Formation of the chain microstructure in the synthesis of adamantane-containing copolyimides in molten benzoic acid

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High-resolution ¹³C NMR spectroscopy was applied to study the chain microstructure of copolyimides obtained at 140 °C by one-pot high-temperature polycondensation in molten benzoic acid from 2,2-propylidene-bis(4-phenylene-4'-oxyphthalic acid) dianhydride (DA, intermonomer) and two comonomers, 1,3-bis(2-aminoethyl)adamantane (ADA) and 9,9-bis(4-aminophenyl)fluorene, varying the order of introduction of components into the system. The experimentally found value of chain microheterogeneity coefficient determined from the ¹³C NMR data is in a good agreement with the values theoretically calculated using the mathematical model developed earlier by the authors and the kinetic data for the model reactions of acylation of amino groups and imidization of amido acid fragments. An ADA—DA-2,2-hexa-fluoropropylidene-bis(phthalic acid) dianhydride system provides another example of the principal possibility of varying orders of introduction of components to control the chain micro-structure of copolyimides.

Key words: polyimides, high-temperature polycondensation, diamines, tetracarboxylic acid dianhydrides, benzoic acid, copolymers, chain microstructure, high-resolution ¹³C NMR spectroscopy, mathematical modeling, kinetics.

The one-pot high-temperature polycondensation (HTPC) of tetracarboxylic acid diamines and dianhydrides in high-boiling solvents (m-cresol, nitrobenzene, etc.) is widely used for the synthesis of soluble homo- and copolyimides.¹⁻⁴ The use of molten benzoic acid (BA) as a catalytically active medium $^{5-7}$ makes it possible to substantially diminish the temperature and duration of the HTPC synthesis (140–150 °C, 1–2 h) and provides a number of other advantages over the traditional synthesis.⁵⁻⁷ A series of multiblock copolyimides (CPI) with five-membered imide rings was obtained in molten BA by the gradual addition of an intermonomer (dianhydride) to a mixture of two comonomers (diamines).5-7 It was shown that for the synthesis in BA the behavior of the reaction system in which several reactions occur simultaneously is similar to the behavior characteristic of the simple process of ideal interbipolycondensation. We earlier⁸ developed a mathematical model describing the formation of the chain microstructure of copolyimides in the HTPC synthesis. The model makes it possible to calculate the parameter of chain microheterogeneity (K_m) on final CPI using the kinetic data for model reactions. These reactions have different orders of introduction of intermonomer (tetracarboxylic acid dianhydride) into the system.

The purpose of this work is to extend the developed model⁸ to calculate the parameter $K_{\rm m}$ from the kinetic data for a new reaction system, 1,3-bis(2-aminoethyl)adamantane (ADA)-9,9-bis(4-aminophenyl)fluorene (AFL)-2,2-propylidene-bis(4-phenylen-4'-oxyphthalic acid) dianhydride (DA). It seemed also interesting to compare the obtained data with the experimental values determined from the ¹³C NMR spectra for the samples of copolyimides synthesized in a BA medium needed for calculations. An intermediate stage of the study is obtaining the kinetic data for acylation of ADA comonomer in acidic medium which are necessary for calculation. The choice of ADA as an object of the study is due to the fact that ADA, being highly basic diamine,⁹ should substantially differ from AFL in effective reactivity, and this would favor an increase in the tendency to the block character of the chain. At the same time, it can be assumed that a combination of the bulky fragment and dimethylene units in ADA would enhance the solubility of copolyimides in organic solvents.

Another aim of the study was to synthesize multiblock CPI in the reaction system in which two dianhydrides act as comonomers and diamine, namely, ADA, acts as an intermonomer.

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 4, pp. 0930–0935, April, 2015. 1066-5285/15/6404-0930 © 2015 Springer Science+Business Media, Inc.

Experimental

9,9-Bis(4-aminophenyl)fluorene (Sigma-Aldrich) was purified by sublimation *in vacuo* ($T_{\rm m} = 237-238$ °C), and 2,2-propylidene-bis[(4-phenylene-4´-oxyphthalic acid) dianhydride (Changzhou Wujin Linchuan Chemical Co.) was recrystallized from acetic anhydride ($T_{\rm m} = 188-189$ °C).

