The Fractal Analysis of Copolymerization Processes

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ABSTRACT: The results obtained in the present article show that the fractal analysis and irreversible aggregation models application allow to obtain a clear physical picture of copolycondensation process and estimate its quantitative characteristics. The basic characteristic, controlling this process, is fractal dimension D_f of macromolecular coil in solution. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 111: 3026–3030, 2009

Key words: copolymerization; glass transition; polyethers; structure; molecular modeling

INTRODUCTION

One of the goals of the copolycondensation theory is the calculation of copolymer compositional heterogeneity described by the distribution of separate macromolecules according to their composition.[1] As a parameter, characterizing this distribution, microheterogeneity coefficient K_M is usually used, which serves as a quantitative characteristic of the sequence of links distribution in copolymer chains. The study of copolymers compositional heterogeneity is solved by both statistical and kinetic methods. These questions were considered in detail in Refs. 1–3. However, we assume that the understanding of this problem can be improved essentially by using fractal analysis and irreversible aggregation models methods owing to the following reasons. As it is known,[4] macromolecular coil in solution is fractal, and its space structure can be described with the aid of fractal dimension D_f. Mechanisms, resulting to such fractal formation, can be described within the framework of irreversible aggregation models cluster–cluster.[5] Registration of such effects as coil structure and its formation mechanism can broaden our representations on the factors influencing on copolymer's compositional heterogeneity. The purpose of the present article is to consider the indicated factors influence by an example of three copolymers: aromatic copolyethersulfoneformals (APESF), diblock copolymers of oligoformal 2,2-di(4-oxiphenyl)-propane and oligosulfone phenolphtaleine (CP-OFD-10/OSP-10), and diblock copolymers of oligoformal 2,2-di(4-oxiphenil)-propane, phenolphtaline, and dichloroanhydride of isophtalic acid (CP-OFD-10/P-1).

EXPERIMENTAL

The aromatic copolyethersulfoneformals (APESF) were synthesized according to Scheme 1.[6]
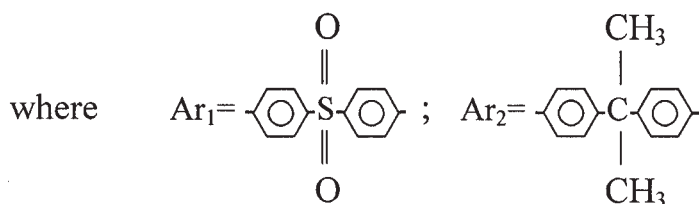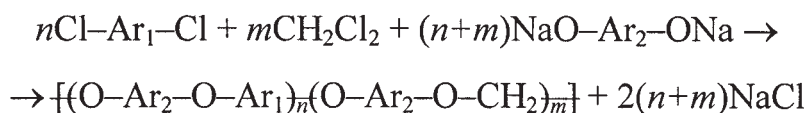
APESF were obtained on the basis of bisphenol A (supplied by the production association "Khimprom," Ufa, Russia) and 4,4′-dichlorodiphenylsulfone (procured by research institute "Khlorproekt," Kiev, Ukraine). The APESF synthesis was made in dimethyl sulfoxide (DMSO) environment in the nitrogen atmosphere during 4–6 h at temperatures 313–433 K.[6] The synthesis method of APESF was stated in more detail in Ref. 6.

Diblock copolymers of oligoformal of 2,2-(4-oxiphenyl)-propane and oligosulfone of phenolphthalein (CP-OFD-10/OSF-10) have been synthesized by the acceptor-catalytic polycondensation according to Scheme 2.[7]

CP-OFD-10/OSF-10 was synthesized according to the following technique. Oligoformal (1.365 g; OFD-10), 2.94 g of oligosulfone (OSF-10), 30 mL of methylene chloride, and 0.3 mL of triethylamine were loaded into a two-neck flask by the capacity of 250 mL, provided with mechanical agitation and stirring. The OFD-10 and OSF-10 were obtained from Kabardino-Balkarian State University, Nalchik, Russia, according to the well-known techniques,[6,8] and triethylamine was supplied by the works "Khimreaktiv," Shostka, Russia.

