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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.

Keywords: C_{60} Polymers; Kinetics of depolymerization; Infra-red spectroscopy; Arrhenius parameters; Reaction models

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 $E_a = 222 \pm 29\,\mathrm{kJ\,mol^{-1}}$ 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 $169 \pm 5\,\mathrm{kJ\,mol^{-1}}$ for O, T and "dimer phase", respectively. The preexponential factors however differed significantly being 7.3×10^{15}, 7.3×10^{14}, $2.6 \times 10^{17}\,\mathrm{s^{-1}}$, 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 $T = 298\,\mathrm{K}$ and $p = 1\,\mathrm{atm}$. 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 ($\pm 1\,\mathrm{K}$) zone in the oven at atmospheric pressure. After certain intervals the samples were taken out and the IR-spectrum was measured at room temperature.

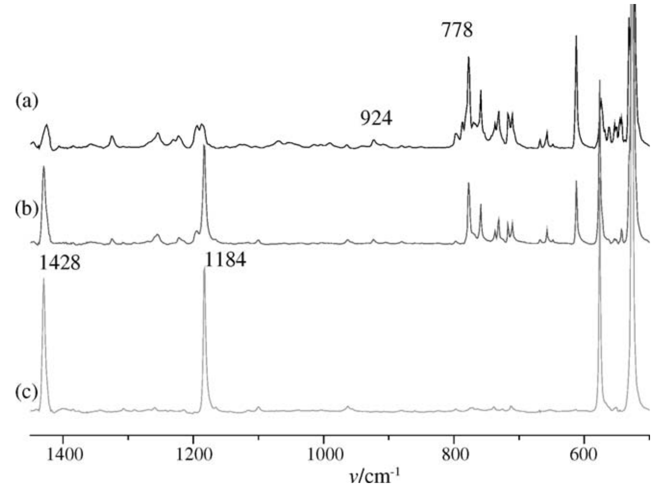

Fig. 1. IR spectrum of O-phase in the course of isothermal ($T = 493\,\mathrm{K}$) depolymerization. Analytical peaks are marked (see text for more details). (a) $\alpha = 0.05$; (b) $\alpha = 0.4$; (c) $\alpha = 1$.

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 $796\,\mathrm{cm^{-1}}$ and 778, $924\,\mathrm{cm^{-1}}$, respectively. The increase of concentration of the C_{60} monomer was independently monitored by measuring of the intensity of the 1428 and $1184\,\mathrm{cm^{-1}}$ 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, $80\,\mathrm{K\,min^{-1}}$ 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:

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

The total heat of transformation ΔH_{tot} and partial heat $\Delta H(T)$ were calculated by integrating of the square under entire DSC peak and under part of the peak up to the temperature T, respectively. The experimental polythermal data were presented as a numerical function:

$$\Psi(a) = T_{\mathrm{exp}} \tag{2}$$

3. Results and discussion

3.1. Kinetic data

Typical DSC traces of DS and O-phase are presented in Fig. 2. Isothermal data for DS and O-phase are given in Figs. 3 and 4, respectively.

3.2. Depolymerization of DS

The kinetic analysis started from the isothermal data. The reaction rate was expressed by the equation:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = f(\alpha)k(T) \tag{3}$$

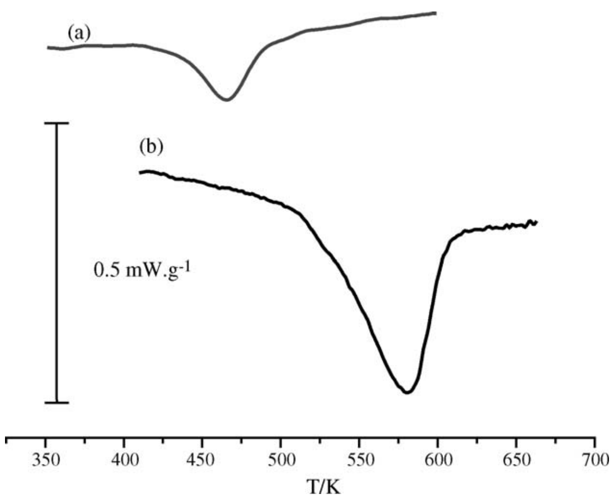

Fig. 2. DSC traces of DS (a) and O-phase (b). Heating rate 20 K min^{-1}.

