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A STUDY ON THE THERMODYNAMIC PROPERTIES OF POLYIMIDE BTDA-ODA BY ADIABATIC CALORIMETRY AND THERMAL ANALYSIS

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Abstract

Polyimide BTDA-ODA sample was prepared by polycondensation or step-growth polymerization method. Its low temperature heat capacities were measured by an adiabatic calorimeter in the temperature range between 80 and 400 K. No thermal anomaly was found in this temperature range. A DSC experiment was conducted in the temperature region from 373 to 673 K. There was not phase change or decomposition phenomena in this temperature range. However two glass transitions were found at 420.16 and 564.38 K. Corresponding heat capacity increments were 0.068 and 0.824 J g^{-1} K^{-1}, respectively. To study the decomposition characteristics of BTDA-ODA, a TG experiment was carried out and it was found that this polyimide started to decompose at ca 673 K.

Keywords: low temperature adiabatic calorimetry, polyimide, thermal analysis, thermodynamic property

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 structures and molecular orders (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 disclosured, polyimides have attracted the attention of the scientific community. Their

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

In the present paper, condensation polyimide poly-benzophenone-3,3',4,4'-tetracarboxylic acid dianhydride and 4,4'-diaminodiphenyl ether (BTDA-ODA) 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.

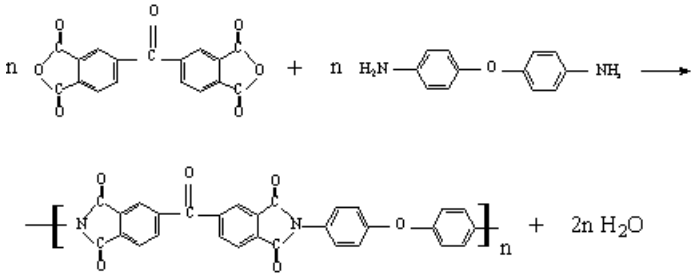
Experimental

Material

In the experiment, all reagents used were of analytical grade. They included benzophenone-3,3',4,4'-tetracarboxylic acid dianhydride (BTDA), 4,4'-diaminodiphenyl ether (ODA) and pyridine.

Sample preparation method

BTDA-ODA was first time synthesized by present authors with polycondensation method. The process is described as following. A certain amount of ODA was dissolved in solvent pyridine. Then the same amount of moles of BPADA was added into the solution. The solution was stirred for 4 h at room temperature and polyamide acid was produced. Heated the mixture to 140°C and kept for 4 h to form polyimide. Then the solid substance was separated from the liquid. By drying the solid material, polyimide BTDA-ODA sample was obtained. The purity of the sample was higher than 98%. The synthesis route is,



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 input 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 international accepted heat capacity standard reference materials, showed a precision of ±0.1 per cent and agreed with those of the National Institute Science and Technology (formerly NBS) to within ±0.2 per cent.

In the present study, 1.1515 g BTDA-*m*-ODA sample was used to measure low temperature heat capacities in temperature region from ca 80 to ca 400 K.

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 9.40 mg sample at a heating rate of 10.0 K min^{-1} in ambient atmosphere. DSC measurements were carried out by 7 Series Thermal Analysis System (Perkin Elmer Instruments). The sample mass was 10.44 mg and heating rate was 10.0 K min^{-1}.

Results and discussion

Heat capacity

Two series of the experiments with different cooling rates of the sample were carried out to determine the heat capacities of the sample in the temperature range from 80 to 400 K. The cooling rate of one series was about 0.1 and another was about 10 K min^{-1}. Some obvious differences between the two situations were found. The experimental results of one of the two series of measurements are listed in Table 1.