1,3-Bis(2-aminoethyl)adamantane (ADA) was synthesized using a previously described procedure.⁹ At room temperature ADA is a viscous liquid ($T_b = 160-162$ °C at 4 Torr). To obtain dibenzoate salt (ADAB), a solution of BA (5.50 g, 0.045 mol) in THF was added to a solution of ADA (5.00 g, 0.02 mol) in THF. A precipitate that formed (ADAB) was filtered, washed with THF, and dried *in vacuo*. A white crystalline substance was obtained with $T_m = 247$ °C (DSC). The composition of ADAB (molar ratio ADA : BA = 1 : 2) was confirmed by the data of potentiometric titration of a weighed sample of ADAB with a solution of HClO₄ in AcOH.

4,4'-(Hexafluoroisopropylidene)diphthalic anhydride (DAF) (Sigma Aldrich) was purified by sublimation *in vacuo* at 200 °C ($T_{\rm m} = 244-247$ °C).

Homopolymers ADA–DA and ADA–AFL were synthesized in molten BA using the procedure similar to that described previously,^{6,7} but diamine was introduced in the form of dibenzoate salt. Copolyimides based on ADA–DA–AFL (CPI-I) and ADA–DA–DAF (CPI-II) were obtained using an earlier described procedure^{5–7} varying order of introduction of components into the system.

 13 C NMR spectra were recorded in a CDCl₃ solution on a Bruker instrument (300 MHz) at a scan increment of 0.001 ppm with a high signal accumulation.

The kinetics of the model reaction of acylation of diamine ADA with phthalic anhydride (PA) was studied in glacial AcOH (100%). The reaction was carried out in a temperature-controlled cell of an APT 09 Akvilon automated potentiometer using a known procedure.⁵ A temperature-controlled solution of PA in AcOH was added to a temperature-maintained solution of ADA in AcOH. The initial concentrations of the reagents were $c_{ADA} = 0.03 \text{ mol } \text{L}^{-1}$ and $c_{PA} = 0.031 \text{ mol } \text{L}^{-1}$. The measurements were carried out at several temperatures in a range of 50–80 °C. Sampling was conducted at specified time intervals to determine the concentration of residual amino groups. Ttiration was carried out at a high rate of titrant introducing to ensure that the duration of sample treatment does not exceed 5–10 s.

A solution of perchloric acid $(0.1 \text{ mol } L^{-1})$ in 100% AcOH was used as a titrant. The kinetic data were analyzed using the second-order reversible reaction and the Maple^R mathematical program.

Results and Discussion

A series of copolyimides were synthesized by the HTCP method in molten BA (140 °C). Two procedures were used for the synthesis: simultaneous introduction of all components into the DA—AFL—ADA system (samples CPI-I-1) and gradual addition of intermonomer DA for 30 min to a solution of comonomers AFL—ADA in molten BA (samples CPI-I-2). The ratio of diamines and intermonomer was ADA : AFL : DA = 1 : 1 : 2 in both cases.

The copolyimides based on ADAB, AFL, and DA were synthesized according to Scheme 1.

The details of the ¹³C NMR spectra of the samples of the CPI-I series are presented in Fig. 1. Microstructure of the chain polymers was characterized using the simplest units, triads. The mole ratio of ACA, ACB, and BCB triads was calculated by signal processing in the structure-sensitive regions (determined earlier in Ref. 7). These signals correspond to the carbon atoms of the anhydride fragment indicated in the chemical formula of the polymer.

By comparing the ¹³C NMR spectra of samples CPI-I with the spectra of homopolyimides the characteristic signals were assigned to triads ACA, BCB, and ACB (Table 1). The relative content of triads and parameter K_m were calculated from the ¹³C NMR spectra. For the simultaneous comonomer introduction, $K_m = 1$ (random sample CPI-I-1). For CPI-I-2, $K_m = 0.51$ (miltiblock sample).