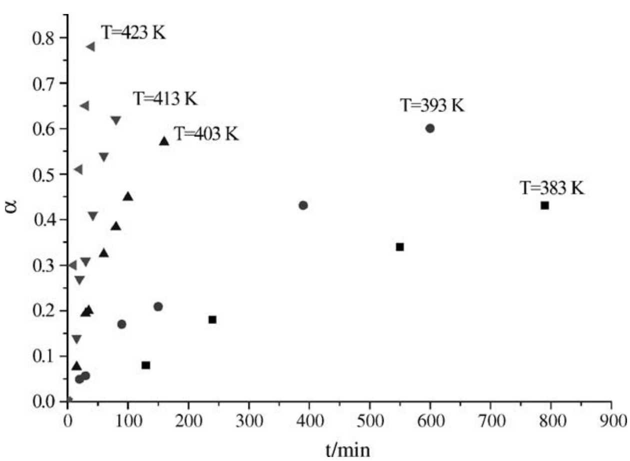

Fig. 3. Extent of conversion (α) vs. time (t). Isothermal depolymerization of DS.

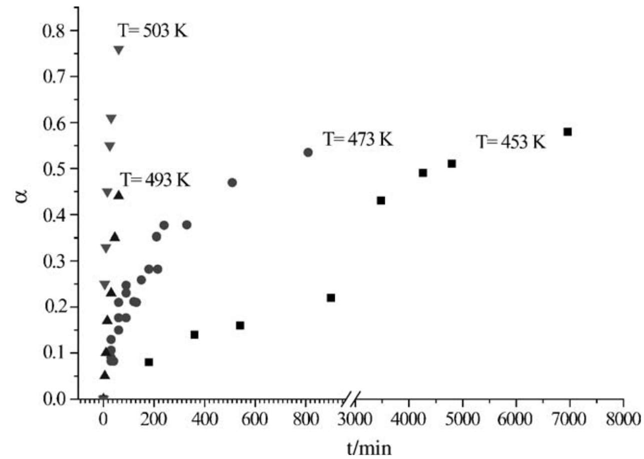

Fig. 4. Extent of conversion (α) vs. time (t). Isothermal depolymerization of O-phase.

or by its integrated form:

$$g(\alpha) = \int_0^{\alpha} \frac{\mathrm{d}\alpha}{f(\alpha)} = kt \tag{4}$$

where $f(\alpha)$ is a particular reaction model function, $k(T)$ is a rate constant.

The temperature dependence of the rate constant was expressed by Arrhenius type equation:

$$k(T) = A\,\mathrm{e}^{-E_{\mathrm{a}}/RT} \tag{5}$$

E_{a} is an activation energy, A is a temperature independent preexponential factor, R is a gas constant. To account for the isothermal data obtained, a number of standard functions $f(\alpha)$ [15] were applied (Table 1). The rate constants $k(T)$ were determined from Eq. (4) by the least-square method for every isotherm and every $f(\alpha)$ in Table 1. The goodness of fit was estimated by using the residual sum of squares:

$$S^2_{r,\mathrm{iso}} = \frac{1}{N-1}\sum_{i=1}^{N}\left(\frac{g(\alpha_i)}{g(\alpha_N)} - \frac{t_i}{t_N}\right)^2 \tag{6}$$

where N is a number of points on the isotherms, t_j the time, corresponding to the extent of conversion α_j, t_N, $g(\alpha_N)$ correspond to the last point on each isotherm. The summation in (6) was over all the isotherms for every reaction model. Different

Table 1
Set of reaction model functions $f(\alpha)$ and the corresponding integral forms $g(\alpha)$