Table 1 Experimental data of heat capacities of polyimide BTDA-ODA 58

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}
78.013	0.362	151.157	0.652	256.575	0.889
78.859	0.366	152.665	0.658	258.577	0.900
79.664	0.371	154.134	0.664	260.538	0.911
80.481	0.374	155.590	0.666	262.523	0.913
81.258	0.378	157.007	0.669	264.468	0.915
82.158	0.384	158.733	0.672	266.436	0.918
83.018	0.391	160.418	0.676	268.365	0.921
83.990	0.397	162.443	0.679	270.313	0.924
84.923	0.403	164.428	0.683	272.221	0.928
85.873	0.409	166.425	0.687	274.145	0.930
86.783	0.415	168.382	0.692	276.029	0.933
87.713	0.419	170.350	0.698	277.931	0.941
88.608	0.424	172.278	0.704	279.793	0.949
89.521	0.429	174.226	0.708	281.672	0.952
90.393	0.435	176.134	0.713	283.512	0.956
91.287	0.437	178.069	0.718	285.372	0.961
92.142	0.439	179.965	0.724	287.191	0.967
93.022	0.442	181.884	0.730	289.061	0.971
93.862	0.446	183.762	0.736	290.892	0.976
94.727	0.450	185.664	0.741	292.742	0.980
95.553	0.454	187.526	0.747	294.552	0.985
96.679	0.460	189.410	0.750	296.494	0.994
97.766	0.466	191.254	0.754	298.396	1.003
99.149	0.477	193.126	0.758	301.493	1.008
100.492	0.489	194.959	0.763	304.550	1.014
101.845	0.495	196.823	0.767	307.589	1.017
103.157	0.501	198.646	0.771	310.589	1.020
104.484	0.506	200.503	0.775	313.569	1.031
105.771	0.511	202.321	0.780	316.509	1.043
107.064	0.518	204.174	0.784	319.439	1.050
108.318	0.526	205.987	0.789	322.329	1.058
109.821	0.528	207.830	0.795	325.217	1.065
111.285	0.531	209.633	0.801	328.065	1.072
113.061	0.536	211.458	0.803	330.916	1.080
114.798	0.542	213.242	0.805	333.727	1.089

Table 1 Continued

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}
116.479	0.547	215.054	0.807	336.543	1.096
118.121	0.553	216.826	0.809	339.318	1.104
119.714	0.561	218.619	0.810	342.104	1.111
121.266	0.569	220.372	0.812	344.850	1.118
122.887	0.575	222.181	0.817	347.634	1.121
124.468	0.581	223.949	0.823	350.378	1.124
126.060	0.586	225.703	0.826	353.175	1.129
127.612	0.591	227.416	0.829	355.932	1.135
129.181	0.595	229.147	0.832	358.727	1.142
130.709	0.599	230.837	0.835	361.483	1.149
132.256	0.602	232.531	0.838	364.273	1.154
133.764	0.606	234.185	0.841	367.023	1.159
135.293	0.610	235.868	0.843	369.803	1.161
136.781	0.614	237.511	0.846	372.543	1.163
138.291	0.617	239.215	0.849	375.293	1.164
139.762	0.621	240.880	0.853	378.002	1.167
141.227	0.625	242.729	0.857	380.727	1.170
142.651	0.629	244.537	0.861	383.412	1.173
144.108	0.633	246.552	0.864	386.139	1.179
145.525	0.637	248.527	0.868	388.826	1.185
146.946	0.640	250.572	0.873	391.536	1.189
148.327	0.644	252.578	0.878	394.206	1.194
149.762	0.648	254.597	0.883	398.827	1.215

The experimental result shows that there is not any heat capacity anomaly in the experimental temperature range. This indicates that polyimide BTDA-ODA has stable molecular and crystalline structures in the temperature between 80 and 400 K.

Thermodynamic function

The above experimental values of heat capacities were fitted with the following polynomial expression with least squares method.

$$C_p=0.85081+0.33691X+0.0746X^2+0.24287X^3-0.14701X^4$$
$$-0.40209X^5+9.10743\cdot10^{-4}X^6+0.24684X^7$$

where transformed temperature $X=(T-238)/160$ and T/K is temperature. The definition of the transformed temperature is $X=[T-(T_2+T_1)/2]/[(T_2-T_1)/2]$, where T_1 and T_2

are the integer values of the start and end temperature of the experiment. In the present study, T_1 and T_2 are 78 and 398 K, respectively.

