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Isothermal and polythermal kinetics of depolymerization of C_{60} polymers

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Abstract

Isothermal depolymerization of the two polymers of C_{60}, i.e. of 1D orthorhombic phase (O) and of "dimer state" (DS) have been studied by means of Infra-red spectroscopy in the temperature ranges 383–423 and 453–503 K, respectively. Differential Scanning Calorimetry (DSC) has been used to obtained depolymerization polytherms for O-phase and DS. Standard set of reaction models have been applied to describe depolymerization behavior of O-phase and DS. The choice of the reaction models was based primarily on the isotherms. Several models however demonstrated almost equal goodness of fit and were statistically indistinguishable. In this case we looked for simpler/more realistic mechanistic model of the reaction. For DS the first-order expression (Mampel equation) with the activation energy $E_a = 134 \pm 7$ kJ mol^{-1} and preexponential factor $\ln(A/s^{-1}) = 30.6 \pm 2.1$, fitted the isothermal data. This activation energy was nearly the same as the activation energy of the solid-state reaction of dimerization of C_{60} reported in the literature. This made the enthalpy of depolymerization close to zero in accord with the DSC data on depolymerization of DS. Mampel equation gave the best fit to the polythermal data with $E_a = 153$ kJ mol^{-1} and preexponential factor $\ln(A/s^{-1}) = 35.8$. For O-phase two reasonable reaction models, i.e. Mampel equation and "contracting spheres" model equally fitted to the isothermal data with $E_a = 196 \pm 2$ and 194 ± 8 kJ mol^{-1}, respectively and $\ln(A/s^{-1}) = 39.1 \pm 0.5$ and 37.4 ± 0.2, respectively and to polythermal data with $E_a = 163$ and 170 kJ mol^{-1}, respectively and $\ln(A/s^{-1}) = 32.5$ and 29.5, respectively.
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1. Introduction

Polymerization of fullerene C_{60} attracted considerable attention in part due to the promising properties of the resulting polymerized materials [1]. Uniform samples of polymeric C_{60} were obtained by pressure/temperature treatment of a pristine fullerene. The synthetic procedures were documented [2]. Three different polymerized phases namely 1D orthorhombic (O), and 2D tetragonal (T) and rhombohedral (R) were identified. Preparation of the polymerized "dimeric state" (DS) was also reported. "Dimer state" consists of the $\{C_{60}=C_{60}\}$ dimer molecules randomly disordered within a cubic lattice derived from that of the monomer [3]. It is not a phase in thermodynamic sense. The structural models of the phases mentioned were supported by numerous theoretical and experimental studies [2,4–6]. The experimental methods jointly used included powder and single-crystal X-ray, Infra-red and Raman spectrometry along with NMR.

At present Infra-red spectrometry (IR) alone can be used for quantitative identification of the polymerized phases. IR is also a useful analytical tool capable for determination of the compositions of mixtures of the polymerized phases [2,7].

Enthalpies of depolymerization [8–11] and heat capacities [10,12] of O-, R-, T-phases and DS were measured by means of differential scanning calorimetry (DSC) and adiabatic calorimetry, respectively. Data on depolymerization enthalpies of O- and R-phases from different groups fall in line. The surprisingly high stability of DS, reported in Ref. [11] was not confirmed [8]. Depolymerization of O, R, T and DS under atmospheric pressure, observed by DSC at temperatures between 450 and 620 K was a spontaneous decomposition of the already nonequilibrium phases, rather than the first order phase transitions [8]. No intermediate species were detected in depolymerization of O-phase, DS and T [9].

Few works were published on the kinetics of polythermal decomposition of the C_{60} polymers. Authors [13] have reported

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polythermal kinetics for O-phase from DSC measurements. The analysis in terms of Avrami equation gave the activation energy $E_a = 222 \pm 29$ kJ mol^{-1} and $n = 1$ (simple exponent). In Ref. [14] thermal expansion was used to study polythermal kinetics of depolymerization of phases O- and T- and of a "dimer state" produced by a solid-state mechanochemical reaction. The data exhibit simple exponent behavior with the almost equal Arrhenius activation energies 183 ± 10, 183 ± 10 and 169 ± 5 kJ mol^{-1} for O, T and "dimer phase", respectively. The preexponential factors however differed significantly being 7.3×10^{15}, 7.3×10^{14}, 2.6×10^{17} s^{-1}, respectively for O, T and DS. This made the rate of decomposition a factor of 10^3 faster for "dimer state" than for O-phase.

The reliability of the kinetic data reported suffered from the insufficient characterization of the samples studied. In Refs. [13,14] polymerized samples were characterized only by the preparation procedure. The choice of the reaction model function was another problem never addressed. In Refs. [13,14] no other model function beside simple exponent was applied for fitting of the experimental data.

