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Study on thermodynamic properties of polypyromellitimide molding powder

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Abstract

Polypyromellitimide molding powder has been prepared. In the 78–370 K range, the dependence of the specific heat capacity (c_p) on the temperature (T) is given by the polynomial: $c_p=0.8163+0.4592X+0.02468X^2+0.1192X^3+0.05659X^4$ (J K^{-1} g^{-1}), where $X=(T-225.5)/144.5$. Thermal decomposition in air starts at 716 K, and is complete at 1034 K. The standard combustion enthalpy is $\Delta_c H=-26.442$ kJ g^{-1}. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Polypyromellitimide molding powder; High-resistant material; Decomposition temperature; Standard combustion enthalpy; Specific heat capacity

1. Introduction

Polyimides have been studied for more than 40 years [1]. These materials can be synthesized by many methods; they have excellent overall properties and can be molded by a variety of processes. They are widely used in aviation, space flight, the chemical industry, microelectronics, mechanics in general and calorimetry [2].

As the science and technology of polyimides has developed, specific properties have been much investigated, in particular flame retardance, fire-prevention and thermal-isolation at high and low temperatures. It has been found that they have excellent thermal stability in the higher and lower temperature ranges [3]. We have prepared a particular polypyromellitimide molding powder. It has been found that its properties are not affected by heat, oxygen and size change. It can be used in an atmosphere of air over a wide temperature range for a long time, it hardly flames and total combustion leaves nothing except a little nontoxic smoke. It can be manufactured into membranes, and has excellent insulating properties [4].

In order to improve the synthesis of this material and carry out relevant application and theoretical research, accurate thermodynamic properties such as specific heat capacity at low temperatures and some thermodynamic data at higher temperatures are urgently needed. This paper reports heat capacities in the temperature range from 78 (liquid nitrogen) to 370 K determined using an adiabatic calorimeter. Also

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reported are the combustion heat and the standard combustion enthalpy at 298.15 K, which were found using DTA, and oxygen bomb calorimetry and the decomposition range, using TGA.

2. Experimental

2.1. Material

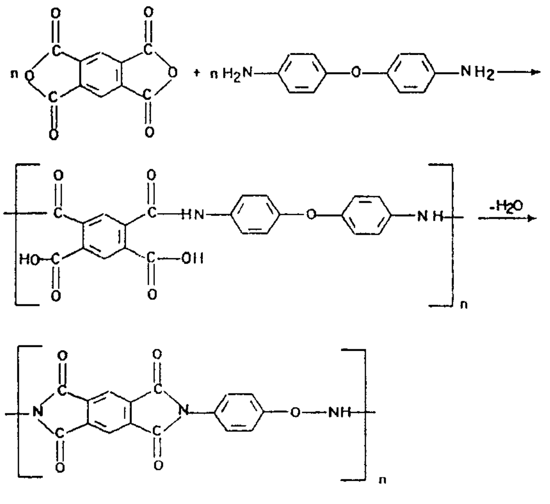
2.1.1. Reagents

Pyromellitic dianhydride, 4,4′-oxydianiline, pyridine.

All reagents used in this work were of analytical grade purity.

2.2. Synthesis

The pyromellitic dianhydride (5.82 g) and the 4,4′-oxydianiline (5.87 g) were mixed and the pyridine solvent (47.6 g) then added. The reaction lasted 1 h at room temperature. After dehydration through distillation, filtration and drying at 413 K, the yellow brown molding powder of polypyromellitimide was obtained. The reaction equation is:



2.3. Measurements

Heat capacities were determined with a precision automatic adiabatic calorimeter. The sample container was a gold-plated copper cylinder with a volume of ca. 6 ml. Within, there was a gold-plated copper vane of a Y-shape. 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 inner and outer walls of the sample cell were screened with brilliant aluminum foil to eliminate heat radiation. A high vacuum was used to prevent heat convection. Differential thermocouples between inner and outer walls were used to control the power supply to the outer walls, thus further reducing heat loss due to conduction and radiation. All processes and calculations were controlled by a computer and completed automatically [6].

