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Thermochimica Acta 433 (2005) 121–127

thermochimica acta

www.elsevier.com/locate/tca

Heat capacity and thermodynamic functions of fullerene-containing derivatives of atactic poly(methyl methacrylate)

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Received 18 January 2005; received in revised form 15 February 2005; accepted 16 February 2005
Available online 19 March 2005

Abstract

In the present work by precision adiabatic vacuum and dynamic scanning calorimetry the heat capacity of covalent-bonded fullerenes C_{60} and C_{70} containing derivatives of atactic poly(methyl methacrylate) has been measured over the range from 6 to 350 K and from 330 to 460 K, respectively. Low-temperature heat capacity has been analyzed on the basis of Debye and Tarasov theories of the heat capacity of solids and the multifractal generalization and, as a result, some conclusions on the heterodynamics of their structures have been drawn. Temperature interval and thermodynamic characteristics of devitrification as well as their thermal stability regions have been determined. The experimental data were used to calculate standard thermodynamic functions, namely, the heat capacity $C_p^\circ(T)$, enthalpy $H^\circ(T)-H^\circ(0)$, entropy $S^\circ(T)$ and Gibbs function $G^\circ(T)-H^\circ(0)$, for the range from $T \to 0$ to 430 K. The thermodynamic characteristics of fullerene-containing derivatives of atactic poly(methyl methacrylate) and a polymer-analog not including C_{60} and C_{70} have been compared.

Keywords: Fullerene-containing atactic poly(methyl methacrylate); Adiabatic vacuum calorimetry; Heat capacity; Thermodynamic functions; Devitrification characteristics

1. Introduction

An intensive growth of researches concerning fullerenes C_{60} and C_{70} and their various functional derivatives is demonstrated in numerous reviews [1–9] and explained, first of all, with an unique structure of fullerenes and wide potential spheres of their application in practice. Fullerene-containing polymers that are formed by the polymerization of neighbouring C_{60} [10] and C_{70} molecules and different modifications of fairly well studied vinyl [11–13], cyclic [14] and organosilicon polymers [7] represent a new fairly promising class of high-molecular compounds. First of all, they evoke interest because of their ability to combine properties of an initial polymer and exceptional characteristics of the fullerene itself. It was found that the fullerene-containing polymers are able not only to preserve a lot of useful properties of the polymer but to noticeably enhance them that allows the expansion of areas of their practical application.

Up to the present, the synthesis methods of fullerene-containing polymers in macroscopic quantities were designed that shows prospects of studying their individual physicochemical features. So, the hydrodynamic and electrooptic properties of the covalent-bonded fullerenes C_{60} and C_{70} containing the atactic poly(methyl methacrylate) derivatives, PMMA-C_{60} and PMMA-C_{70}, were examined [15] The thermodynamic properties of PMMA-C_{60} and PMMA-C_{70} have not been studied yet. In this connection, the goal of the given work is to calorimetrically determine the temperature dependence of isobaric heat capacity for PMMA-C_{60} and PMMA-C_{70} between 6 and 460 K, to detect possible physical transformations on heating and cooling the samples, to determine and interpret in terms of physical chemistry their thermodynamic characteristics, to calculate from the data obtained the thermodynamic functions $C_p^\circ(T)$, $H^\circ(T)-H^\circ(0)$, $S^\circ(T)$ and $G^\circ(T)-H^\circ(0)$ over the range from $T \to 0$ to 430 K

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doi:10.1016/j.tca.2005.02.022

and to compare the thermodynamic properties of PMMA-C_{60} and PMMA-C_{70} with appropriate data for the analog not containing fullerenes C_{60} and C_{70}, i.e. the atactic poly(methyl methacrylate) studied earlier [16].

2. Experimental

2.1. Sample

The examined samples of PMMA-C_{60} and PMMA-C_{70} were synthesized at the Organometallic Chemistry Institute of Russian Academy of Sciences by the method of block polymerization of MMA analogous to those described elsewhere [15], the fullerenes being introduced into the monomer as a dichlorobenzene solution at the starting stage prior to the addition of an initiator. The polymer macromolecules were molecules of fullerene C_{60} and C_{70} covalent-bonded with PMMA chains. Spectral properties of polymer films were characterized by UV- and NMR-spectroscopy (a Perkin-Elmer Lambda 25 UV–vis and a Bruker Avance DPX-200 (200 Mhz) spectrometers) at 25 °C [17]. The concentration of C_{60} and C_{70} in the samples of PMMA-C_{60} and PMMA-C_{70} was found to be 0.043 and 0.0053 mass%, respectively, i.e. on the average one molecule of C_{60} or C_{70} per 1.67×10^4 (1.58×10^5) monomeric units of the macromolecules. According to our calorimetric data, the samples of PMMA-C_{60} and PMMA-C_{70} were amorphous. The intrinsic viscosity $[\eta]$ of the tested samples was 2.0 and 2.87 dl/g, respectively (as determined in benzene at 299 K).