After oligomer solution, 0.3709 g of bischloroformiate 2,2-di(4-oxyphenyl)-propane procured by Mendeleev Russian Chemical-Technological University, Moscow, Russia, was added to the mixture. The reaction lasted for 3 h, and then the reactive mixture

$$n\text{Cl--Ar}_1\text{--Cl} + m\text{CH}_2\text{Cl}_2 + (n+m)\text{NaO--Ar}_2\text{--ONa} \rightarrow$$

$$\rightarrow [(\text{O--Ar}_2\text{--O--Ar}_1)_{\overline{n}}(\text{O--Ar}_2\text{--O--CH}_2)_{\overline{m}}] + 2(n+m)\text{NaCl}$$

where $\text{Ar}_1 = $ ⟨O⟩–S(=O)(=O)–⟨O⟩ ; $\text{Ar}_2 = $ ⟨O⟩–C(CH₃)(CH₃)–⟨O⟩

Scheme 1 The schedule of copolyethersulfoneformals synthesis.

was diluted by methylene chloride and was precipitated in isopropyl alcohol. The precipitated copolymer was filtrated and washed by water till the chlorine ions disappeared completely.
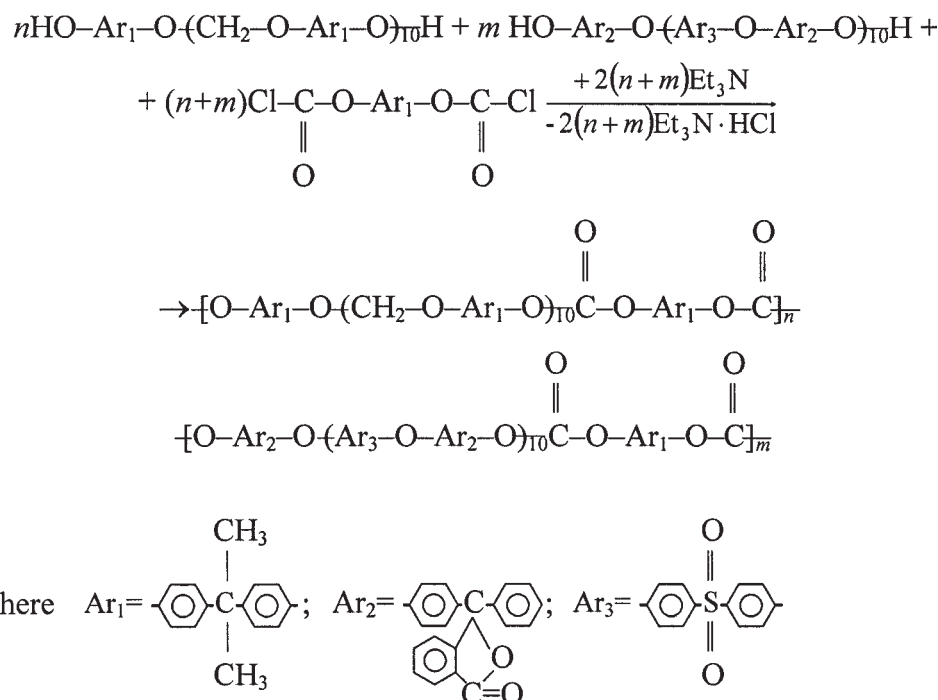
The diblock copolymers of oligoformal of 2,2-di(4-oxiphenyl)-propane, phenolphthalein, and dichloranhydride of isophthalic acid (CP-OFD-10/P-1) were synthesized by the acceptor-catalytic polycondensation according to Scheme 3.[7]

Phenolphthalein was supplied with the alkaloid works (Moscow, Russia), and dichloroanhydride of isophthalic acid was procured with the research institute "Khlorproekt" (Kiev, Ukraine).

Solvents were purified according to the techniques mentioned in Ref. 9. The synthesis technique of

diblock copolymer of CP-OFD-10/P-1 is similar to the one described earlier for CP-OFD-10/OSP-10.