Reaction model	$f(\alpha)$	$g(\alpha)$	n
1	$n(1-\alpha)(-\ln(1-\alpha))^{1-1/n}$	$(-\ln(1-\alpha))^{1/n}$	0.5, 1, 1.5, 2, ... 4
2	$n(1-\alpha)^{(n-1)/n}$	$1-(1-\alpha)^{1/n}$	2, 3
3	$(1/n)\alpha^{(1-n)}$	α^n	1/4, 1/3, 1/2, 3/2

reaction models were compared by F-test:

$$F_i = \frac{S^2_{r,\mathrm{iso}}}{S^2_{r,\mathrm{iso}}(\min)} < F_{1-p,1-N,1-N} \quad (7)$$

where $F_{1-p,1-N,1-N}$ is a percentile of the F-distribution for $(1 \pm p)100\%$ confidence probability. According to the F-test, only those reaction models for which:

$$F_i > F_{1-p,1-N,1-N} \quad (8)$$

should be discriminated. The reaction models which obeyed Eq. (7) fit experimental data as accurately as the model that gives the minimum residual sum of squares, $S^2_{r,\mathrm{iso}}(\min)$.

The kinetic data on depolymerization of DS are presented in Table 2. The table includes the kinetic data for four reaction models with the lowest F_i (see the fifth column in Table 2). The rate constants $k(T)$, derived from different isotherms were used than to evaluate E_a and A of Eq. (5) for every model function $f(\alpha)$ by the least square method (columns 3 and 4 in Table 2, respectively). Two reaction models are characterized by almost equal $S^2_{r,\mathrm{iso}}$, namely reaction model 1 with $n = 1$ (Mampel equation) and model 3 with $n = 3/2$ (power law). From the point of view of F-test they are equally probable.

These two reaction models were taken for additional fitting of the Arrhenius parameters. This fitting was performed using the polythermal DSC data. From Eqs. (4) and (5) one gets:

$$g(\alpha) = \frac{A}{\beta} \int_0^T \mathrm{e}^{-E_a/RT}\, \mathrm{d}T \quad (9)$$

where β is a scanning rate in DSC run ($T = \beta t$), E_a and A are kinetic parameters, calculated from the isothermal data with the particular $f(\alpha)$. The numerical function:

$$T_{\mathrm{theor}} = H(\alpha, \beta, E_a, A) \quad (10)$$

was computed for every polytherm by means of Eq. (9).

The experimental DSC curve ($T_{\exp,\beta} = \Psi(\alpha)$) taken with the scanning rate β was fitted with the numerical function T_{theor} given by Eq. (10). The sum:

$$\frac{1}{N-1}\sum_{i=1}^{N}(T_{\exp,b} - T_{\mathrm{theor}}(\alpha_i, \beta, E_a, A))^2 \quad (11)$$

was calculated for every polytherm. The goodness of fit was estimated using the residual sum:

$$S^2_{r,\mathrm{poly}} = \sum_{\beta}\left(\frac{1}{N-1}\sum_{i=1}^{N}(T_{\exp,b} - T_{\mathrm{theor}}(\alpha_i, \beta, E_a, A))^2\right) \quad (12)$$

Table 2
Kinetics parameters of depolymerization of DS, calculated from isothermal data

Reaction model	n	E_a (kJ mol^{-1})	ln(A/s^{-1})	F_i[a]
1	1	133.8 ± 7.1	30.6 ± 2.1	1.2
2	2	129.1 ± 7.5	28.3 ± 2.3	3.7
2	3	130.4 ± 7.4	28.3 ± 2.2	2.6
3	3/2	133.3 ± 6.4	29.7 ± 1.9	1.0

[a] $F_{1-p,1-N,1-N} = 2.38$, $N = 32$, $p = 0.01$.