Thermogravimetric measurements (TGA) were made using a DT-20B (Shimadzu, Japan) TGA. The recorder rate was 1.25 mm/min. Differential thermal analysis (DTA) was carried out with a DTA-2 (Beijing No.2 Factory of Optical Instruments, China). The recorder rate was 6 mm/min. Both TGA and DTA measurements were carried out in an atmosphere of static air with a common heating rate of 10 K/min.

The heat of combustion was found using a self-made oxygen bomb calorimeter. The pelletized sample was ignited electrically with nickel wire under an initial pressure of 3×10^6 Pa oxygen. Water was used as heat-conducting medium with air as thermal insulation. A thermocouple was used to indicate the temperature difference between the outer and inner cylinders. When the temperature in the inner cylinder began to rise due to combustion, the thermocouple delivered a differential temperature signal to the heater in the outer cylinder so that this was heated and kept at the same temperature as that of the inner cylinder. The temperature of the inner cylinder was measured by a precision Pt resistance thermometer linked with a digital multimeter (7150, Schlumberger Electronics (UK) Ltd. Farnborough, Hampshire, England). The energy equivalent of the empty calorimeter was determined by burning a benzoic acid calorimetric standard (purity 99.992%, 26.437 kJ g^{-1}). The experimental results were corrected using a Reginald diagram. The acid–base titration and the correction for electrical ignition heat of nickel wire were made with the aid of a computer [5]. The measuring inaccuracy of the calorimeter was ±0.1%.

3. Results and discussion

The precision automatic adiabatic calorimeter was used to measure 86 heat capacities in the temperature range from 78–370 K. They are shown in Table 1 and Fig. 1.

The polynomial equation showing the change of heat capacity with temperature was obtained by a least squares procedure:

$$c_p = 0.8163 + 0.4592X + 0.02468X^2 + 0.1192X^3 + 0.05659X^4 \quad (\mathrm{JK^{-1}\,g^{-1}})$$

where $X=(T-225.5)/144.5$.

The smoothed values of specific heat capacities from 78–370 K can be calculated from the above equation. The relative error between the measured experimental values and the smoothed values was within ±0.3%.

TGA and DTA curves for the polypyromellitimide molding powder are shown in Figs. 2 and 3, respectively. It is clear from the TGA results that the molding powder was stable in air below 716 K, but began to decompose intensely at 767 K. There was an inflexion at 823 K and decomposition was complete (100%) at 1034 K.

DTA results (Fig. 3) confirm that polypyromellitimide molding powder was stable in air below 716 K. Two angular and intense exothermic bands, peaking at 832 and 1020 K, respectively, start at 767 and end at 1033 K. The start and end temperatures of mass loss in the TG curve are nearly equal to the onset and end temperatures in the DTA curve.

The released heat of polypyromellitimide molding powder at 767 K, 5.56 kJ g^{-1}, was obtained by diagrammatic area integration. This can be converted to the value at 298.15 K, ca. 26 kJ g^{-1}, by the use of Kirchhoff‘s law [7].

The standard combustion enthalpy of the molding powder was calculated from the oxygen bomb combustion experiment as 26.442 kJ g^{-1} at 298.15 K. There is, therefore, a good agreement between the two types of calorimetric measurements.

Both TGA and DTG curves show that the polypyromellitimide molding powder has a much higher

