

Thermochemical study on the properties of polyimide BPADA-*m*-PDA

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Abstract

The heat capacity of a polyimide BPADA-*m*-PDA sample, prepared by polycondensation or step-growth polymerization method, is reported for the temperature range between 80 and 380 K. No thermal anomaly was found in this temperature range. A complementary DSC experiment was conducted in temperature region from 373 to 623 K. There was no phase change in this temperature range. A glass transition was observed at 492.42 K. To study the decomposition characteristics of BPADA-*m*-PDA, a TG experiment was carried out and it was found that this polyimide started to decompose at 630 K. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Polyimides belong to a class of polymers known as polyheterocyclics. Since their initial disclosure in the later 1950s, hundreds of polyimides with different chemical structure and molecular order (morphology) and accordingly, different physical, mechanical and chemical properties have been reported [1–3]. Polyimides possess excellent stability in a high temperature environment. Initial applications were in the electrical field where higher temperature insulation was needed. High temperature organic polymers were also required for use in structural components in advanced high speed aircraft, weapon systems and space vehicles.

Although many different families of high temperature polymers have been discovered, polyimides have attracted the attention of the scientific community. Their popularity arises as a result of a unique combination of thermal stability, chemical and solvent resistance, mechanical properties, reasonable cost and the ability to be processed into useful forms. Unlike most other high temperature polymers, polyimides can be prepared from a variety of inexpensive monomers by several synthetic routes. By judicious choice of starting materials, a polyimide can be tailor-made for a specific application. For example, the glass transition and crystalline melt temperature, thermo-oxidative stability, toughness, dielectric constant, coefficient of thermal expansion, chemical stability, mechanical performance, etc. of polyimides can be controlled within certain boundaries. This versatility has permitted the development of various forms of polyimides. These

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include adhesives, composite matrices, coatings, films, moldings, fibers, foams and membranes.

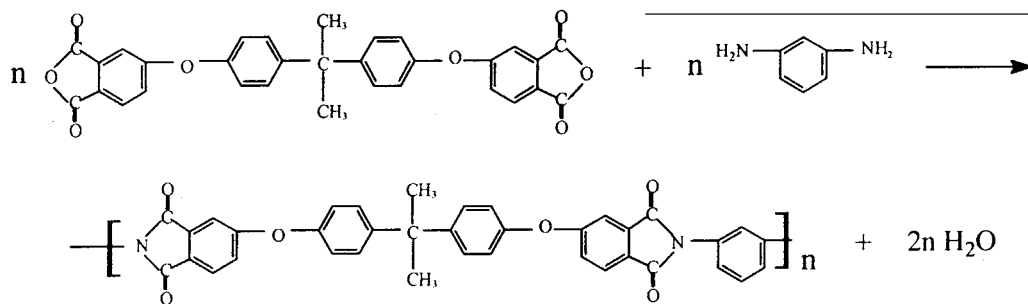
In the present paper, condensation polyimide bisphenol A dianhydride *m*-phenylene diamine (BPADA-*m*-PDA) sample was prepared. Some thermodynamic properties such as low temperature heat capacity and thermal stability at higher temperature were studied by calorimetry and thermal analysis methods. The reported results may be helpful for further study and application of polyimides.

2. Experimental

2.1. Sample preparation

All reagents used, *m*-phenylene diamine (*m*-PDA), *o*-dichlorobenzene, bisphenol A dianhydride (BPADA) were of analytical grade.

A certain amount of *m*-PDA was dissolved in *o*-dichlorobenzene. Then same moles of BPADA were added into the solution, that was heated to 180 °C for 4 h. The solid substance was separated from the liquid and washed by distilled water and subsequently dried. The synthesis route is,



The density of modeled material of the sample was measured to be 1.359 g cm⁻³. To characterize the structure of the sample, an X-ray diffraction measurement was carried out as shown in Fig. 1. The result indicates that this sample was a glassy state polymer basically.