We have earlier⁸ analyzed the generalized kinetic scheme of chain microstructure formation in the synthesis of CPI in a catalytic medium formed by two symmetrical bifunctional comonomers specifically, diamines (A, B) with independent groups (a, b), and symmetrical bifunctional intermonomer (for example, dianhydride C) also with independent groups (c) were used. The scheme includes the following main reactions: acylation of amino



Scheme 1



groups with anhydride groups to form amido acid fragments, decomposition of these fragments to the initial groups, and imidization of the amido acid fragments to form imide cycles. Since the synthesis of CPI by the HTCP method is carried out in the regime of effective removal of evolved water from the system with an inert gas flow, the imidization was considered in the first approximation as an irreversible reaction. An important distinction of the





Table 1.	Assignment	of the	characteristic	^{13}C	NMR
signals (a	δ) to triads in	samples	s CPI-I		

Triad	C(1)	C(2)	C(3)	
ACA	147.31	111.57	42.45	
ACB	147.27, 147.51	111.54, 111.82	42.47	
BCB	147.48	111.79	42.49	

CPI synthesis in a BA medium from the synthesis in "inert" solvents (*m*-cresol, nitrobenzene) is the pronounced catalytic character of the first step (acylation—decomposition of PAA). The mathematical model⁸ corresponding to this kinetic scheme consists of a system of kinetic equations describing the change in the independent variables: current concentrations of free amino groups of two types (a, b), anhydride groups (c), amido acid fragments of two types (ac₁, bc₁), and imide cycles (ac₂, bc₂). The material balance and different characters of introduction of intermonomer into the system were taken into account in the model. The model also contains equations for the calculation of the concentrations of triads with difference sequences of units ACA, ACB, and BCB; the average current length of blocks ...ACAC... and ...BCBC...; and parameter K_m .

To calculate $K_{\rm m}$ for copolyimide CPI-I-2 synthesized by the HPCP method from ADA-DA-AFL in molten BA, kinetic data for the steps of acylation and imidization of ADA under the conditions of CPI synthesis are needed that are unavailable in literature. The expected rate for ADA acylation at 140 °C is very high and, in addition, acylation and imidization under these conditions are conjugated reactions. Therefore, to obtain the necessary kinetic information, imaginary separation of these steps was introduced. For this purpose, the model reaction of ADA acylation with phthalic anhydride in glacial AcOH was studied at several temperatures below 100 °C, i.e., under the conditions where the rate of the conjugated reaction (imidization of the amido acid fragment) is negligible (Scheme 2). The obtained rate constants were extrapolated to the temperature of CPI synthesis equal to 140 °C.

The kinetic curves for the acylation of ADA (50-80 °C) with phthalic anhydride in 100% AcOH are presented in Fig. 2 in the conversion—time coordinates. The retardation of the reaction rate was observed until equilibrium at 30-40% conversions was achieved.

The rate constants of the forward (k_1) and backward (k_{r1}) acylation reactions were calculated from the Arrhenius dependences extrapolated to the temperature of the CPI synthesis equal to 140 °C (Fig. 3). The values of the rate constants are presented in Table 2 along with the values of activation energy of the acylation of amino groups (E_{a1}) and the decomposition of amido acid fragments (E_{a10}) , as well as the equilibrium constants (K_p) and changes in the enthalpy of the acylation step (ΔH_1) . The value of k_2 was accepted to be equal to the corresponding value

Scheme 2



 $k_2 = 0.5 \text{ min}^{-1}$ for the model bis(amido acid) obtained from hexamethylenediamine and PA.¹⁰ Similar kinetic data for AFL were presented earlier.⁸

Using the mathematical model presented in Ref. 8 for final CPI-I-2 and the kinetic data (Table 2), we calculated the average length of the blocks $l \sim 4$ and $K_{\rm m} = 0.506$. For the regime of simultaneous introduction of comonomers and intermonomer into the system, the calculated values were l = 2 and $K_{\rm m} = 1$, which corresponds to the formation of random CPI.