Gross-formulae of monomeric units of the polymers (PMMA-C_{60} and PMMA-C_{70}) are $C_{5.003}H_8O_2$ and $C_{5.0004}H_8O_2$ with $M = 100.154$ and 100.122 g/mol, respectively. All consequent calculations were made for them. The elemental analysis data for the synthesized samples of PMMA-C_{60} and PMMA-C_{70} correspond to formula calculations.

2.2. Apparatus and measurement procedure

To study the temperature dependence of the heat capacity, temperatures of physical transitions of PMMA-C_{60} and PMMA-C_{70} samples in the range from 6 to 350 K a VST-3 thermophysical automatic device designed and manufactured in “Termis” (Mendeleevo, Moscow Region) was employed. The calorimeter design and the operation procedure were described earlier [18,19]. The reliability of the calorimeter operation was checked by measuring C_p° of standard samples of special-purity copper, corundum and K-2 benzoic acid. It was ascertained that the apparatus and the measurement technique enable to determine the heat capacity C_p° of substances with an uncertainty of not more than ± 1.5% nearby 10 K, ± 0.5% between 15 and 40 K and ± 0.2% in the range from 40 to 350 K and to measure the physical transition temperatures within to about ± 0.01 K.

To examine the relation $C_p^{\circ} = f(T)$ and temperatures of physical transformations in the range from 300 to 450 K a thermoanalytical device operating by the principle of triple thermal bridge, an ADCTHB differential scanning calorimeter, was used [20,21]. The reliability of the calorimeter operation was tested by measuring the heat capacity of standard samples of synthetic corundum and special-purity copper and temperatures and enthalpies of melting of indium, tin and lead. It was found that the apparatus allows the measurements of C_p° of substances with an uncertainty of ± 1.5% in the whole temperature interval, the temperatures of physical transitions within to ca. ± 0.5 K. However, since the heat capacity of the examined substances in the range from 300 to 350 K was measured also in the adiabatic vacuum calorimeter with an error of ±0.2% and the measurement conditions in the dynamic calorimeter were chosen so that in the above temperature range the C_p° values obtained in two calorimeters coincided, it was assumed that at $T > 350$ K the heat capacity was determined within to ±0.5–1.5%.

3. Results and discussion

3.1. Heat capacity

The heat capacity of PMMA-C_{60} was measured in the range from 6.9 to 456 K and for PMMA-C_{70} between 7.3 and 406 K. The masses of the examined samples located in a calorimetric ampoule were 0.3845 and 0.4337 g for PMMA-C_{60} and PMMA-C_{70}, respectively. In the adiabatic vacuum calorimeter in four series of measurements 228 experimental C_p° points were obtained for PMMA-C_{60} and 197 experimental values of C_p° for PMMA-C_{70} (Fig. 1). The heat capacity over the range 330–460 K was measured at an average heating rate of the calorimeter with the substance 0.0133 K/s. In the whole temperature interval the heat capacity of the fullerene-containing polymer PMMA-C_{60} was from 20 to 40% of the total heat capacity of the calorimetric ampoule and the substance and for PMMA-C_{70} from 20 to 60%. A computer-assisted averaging of the experimental C_p° values was made by means of degree and semilogarithmic polynomials. The root mean square deviation of them from the averaging $C_p^{\circ} = f(T)$ curve was ±0.5% in the range 6–80 K, ±0.04% from 80 to 340 K and ±0.6% between 330 and 460 K.

The experimental C_p° values and the averaging $C_p^{\circ} = f(T)$ plots are illustrated in Fig. 1 for PMMA-C_{60} (curve 1) and PMMA-C_{70} (curve 2) and for comparison, the temperature dependence of C_p° for the atactic poly(methyl methacrylate) (curve 3) is shown too [16]. It is seen that in the studied temperature range the devitrification of the samples of PMMA-C_{60}, PMMA-C_{70} and the polymer-analog not containing fullerenes C_{60} and C_{70} occurs in the interval from 360 to 400 K (section BE, Fig. 1).

The heat capacity of the PMMA-C_{60} and PMMA-C_{70} samples in a glassy state as well as of the atactic PMMA shows no peculiarities: it smoothly increases with rising tem-