Table 3
Dimer state: fitting of the polytherms of depolymerization

Reaction model	n	Optimized parameters	E_a (kJ mol^{-1})	ln(A/s^{-1})	S_r (K)
3	3/2	None	133.3	29.7	6.11
3	3/2	E_a, A	174.2	40.7	4.56
1	1	None	133.8	30.6	3.38
1	1	E_a, A	152.8	35.8	2.61

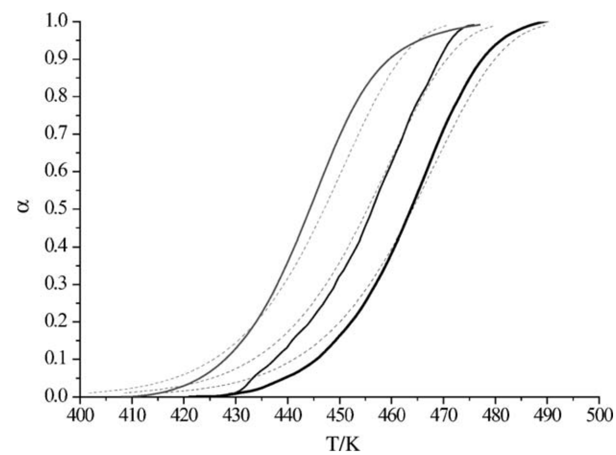

Fig. 5. Polythermal depolymerization of DS, extent of conversion (α) vs. temperature (T). The solid and the dashed lines correspond to the experimental and calculated data, respectively. The scanning rates were (from left to right) 5, 10, 20 K min^{-1}.

where $S^2_{r,\mathrm{poly}}$ was calculated by summation over polytherms taken with different scanning rates β and N was a number of experimental points on the polytherm. The residual sums (12) were calculated for both reaction models (see lines 1, 3 in Table 3).

At the next step $S^2_{r,\mathrm{poly}}$ was minimized by additional variation of E_a and A. The procedure was performed by means of the gradient method and was started from the isothermal parameters. The results of optimization are given in lines 2, 4 of Table 3. Experimental and calculated polytherms of DS are compared in Fig. 5. The calculations were based on Mampel equation with the optimized parameters (see line 4 in Table 3).

3.3. Depolymerization of O-phase

Isothermal and polythermal data on depolymerization of O-phase were handled similarly to the data on DS. Table 4 presents

Table 4
Kinetics parameters of depolymerization of O-phase, calculated from isothermal data

Reaction model	n	E_a (kJ mol^{-1})	ln(A/s^{-1})	F_i[a]
1	0.5	207.7 ± 24.6	41.5 ± 6.2	1.0
1	1	195.9 ± 2.1	39.1 ± 0.5	4.3
3	3/2	194.5 ± 0.5	38.0 ± 0.6	2.8
2	2	193.3 ± 2.0	37.6 ± 0.5	6.5
2	3	194.1 ± 8.4	37.4 ± 0.2	5.7

[a] $F_{1-p,1-N,1-N} = 2.3$, $N = 36$, $p = 0.01$.

Table 5
O-phase: fitting of the polytherms of depolymerization

Reaction model	n	Optimizable parameters	E_a (kJ mol^{-1})	ln(A/s^{-1})	S_r (K)
3	3/2	None	194.5	38.0	14.24
3	3/2	E_a, A	183.9	34.6	4.55
2	3	None	194.1	37.4	12.62
2	3	E_a, A	162.5	29.5	2.67
1	0.5	None	207.7	44.5	13.23
1	0.5	E_a, A	139.4	25.4	7.52
1	1	None	195.9	39.1	12.67
1	1	E_a, A	170.3	32.5	1.87

isothermal parameters of depolymerization, evaluated by Eq. (5) for the reaction models with the lowest F_i.

As it is seen from the table, the reaction model 1 with $n = 0.5$ (Avrami–Erofeev equation, [16]) demonstrated the best fit to the experimental data. Three other models, namely model 3 with $n = 3/2$, model 1 with $n = 1$ and model 2 with $n = 3$ were statistically equal. The four models mentioned were taken for additional fitting of the polythermal data.

The additional fit of the Arrhenius parameters A and E_a was performed using the polythermal DSC data. The procedure was described above (see Eqs. (9)–(12)). The resulting parameters are presented in Table 5. As it is seen from the table, the reaction model 1 with $n = 0.5$ failed to fit the polythermal data. The lowest residual sum $S_{r,\mathrm{poly}}$ was achieved with Mampel equation (model 1, $n = 1$).