2.2. Measurements

A low-temperature adiabatic calorimeter was used to measure the heat capacity of the sample. The calorimetric apparatus and measuring technique have

been described in detail [4,5]. Briefly, it is an adiabatic calorimeter with intermittent energy inputs and temperature equilibration after each input. The calorimeter cell, with an internal volume of ca. 6 ml, was made of gold plated silver with a Y-shape fin inside. Adhesive was used to seal the lid, which contained a copper capillary tube, to the loaded calorimeter. This assembly was evacuated through the capillary and then filled with helium gas in order to keep good thermal conductivity. The capillary was pinched off and soldered with tin. The outer wall of the sample cell was screened with brilliant aluminum foil to eliminate heat radiation.

The calorimeter-cell assembly was suspended inside an inner adiabatic shield, which was in turn surrounded by an outer adiabatic shield. All of these were housed in a high vacuum vessel. The temperature differences between the calorimeter cell and the inner shield and between the inner and outer shields were measured by means of two sets of eight junctions of chromel–constantan thermopiles installed between them. The amplified signals were used for automatic control of the shield heaters in a PID (proportional-integral-differential) mode during energy input and drift periods. The electrical energy supplied to the calorimeter cell and the temperature of the calorimeter

of the cell were measured and processed automatically by a personal computer with a digital multimeter. Measurements of the heat capacities of α -alumina and *n*-heptane, two internationally accepted heat capacity standard reference materials, showed a precision of $\pm 0.1\%$ and agreed with those of the National Institute Science and Technology (formerly NBS) to within $\pm 0.2\%$.

In the present study, 1.6457 g BPADA-*m*-PDA sample was used to measure low temperature heat capacities in temperature region from ca. 80 to ca. 380 K.

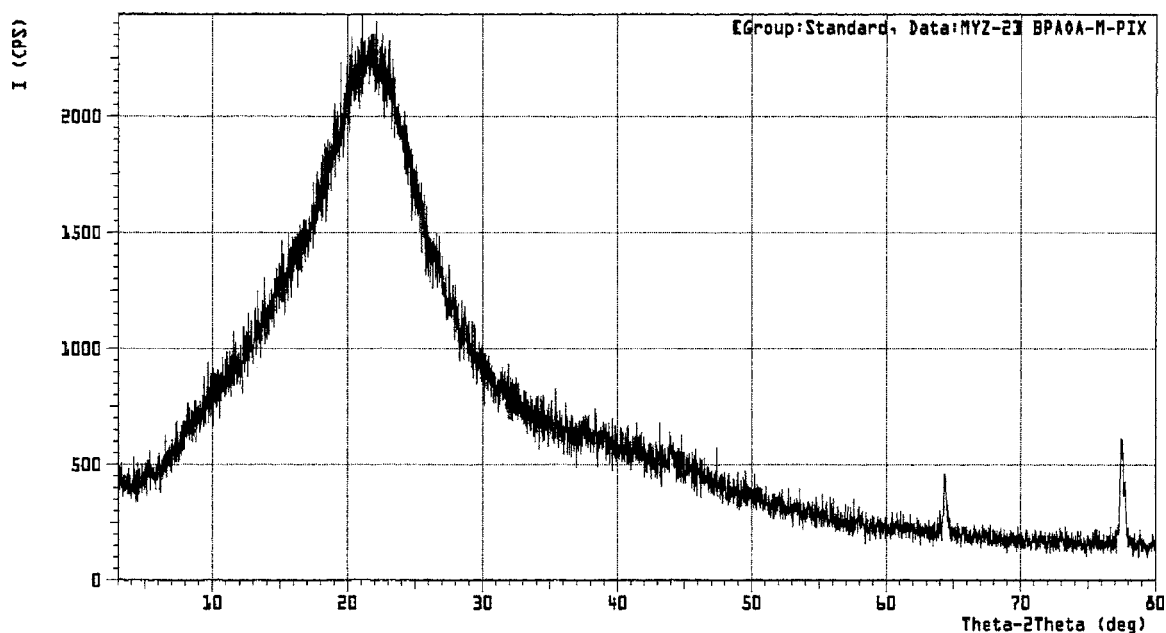


Fig. 1. Result of X-ray diffraction of BPADA-*m*-PDA.