In the present study, the heat capacity near thermodynamic zero point was difficult to obtain. Therefore, only the thermodynamic function data in temperature range from 80 to 400 K were given based on standard state (298.15 K). The results of thermodynamic function $H_{(T)}$–$H_{(298.15)}$, $S_{(T)}$–$S_{(298.15)}$, and $G_{(T)}$–$G_{(298.15)}$ are listed in Table 2.

Table 2 Calculated thermodynamic function results of polyimide BTDA-ODA

T/K	C_p/J K^{-1} g^{-1}	$H_{(T)}$–$H_{(298.15)}$/J g^{-1}	$S_{(T)}$–$S_{(298.15)}$/J K^{-1} g^{-1}	$G_{(T)}$–$G_{(298.15)}$/J g^{-1}
80	0.370	–159.144	–0.878	–88.896
85	0.403	–157.210	–0.855	–84.564
90	0.433	–155.118	–0.831	–80.351
95	0.459	–152.886	–0.807	–76.257
100	0.483	–150.529	–0.782	–72.284
105	0.505	–148.058	–0.758	–68.433
110	0.525	–145.484	–0.734	–64.701
115	0.543	–142.814	–0.711	–61.088
120	0.561	–140.054	–0.687	–57.594
125	0.577	–137.210	–0.664	–54.216
130	0.593	–134.285	–0.641	–50.954
135	0.608	–131.282	–0.618	–47.806
140	0.623	–128.206	–0.596	–44.770
145	0.637	–125.056	–0.574	–41.846
150	0.651	–121.837	–0.552	–39.031
155	0.664	–118.550	–0.530	–36.325
160	0.677	–115.196	–0.509	–33.726
165	0.690	–111.777	–0.488	–31.233
170	0.703	–108.295	–0.467	–28.844
175	0.715	–104.752	–0.447	–26.559
180	0.727	–101.148	–0.427	–24.376
185	0.738	–97.485	–0.406	–22.293
190	0.750	–93.765	–0.387	–20.311
195	0.761	–89.989	–0.367	–18.427
200	0.772	–86.158	–0.348	–16.641
205	0.782	–82.274	–0.328	–14.951
210	0.793	–78.336	–0.309	–13.356
215	0.803	–74.346	–0.291	–11.856

Table 2 Continued

T/K	C_p/J K^{-1} g^{-1}	$H_{(T)}$–$H_{(298.15)}$/J g^{-1}	$S_{(T)}$–$S_{(298.15)}$/J K^{-1} g^{-1}	$G_{(T)}$–$G_{(298.15)}$/J g^{-1}
230	0.834	–62.067	–0.235	–7.913
235	0.845	–57.870	–0.217	–6.781
240	0.855	–53.621	–0.200	–5.738
245	0.866	–49.320	–0.182	–4.785
250	0.877	–44.964	–0.164	–3.920
255	0.888	–40.553	–0.147	–3.143
260	0.899	–36.086	–0.129	–2.453
265	0.911	–31.562	–0.112	–1.849
270	0.923	–26.978	–0.095	–1.332
275	0.935	–22.334	–0.078	–0.899
280	0.948	–17.627	–0.061	–0.552
285	0.960	–12.857	–0.044	–0.289
290	0.974	–8.022	–0.027	–0.111
295	0.987	–3.121	–0.011	–0.017
298.15	0.995	0.000	0.000	0.000
300	1.000	1.846	0.006	–0.006
305	1.014	6.880	0.023	–0.078
310	1.027	11.982	0.039	–0.234
315	1.041	17.152	0.056	–0.472
320	1.054	22.387	0.072	–0.793
325	1.067	27.688	0.089	–1.196
330	1.079	33.053	0.105	–1.682
335	1.091	38.479	0.122	–2.249
340	1.103	43.965	0.138	–2.898
345	1.114	49.507	0.154	–3.627
350	1.124	55.102	0.170	–4.438
355	1.134	60.746	0.186	–5.328
360	1.143	66.437	0.202	–6.299
365	1.151	72.171	0.218	–7.348
370	1.159	77.945	0.234	–8.477
375	1.166	83.757	0.249	–9.684
380	1.173	89.605	0.265	–10.969
385	1.181	95.490	0.280	–12.331
390	1.189	101.412	0.295	–13.769
395	1.198	107.377	0.311	–15.284
400	1.208	113.392	0.326	–16.874