4. Discussion

As it is seen from Tables 2 and 3 both isothermal and polythermal data for DS were reasonably fitted within the first-order kinetics. The isothermal Arrhenius parameters are $E_a = 134 \pm 7$ kJ mol^{-1} and $A = 1.9 \times 10^{13}$ s^{-1}. According to the F-test $F_i < F_{1-p,1-N,1-N} = 2.38$ one other model in Table 2 fits the isothermal experimental data as accurate as Mampel equation, giving almost the same Arrhenius parameters. The Mampel equation is preferable from the point of view of possible reaction mechanism. It could be assumed that the samples consisted of dimer units randomly distributed within a basic matrix of monomeric fcc C_{60} [3]. There is no phase boundary between dimers and monomeric C_{60}. If so the reaction rate may be assumed proportional to the number of moles of a dimer $(1 - \alpha)$ i.e. the first-order kinetic equation is valid. The Mampel equation also gave the best fit to polythermal data (see Table 3) though the Arrhenius parameters obtained were different from the isothermal ones.

Nagel et al. [14] have studied polythermal depolymerization of DS using dilatometric method. The reaction model used was also Mampel equation. Compared to this study the activation energy and the preexponential factor in Ref. [14] were much greater, 169 ± 10 kJ mol^{-1} and 2.6×10^{17} s^{-1}, respectively. The rate constants at $T = 423$ K, were however rather close (5.8×10^{-4} s^{-1}, 3.6×10^{-4} s^{-1}, from isothermal and from Nagel et al., respectively.). At $T = 383$ K (the lowest temperature of the isotherms) the rate constant measured in this study is greater than the one, calculated from the parameters determined in Ref. [14] already by a factor of four (1.1×10^{-5} and 2.3×10^{-6} s^{-1}, respectively). This difference is significant, since isothermal depolymerization at $T = 383$ K was observed in this study. This was unlikely to occur with the slow rate constant, predicted in Ref. [14].

Authors of Ref. [17] used IR-spectroscopy to study kinetics of dimerization of C_{60}. Simple second order kinetic equation was assumed as a reaction model. The activation energy of dimerization (134 ± 6 kJ mol^{-1}, [17]) combined with the "isothermal" activation energy of depolymerization of DS from this study (134 ± 7 kJ mol^{-1}) make the enthalpy of dimerization in the solid state almost equal to zero. This is in reasonable agreement with the DSC data obtained in Ref. [8] ($\Delta H = -7 \pm 5$ kJ mol^{-1}) and in Ref. [10] ($\Delta H = -9$ kJ mol^{-1}). DFT (SVWN) calculations of the dissociation energy of a dimer molecule combined with the lattice energies of DS and fcc C_{60} gave almost the same value for the enthalpy of a solid state dimerization [18]. The energy barrier for dissociation of the individual dimer $\{C_{60}{=}C_{60}\}$ calculated in Ref. [19], was 154 kJ mol^{-1}. It was suggested [20] to present the rate constants for several activated "jump processes" in the solid phase in the form given by Eyring rate constant theory:

$$k = f_0\, \mathrm{e}^{(-\Delta H/RT)} \mathrm{e}^{(\Delta S/R)} \tag{13}$$

For the first order process ΔH of activation relates to experimental activation energy E_a calculated from the Arrhenius plots, as

$$\Delta H + RT \approx E_a \tag{14}$$

The relation for k is

$$k = f_0\, \mathrm{e}^{(-\Delta E_a/RT)}\, \mathrm{e}^{1+(\Delta S/R)} \tag{15}$$

The frequency f_0 is associated with the certain lattice frequency and has to be of the order of 10^{13} s^{-1} the "isothermal" preexponential factor measured in this study is

$$A = 1.9 \times 10^{13}\ \mathrm{s}^{-1} \approx 10^{13}\, \mathrm{e}^{1+(\Delta S/R)} \tag{16}$$

This makes the entropy of activation ΔS almost equal to zero. Such low activation entropies are typical for simple monomolecular transformations.