Table 1
The experimental heat capacities of polypyromellitimide molding powder

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})	T (K)	c_p (J K^{-1} g^{-1})
81.275	0.3104	143.807	0.5471	226.955	0.8287	303.446	1.0900
83.635	0.3182	147.725	0.5621	230.716	0.8432	306.849	1.1044
85.907	0.3324	151.580	0.5743	234.478	0.8526	310.361	1.1196
88.152	0.3448	155.378	0.5880	238.166	0.8698	313.849	1.1425
90.345	0.3526	159.124	0.5980	241.781	0.8817	317.316	1.1492
92.634	0.3577	162.856	0.6084	245.395	0.8880	320.780	1.1696
94.995	0.3717	166.470	0.6202	249.009	0.9036	324.173	1.1854
97.355	0.3811	170.088	0.6302	252.550	0.9155	327.640	1.2032
99.642	0.3910	173.658	0.6428	256.164	0.9186	331.033	1.2165
101.928	0.4045	177.165	0.6551	259.654	0.9328	334.426	1.2410
104.142	0.4117	180.706	0.6654	263.155	0.9429	337.745	1.2633
106.649	0.4190	184.173	0.6727	266.635	0.9541	341.064	1.2862
109.526	0.4341	187.567	0.6895	270.091	0.9689	344.384	1.3077
112.255	0.4435	191.349	0.6985	273.521	0.9769	347.629	1.3283
115.501	0.4528	195.478	0.7153	276.925	0.9887	351.096	1.3475
119.262	0.4663	199.563	0.7237	280.309	0.9991	354.784	1.3735
122.891	0.4842	203.604	0.7395	283.676	1.0136	358.398	1.4011
126.464	0.4968	207.604	0.7500	287.027	1.0231	362.013	1.4208
129.973	0.5064	211.563	0.7672	290.389	1.0424	365.627	1.4401
133.425	0.5148	215.480	0.7840	293.635	1.0563	369.241	1.4707
136.822	0.5277	219.357	0.7975	296.955	1.0678		
140.169	0.5357	223.193	0.8167	300.200	1.0762		

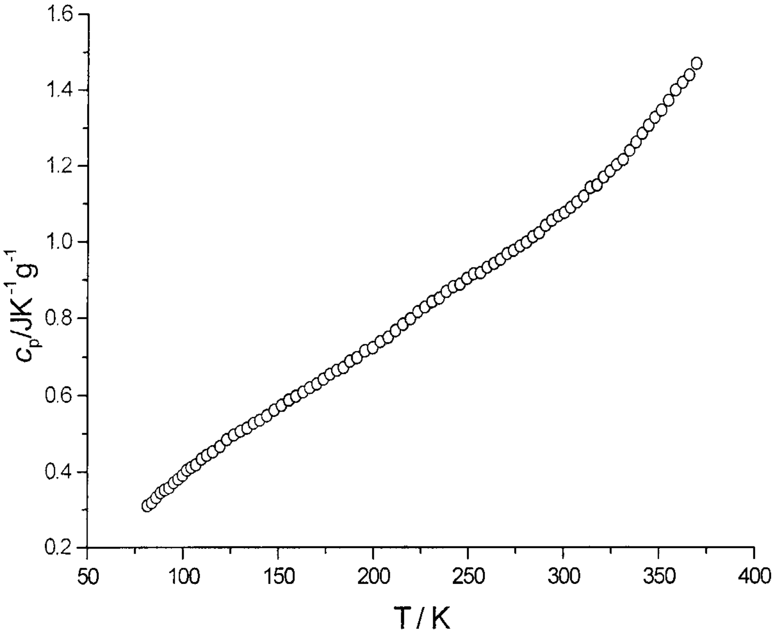


Fig. 1. c_p–T curve of the polypyromellitimide molding powder.