DSC and TG results

To examine the thermal activity of BTDA-ODA in higher temperature range and its thermal decomposition characteristics, DSC and TG experiments were carried out. The results are shown in Figs 1 and 2, respectively.

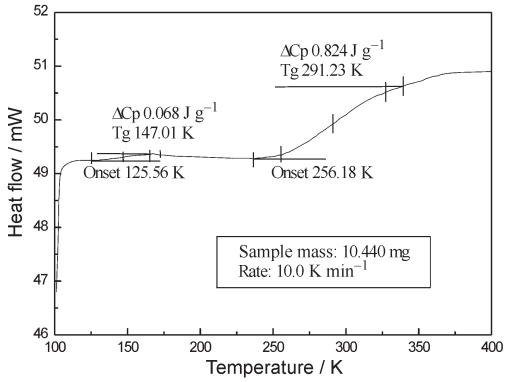


Fig. 1 DSC experiment result of polyimide BTDA-ODA

The DSC result (Fig. 1) indicates that BTDA-ODA was thermally stable in the temperature range between 373 and 673 K. There was not phase change or decomposition in this temperature range. However, there were two glass transitions in this temperature region. The first glass transition occurred at 420.16 K and corresponding heat capacity increment was 0.068 J g^{-1} K^{-1}. This glass transition started at 398.71 and ended at 438.46 K. The second glass transition temperature was 564.38 K and the corresponding heat capacity increment was 0.824 J g^{-1} K^{-1}. The glass transition started at 529.33 and ended at about 600.16 K.

Figure 2 shows the TG and DTG result. It is obvious that polyimide BTDA-ODA was thermally stable in air below 673 K. This temperature is about 40 K lower than that of another polyimide–poly(pyromellitimide) [6]. BTDA-ODA started

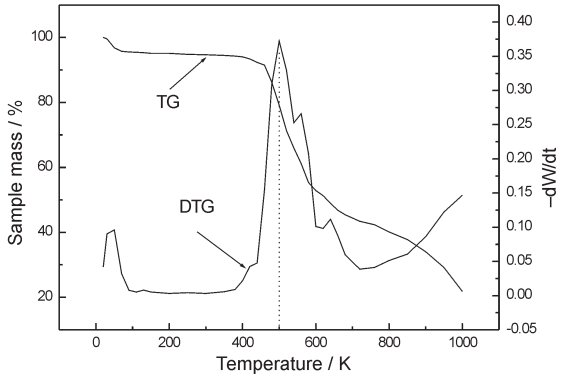


Fig. 2 TG experiment result of polyimide BTDA-ODA

to decompose at ca 673 and the peak temperature was ca 773 K. In DTG curve a small peak was found at 323 K. This sample mass loss peak was attributed to water.

The above experimental results reveal that polyimide BTDA-ODA has not only excellent thermal stability in higher temperature ambient up to 673 K but also possesses good performance in lower temperature down to ca 80 K. Small glass transitions will not have essential effects on its mechanical property and thermal stability. This information may be very helpful to the utilization of polyimide BTDA-ODA in engineering and industries.

Conclusions

Polyimide BTDA-ODA is a polymer with excellent thermal stability both in higher and lower temperature environment. From temperature down to 80 to temperature up to 673 K, there was not phase change and other thermal anomaly except for two small glass transitions at 420.16 and 564.38 K. BTDA-ODA began to decompose at ca 673 K and the decomposition peak temperature was ca 773 K.

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