Depolymerization behavior of O-phase was more complicated. When handling the isotherms the F-test formally indicated the Avrami–Erofeev equation (model 1, $n = 0.5$) as the best fit. Three other models are equally probable. The Arrhenius parameters determined vary from model to model but these variations are within the limits of errors. The same reaction models with the "isothermal" Arrhenius parameters determined failed to fit polytherms. Additional optimization resulted in markedly different values of the activation energies and preexponential factors (see Table 5). The Mampel equation and the model of contracting spheres gave the best fit to the polythermal data while the Avrami–Erofeev equation ($n = 0.5$) gave the worse. The situation is typical for many solid-state reactions. As a rule it is not possible to fit both isothermal and polythermal data with one reaction model and one set of Arrhenius parameters. The model-fitting procedures do not allow to conclusively deciding between the

Table 6
Kinetic parameters of depolymerization of O-phase

Reaction model/type of data	E_a (kJ mol^{-1})	ln(A/s^{-1})	k (s^{-1})	T (K)	Reference
Mampel equation/polythermal	183	36.5	0.124; 8.87×10^{-5}	570, 480	[14]
Contracting spheres/isotherms	194 ± 9	37.4 ± 0.2	0.028; 1.31×10^{-5}	570, 480	This study
Mampel equation/isothermal	196 ± 2	39.1 ± 0.5	0.102; 4.37×10^{-5}	570, 480	This study
Avrami–Erofeev, $n = 0.5$/isothermal	208 ± 25	41.5 ± 6.2	0.086; 2.38×10^{-5}	570, 480	This study

competing reactions models [15]. The mechanism of depolymerization process of the O-phase could be better understood in terms of the model of "contracting spheres" in which the reaction proceeds on the surface of the depolymerized phase and its rate is proportional to the surface square $(1-\alpha)^{2/3}$. The Avarmi–Erofeev model ($n = 0.5$) is the least probable, since it corresponds to the rare case of the diffusion control over the growth mechanism of the product phase. The model has been found [16] to describe thickening of the large plates and could hardly be applied for solid–solid depolymerization process. The Mampel equation is the simplest model and was already used in the literature for fitting of the experimental data on depolymerization of the O-phase [14].

In Table 6 the isothermal data from this study are compared with the polythermal data on depolymerization of O-phase reported by Nagel et al. [14]. In the fourth column (Table 6) the rate constants, calculated at the highest and at the lowest temperatures of the isotherms are presented. One can see that if Mampel equation was used as a reaction model, similar values were derived in this study and in Ref. [14]. The difference in Arrhenius parameters is more pronounced. They coincided within limits of errors. It could be stated that Mampel equation formally gives the reasonable description of all the kinetic data on depolymerization of phase O-, reported so far.

5. Conclusion

In this work isothermal depolymerization kinetics of the two C_{60} polymers, i.e. O and DS was studied for the first time. The simplest first order rate equation (Mampel equation) formally accounts for the isothermal data in both phases. It is worth noting that the choice of the reaction model was not unambiguously determined. From the point of view of F-test several other reaction models were equally probable for DS and O-phase. To choose the reasonable model we looked for additional arguments, e.g. tried to fit polytherms and consider the basis on which competing rate equations were derived. For DS the Mampel equation was the best from several points of view. It gave simple and realist picture of the depolymerization process. The Arrhenius parameters found showed that DS exhibits simple depolymerization behavior with the preexponent A of the order of the Eyring universal factor 10^{13} s^{-1}. The activation energy, derived in this study disagreed with the one reported in the literature but correlated well with the sum of the activation energy of dimerization and the enthalpy of depolymerization.

For O-phase the model of "contracting spheres" and Mampel equation provided comparable fits for both isotherms and polytherms while the former model gave more clear understanding of the reaction mechanism. The activation energy derived from the set of the isotherms was almost equal for these two reaction models (195 ± 10 kJ mol^{-1}). The activation energy of 183 ± 15 kJ mol^{-1} was reported in the literature for depolymerization of O-phase from the polythermal data.

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