time t) and the total weight loss of the imidization reaction,

$$P=(G_t-G_0)/(G_E-G_0)$$

where G_0 is the weight of the remaining solvent and the moisture absorbed, or the weight loss in part 1 of Figure 1; G_E is the total weight loss of the process, which is the sum of the weight loss of the three parts. Then the speed of the imidization reaction is

$$dP/dt = (dGt/dt)/(G_E-G_0)$$

where dP/dt is the speed of the imidization reaction and dGt/dt is the speed of the weight loss at time t. From the basic kinetic equation of a chemical reaction and Areniuss Equation, we have

$$\ln(dP/dt) = \ln K + n\ln(1-P) \text{ and}$$

$$\ln K = \ln A + E/RT$$

where n is the order of the reaction.

ln(dP/dt) ～ ln(1-P) and the fitted lines were plotted in Figure 2. lnK ～ 1/T and the fitted lines were plotted in Figure 3. From the two figures, following kinetic parameters of the imidization reaction were obtained:

The average order of the reaction (n) is 1.99; A is 4 × 106s-1; The activation energy of the imidization reaction E is 57.2kJ/mol.

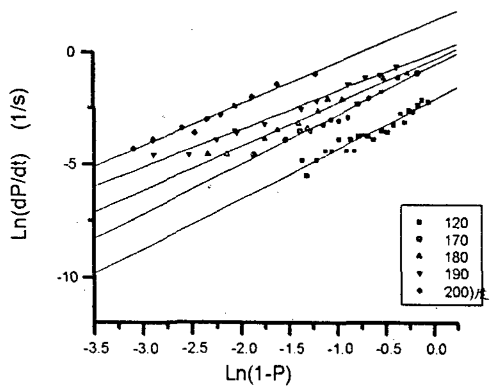

Fig.2 ln(dp/dt) ～ln(1-P) and Fitted Lines

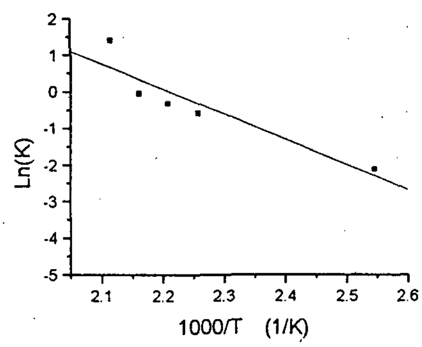

Figure 3 ln(K)～ 1000/T and Fitted Lines

3. Conclusions

(1). The imidization reaction of PSPI-1 happens mainly at a temperature range of 120 ～ 250 ℃.

(2). The reaction order of the imidization of PSPI-1 is a non-integral number between 1.5 and 2.5 and changes with the change of the temperature.

(3). The activation energy of the imidization reaction is 57.2kJ/mol.

(4). The imidization reaction of PSPI-1 can be finished at 200 ℃ for 1 hour.