To study the thermal stability, TG and DSC experiments were carried out. The thermogravimetric measurements were conducted on a DT-20B (Shimadzu, Japan) instrument with 9.50 mg sample at a heating rate of 10.0 K min⁻¹ in nitrogen ambient. The DSC measurements were carried out by 7 Series Thermal Analysis System (PERKIN-ELMER Instruments). The sample weight were 10.24 mg and heating rate was 10.0 K min⁻¹.

3. Results and discussion

Two series of experiments were carried out to determine the heat capacities of the sample in the temperature range from 80 to 380 K. The sample was cooled down to ca. 80 K using different cooling rates, ca. 0.1 and 10 K min⁻¹, in the two series. No difference between the two series was found. The maximum deviation between the two series was not more than 0.1%. The experimental results of one (cooling rate: 0.1 K min⁻¹) of the two series of measurements are shown in Fig. 2 and listed in Table 1.

Fig. 2 shows that there is no heat capacity anomaly in the experimental temperature range. This indicates

that polyimide BPADA-*m*-PDA has stable molecular structure in the temperature between 80 and 380 K.

To examine thermal activity of BPADA-*m*-PDA in higher temperature range and its thermal decomposition characteristics, DSC and TG experiments were carried out. The results are shown in Figs. 3 and 4, respectively.

The DSC result (Fig. 3) indicates that BPADA-*m*-PDA was thermally stable in the temperature range between 373 and 623 K, except a small glass transition. The glass transition temperature was 492.42 K and corresponding heat capacity increment was 0.280 J g⁻¹ K⁻¹. The glass transition started at 471.55 K and ended at 504.65 K. Compared with similar structure polyimide [6] poly-*s*-benzene tetracarboxylic acid anhydride *p*-phenylene diamine ($T_g = 280^\circ\text{C}$) BPADA-*m*-PDA glass transition temperature was about 82 K lower than that the reason may be the introduction of ether bond in the molecular structure. Therefore, BPADA-*m*-PDA is easier to process at lower temperature.

Fig. 4 shows the TG result. It is obvious that polyimide BPADA-*m*-PDA was thermally stable in air below 630 K. This temperature is about 100 K lower than that of another polyimide—polypyromellitimide

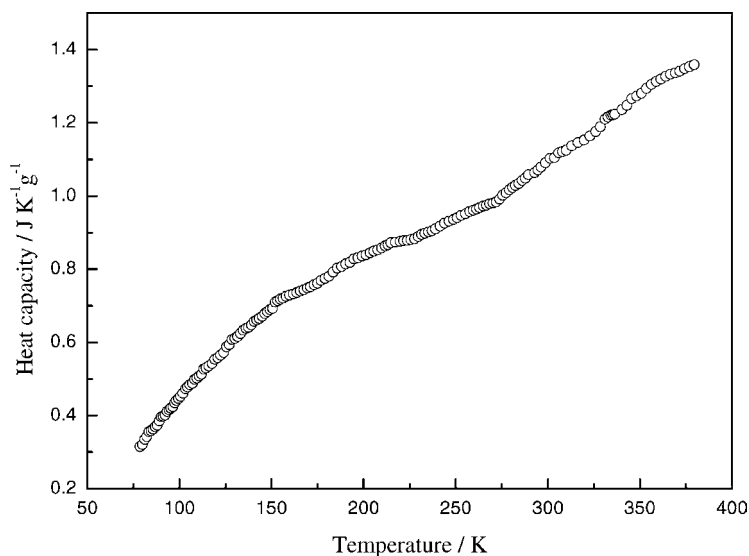


Fig. 2. Heat capacity of polyimide BPADA-*m*-PDA.