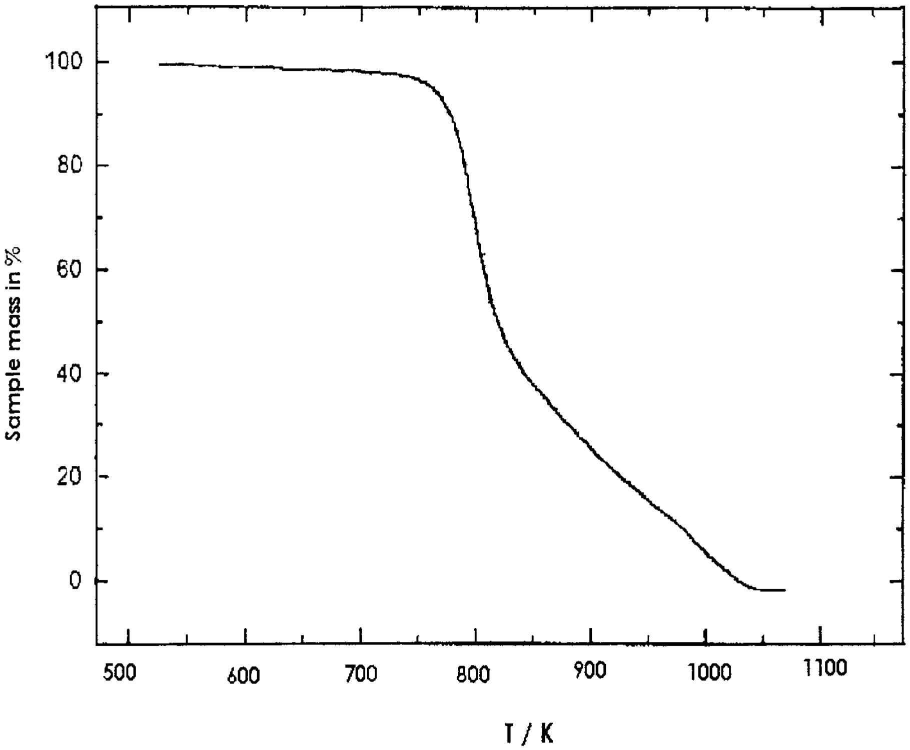


Fig. 2. TG curve of the polypyromellitimide molding powder.

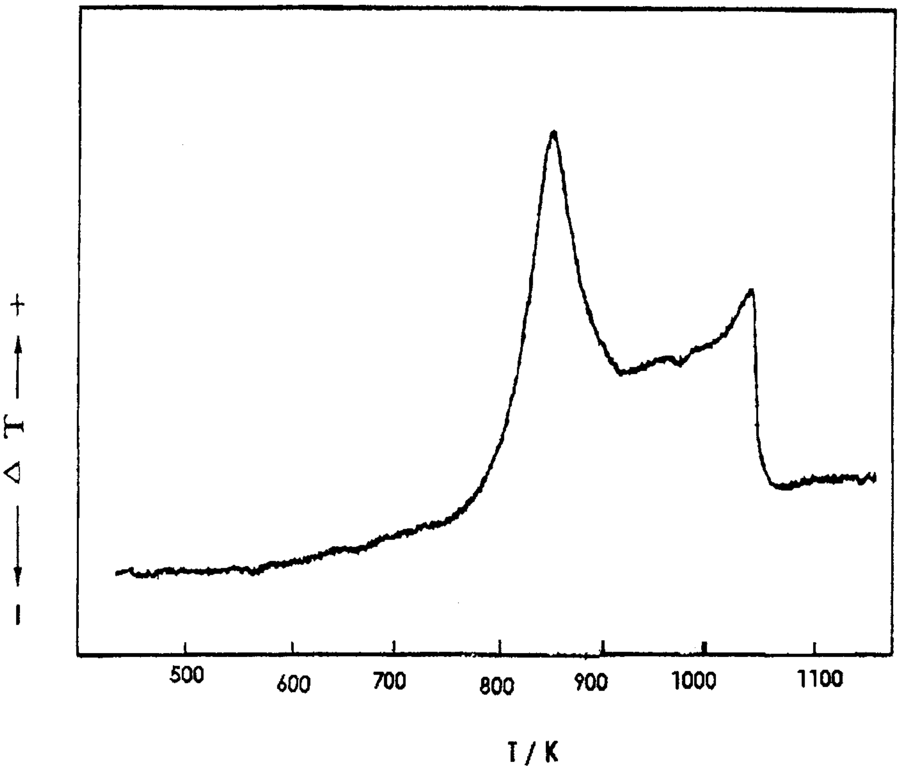


Fig. 3. DTA curve of the polypyromellitimide molding powder.

combustion temperature than that of normal organic compounds.

4. Conclusions

Polypyromellitimide molding powder is easily synthesized and is stable up to high temperatures. It is a valuable high temperature material, but is also useful at low temperatures.

Acknowledgements

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