The primary goal of this work was to study isothermal kinetics of depolymerization of O-phase and of DS at atmospheric pressure. IR was used to follow the rate of isothermal depolymerization. In addition polytherms of depolymerization were extracted from DSC traces. A number of standard reaction models were tested in order to account for isothermal data. The final choice of the model kinetic equations and adjustment of the kinetic parameters were based on both isothermal and polythermal data.

2. Experimental

2.1. Samples

Crystalline C_{60} powder with less than 0.1% impurity was taken as starting material. The polymerized phases were obtained through high pressure-high temperature treatment of C_{60} in piston-cylinder and toroid-type HP devices. The methods of synthesis of O and DS were described in Refs. [2,3]. The identification of the polymerized samples was based on the IR-data, presented in Refs. [2,7]. The IR spectra of the samples pelleted in KBr were obtained on a Bruker Tensor 27 FT-IR spectrometer at $T = 298$ K and $p = 1$ atm. Taking into account the sensitivity of the IR measurements conservative estimation of the purity of the O-phase was about 95%. The samples were contaminated with the "small oligomers" of C_{60}, short polymeric chains not completely converted into the linear polymer. DS samples were mixtures of C_{60} dimers (from 60 up to 70 mol.%) and of C_{60} monomers. According to Ref. [3] the dimer molecules in DS are incorporated into the fcc lattice of C_{60}.

2.2. Isothermal kinetics

Samples of the polymerized phases pelleted already in KBr were kept inside the isothermal (± 1 K) zone in the oven at atmospheric pressure. After certain intervals the samples were taken out and the IR-spectrum was measured at room temperature.
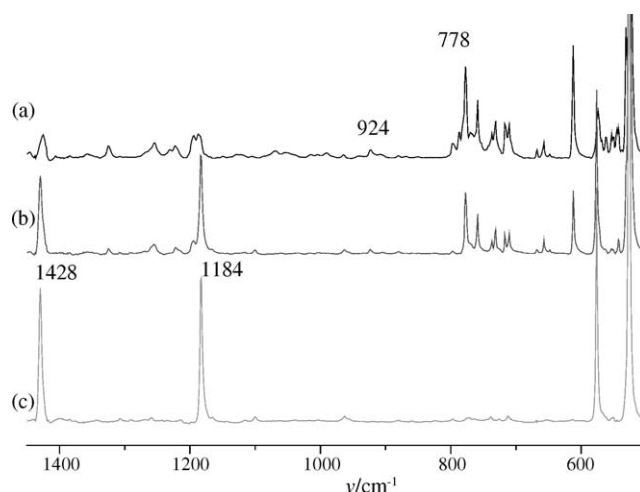

Fig. 1. IR spectrum of O-phase in the course of isothermal ($T = 493$ K) depolymerization. Analytical peaks are marked (see text for more details). (a) $\alpha = 0.05$; (b) $\alpha = 0.4$; (c) $\alpha = 1$.

The samples then were put back into the oven and the isothermal run was continued. Measurements with one and the same pellet significantly improved the accuracy of the data obtained. The isothermal data were reproducible within 6%. With such a procedure it was possible to get 4–20 points on each isotherm. Additional runs were performed to prove that presence of KBr did not influence the rate of decomposition. The extent of conversion, α of DS and O-phase was calculated from the intensity of IR bands at 796 cm^{-1} and 778, 924 cm^{-1}, respectively. The increase of concentration of the C_{60} monomer was independently monitored by measuring of the intensity of the 1428 and 1184 cm^{-1} bands. It was another source of calculating of α. The typical IR spectra of O-phase taken in the course of the isotherm are presented in Fig. 1. It is worth noting that though admixtures of other polymeric forms were present in the initial samples (see above), the rate of decomposition of the targeting polymer (e.g. O-phase or DS) was readily measured by IR.

Isotherms were obtained at 383, 393, 403, 413, 423 K and at 453, 473, 493, 503 K for DS and O, respectively.

2.3. Polythermal kinetics

DSC-30 Mettler and DSC Mettler 822e instruments were used to capture DSC traces from 180 to 670 K with the scanning rates 5, 10, 20 and 10, 15, 30, 50, 80 K min^{-1} for DS and O-phase, respectively. Indium, tin, and zinc were used for temperature calibration. The heat of fusion of In was used for heat flow calibration. The instrumental error was less then 1.5 K in temperature. The completeness of the depolymerization of the samples was checked by IR after each run. Extent of conversion $\alpha(T)$ of the polymerized phase at temperature T, was extracted from the DSC traces by the equation:

$$\alpha(T) = \frac{\Delta H(T)}{\Delta H_{\text{tot}}} \tag{1}$$

The total heat of transformation ΔH_{tot} and partial heat $\Delta H(T)$ were calculated by integrating of the square under entire DSC