[7]. However, polypyromellitimide decomposition was completed in a temperature interval of about 318 K (began at 716 K and ended at 1034 K) and polyimide BPADA-*m*-PDA decomposition was not completed even in a broad temperature interval of about 646 K (from 630 K to 1276 K). This difference is caused by their different molecular structure.

The above experimental results reveal that polyimide BPADA-*m*-PDA has not only excellent thermal stability in higher temperature ambient up to 630 K, but also possess good performance in lower temperature down to ca. 80 K. This information may be very helpful to the utilization of polyimide BPADA-*m*-PDA in engineering and industries.

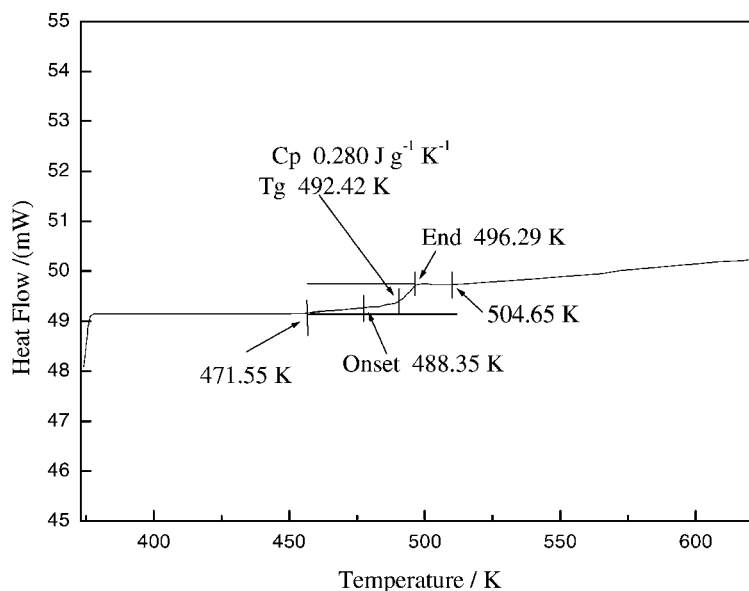


Fig. 3. DSC experiment result of polyimide BPADA-*m*-PDA.