Thus, for sample CPI-I-2, the calculated and experimental values of $K_{\rm m}$ coincide with a fairly high accuracy. All earlier considered^{5–8} CPI were obtained in the sys-

All earlier considered ${}^{5-8}$ CPI were obtained in the systems in which orthodicarboxylic acid dianhydrides were used as an intermonomer and diamines with different re-



Fig. 2. Kinetic curves for ADA acylation ($C_0 = 0.03 \text{ mol } \text{L}^{-1}$) with phthalic anhydride at temperatures 50 (1), 60 (2), 70 (3), and 80 (4) °C. Inset: the initial region is marked with hatched rectangular (a).



Fig. 3. Temperature dependences of the rate constant (a) and equilibrium constant (b) for the acylation reaction.

activities served as comonomers. Random or multiblock CPI were obtained depending on the method of intermonomer introduction into the system (simultaneous or gradual introduction, respectively). In this work, a similar approach was also applied to the reaction system in which diamine ADA was used as an intermonomer and two orthodicarboxylic acid dianhydrides (DA and DAF) served as comonomers. The choice of DAF was motivated by the expectation that this dianhydride bearing a strong electron-acceptor bridging substituent should be more reactive in acylation than DA.

A series of CPI-II samples based on DA—DAF—ADA was also synthesized using two methods of introduction of components. The first method involved simultaneous introduction of a DA—DAF comonomer mixture into a solution of intermonomer ADAB in molten BA (samples CPI-II-1). The second method included gradual introduction for 30 min of intermonomer ADAB into a solution of a DA–DAF comonomer mixture in molten BA (samples CPI-II-2).

The microstructure of the synthesized samples was studied by ¹³C NMR spectroscopy. A signal in a structuresensitive region (46 ppm) was revealed corresponding to the C atom indicated in the formula of diamine moiety.

Figure 4 shows that in the structure-sensitive region of the spectra of CPI a new signal appears between the signals of the C(4) atom (in the CPI-II structure) assigned to homotriads (ppm): 46.51 (C(4), ACA), 46.63 (C(4), ACB), and 46.71 (C(4), BCB). The intensity ratio of these signals changes depending on the order of introduction.

The values of $K_{\rm m}$ were calculated from the high-resolution ¹³C NMR spectra: 0.91 for CPI-II-1 and 0.76 for CPI-II-2. The change in the method of introduction of intermonomer from the simultaneous to gradual one resulted in an increase in the average length of the block from 2 to 3, indicating a tendency for the formation of



Table 2. Calculated parameters for the acylation of diamines ADA and AFL with phthalic anhydride in AcOH at 140 $^\circ$ C

Com-	K _p	k_1	k _{r1}	<i>k</i> ₂	E _{a1}	E _{ar1}	$-\Delta H_1$
pound	$/L mol^{-1}$	$/L \pmod{\min^{-1}}$	min ⁻¹		kJ mol ⁻¹		
ADA AFL ⁸	9 28	294 4800	32.6 170	0.5 0.8	77.4 28.8	97.5 65.7	20.1 36.9



Fig. 4. Signals in the structure-sensitive regions of the ¹³C NMR spectra for samples ADA–DAF (*1*), ADA–DA (*2*), CPI-II-1 (*3*), and CPI-II-2 (*4*).

a multiblock microstructure, but the latter is not very pronounced. This can be explained by a substantially lower influence of the nature of the bridging substituent in diphthalic anhydrides on their reactivity in acylation compared to a similar effect in a series of diamines.¹¹

Thus, in this work we synthesized two series of samples, CPI-I and CPI-II, containing the fragment of 1,3-bis(2-aminoethyl)adamantane. In the first series, diamine acted as one of the comonomers. In the second series, diamine served as an intermonomer. In both series, CPI with the random chain microstructure was obtained by simultaneous introduction of intermonomer into the system, whereas multiblock CPI were obtained with gradual introduction. Therefore, the chain microstructure can be purposefully affected by different introduction of intermonomer, no matter what compound acts as an intermonomer, diamine or orthodicarboxylic acid dianhydride.

The parameter $K_{\rm m}$ calculated from the kinetic data for the model system ADA—DA—AFL is well consistent with the experimental values obtained from the ¹³C NMR spectra. This work was financially supported by the Russian Foundation for Basic Research (Project No. 13-03-00915).

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Received December 17, 2014; in revised form February 5, 2015