Table 1
 Experimental data of heat capacities of polyimide BPADA-*m*-PDA

T (K)	c_p (J K ⁻¹ g ⁻¹)	T (K)	c_p (J K ⁻¹ g ⁻¹)	T (K)	c_p (J K ⁻¹ g ⁻¹)
78.765	0.315	150.616	0.698	261.328	0.964
79.991	0.321	151.997	0.709	263.133	0.968
81.213	0.335	153.359	0.714	264.935	0.973
82.394	0.343	154.717	0.718	266.729	0.975
83.571	0.356	156.258	0.721	268.520	0.979
84.711	0.359	158.000	0.726	270.304	0.981
85.847	0.363	159.928	0.729	272.081	0.984
86.962	0.369	161.851	0.732	273.849	0.992
88.074	0.374	163.755	0.736	275.613	1.002
89.162	0.385	165.654	0.741	277.372	1.009
90.247	0.397	167.534	0.744	279.126	1.017
91.307	0.399	169.408	0.749	280.878	1.023
92.366	0.402	171.295	0.752	282.624	1.029
93.406	0.411	173.181	0.758	284.360	1.034
94.442	0.416	175.077	0.762	286.090	1.042
95.462	0.420	176.974	0.769	287.809	1.049
96.478	0.424	179.055	0.775	289.523	1.058
97.480	0.435	181.171	0.781	291.231	1.061
98.480	0.441	183.470	0.792	292.930	1.064
99.519	0.446	185.766	0.803	294.629	1.071
100.755	0.453	188.033	0.807	296.325	1.079
102.031	0.461	190.295	0.814	298.635	1.091
103.302	0.473	192.538	0.819	301.259	1.103
104.561	0.478	194.778	0.828	303.572	1.105
105.817	0.484	196.993	0.831	305.880	1.118
107.073	0.488	199.204	0.836	307.921	1.121
108.325	0.499	201.352	0.839	309.957	1.125
109.585	0.502	203.497	0.845	313.074	1.137
110.815	0.508	205.587	0.849	316.361	1.146
112.036	0.513	207.673	0.853	319.629	1.153
113.253	0.527	209.718	0.858	322.883	1.164
114.472	0.530	211.760	0.864	325.991	1.176
116.078	0.535	213.277	0.867	328.582	1.189
117.687	0.542	214.790	0.872	331.074	1.21
119.292	0.554	217.295	0.874	332.733	1.216
120.882	0.558	219.798	0.876	334.387	1.221
122.470	0.565	221.781	0.878	335.292	1.222
124.043	0.572	223.759	0.879	336.357	1.224
125.611	0.588	225.729	0.881	340.229	1.236
127.156	0.594	227.695	0.883	342.935	1.248
128.694	0.608	229.633	0.889	345.629	1.266
130.208	0.611	231.568	0.895	348.290	1.273
131.718	0.616	233.455	0.898	350.947	1.281
133.213	0.624	235.339	0.902	353.591	1.294
134.702	0.633	237.186	0.905	356.225	1.305
136.178	0.638	239.028	0.910	358.834	1.313
137.648	0.641	241.516	0.918	361.439	1.320
139.108	0.648	243.999	0.926	364.022	1.327
140.565	0.657	246.405	0.931	366.600	1.333
142.026	0.661	248.806	0.936	369.155	1.337
143.484	0.666	250.894	0.941	371.707	1.341
144.941	0.671	252.978	0.947	374.286	1.348
146.392	0.679	255.335	0.952	376.827	1.353
147.813	0.684	257.691	0.958	379.365	1.359
149.231	0.690	259.511	0.961		

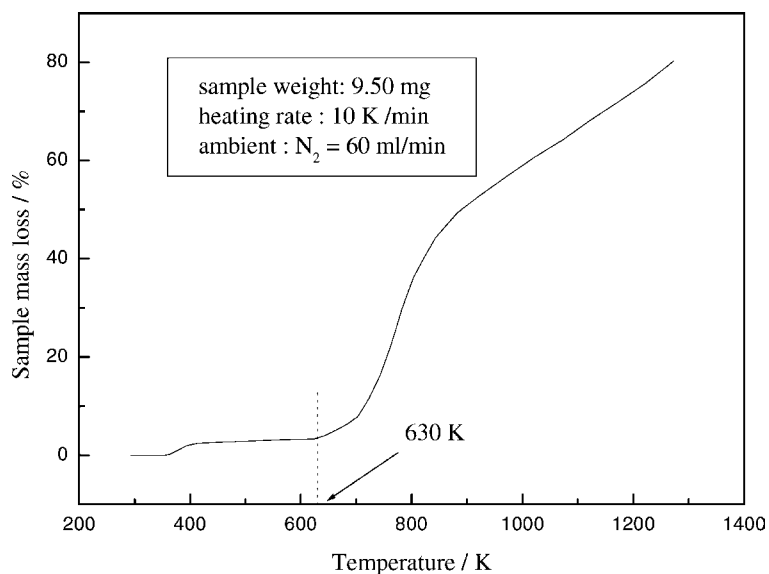


Fig. 4. TG experiment result of polyimide BPADA-*m*-PDA.

4. Conclusions

Polyimide BPADA-*m*-PDA is a polymer with excellent thermal stability, both in higher and lower temperature environment. From temperature down to 80 K to temperature up to 630 K, there was no phase change and other thermal anomaly except a small glass transition at 492.42 K. This polymer began to decompose at ca. 630 K, but the decomposition was not completed until ca. 1276 K.

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