The copolymer's structure is confirmed by the elementary analysis and IR-spectroscopy data. IR spectrums were obtained on the spectrometer UR-20 in tablets with KB. So, for example, APESF IR-spectrums contain the absorbtion IR-bands at 2970, 2870 cm^{-1} (—CH₃—), 1275–1200 cm^{-1} (Ar₂—O—Ar₁); 1240, 1020 cm^{-1} (Ar₂—O—CH₂); 1300, 1157 cm^{-1} $\left(-\overset{\text{O}}{\underset{\text{O}}{\overset{\|}{\underset{\|}{S}}}}-\right)$, 3000, 2800, 1420 cm^{-1} (—CH₂—). The adduced viscosity of APESF depending on the composition changes within the limits 0.094–0.040 m^3/kg, and the limiting conversion degree Q_{lim} is from 82 up to 92%.[6]

$$n\text{HO--Ar}_1\text{--O}(\text{CH}_2\text{--O--Ar}_1\text{--O})_{\overline{10}}\text{H} + m\,\text{HO--Ar}_2\text{--O}(\text{Ar}_3\text{--O--Ar}_2\text{--O})_{\overline{10}}\text{H} +$$

$$+ (n+m)\text{Cl--}\underset{\text{O}}{\overset{\|}{\text{C}}}\text{--O--Ar}_1\text{--O--}\underset{\text{O}}{\overset{\|}{\text{C}}}\text{--Cl} \xrightarrow[\text{-2}(n+m)\text{Et}_3\text{N}\cdot\text{HCl}]{+2(n+m)\text{Et}_3\text{N}}$$

$$\rightarrow [\text{O--Ar}_1\text{--O}(\text{CH}_2\text{--O--Ar}_1\text{--O})_{\overline{10}}\underset{\text{O}}{\overset{\|}{\text{C}}}\text{--O--Ar}_1\text{--O--}\underset{\text{O}}{\overset{\|}{\text{C}}}]_{\overline{n}}$$

$$[\text{O--Ar}_2\text{--O}(\text{Ar}_3\text{--O--Ar}_2\text{--O})_{\overline{10}}\underset{\text{O}}{\overset{\|}{\text{C}}}\text{--O--Ar}_1\text{--O--}\underset{\text{O}}{\overset{\|}{\text{C}}}]_{\overline{m}}$$

where $\text{Ar}_1 = $ ⟨O⟩–C(CH₃)(CH₃)–⟨O⟩; $\text{Ar}_2 = $ ⟨O⟩–C–⟨O⟩ (phthalide); $\text{Ar}_3 = $ ⟨O⟩–S(=O)(=O)–⟨O⟩

Scheme 2 The schedule of diblock copolymers of oligoformal of 2,2-di(4-oxiphenyl)-propane and oligosulfone of phenolphthalein synthesis.

$$n\text{HO–Ar}_1\text{–OH} + (n+m)\text{Cl–}\overset{\overset{O}{\|}}{\text{C}}\text{–Ar}_2\text{–}\overset{\overset{O}{\|}}{\text{C}}\text{–Cl} +$$

$$m\ \text{HO–Ar}_3\text{–O}\text{(CH}_2\text{–O–Ar}_3\text{–O)}_{\overline{10}}\text{H} \xrightarrow[\,-2(n+m)\text{Et}_3\text{N}\cdot\text{HCl}\,]{+2(n+m)\text{Et}_3\text{N}}$$

$$\rightarrow \overline{}\text{O–Ar}_3\text{–O}\text{(CH}_2\text{–O–Ar}_3\text{–O)}_{\overline{10}}\overset{\overset{O}{\|}}{\text{C}}\text{–Ar}_1\text{–}\overset{\overset{O}{\|}}{\text{C}}\overline{]_m}\overline{}\text{O–Ar}_1\text{–O–}\overset{\overset{O}{\|}}{\text{C}}\text{–Ar}_3\text{–}\overset{\overset{O}{\|}}{\text{C}}\overline{]_n}$$

where $\text{Ar}_1 =$ [structure]; $\text{Ar}_2 =$ [structure]; $\text{Ar}_3 =$ [structure]

Scheme 3 The schedule of diblock copolymers of oligoformal of 2,2-di(4-oxiphenyl)-propane, phenolphthalein, and dichloranhydride of isophthalic acid synthesis.

For the diblock copolymer of CP-OFD-10/OSF-10 η_{red} = 0.036–0.080 m^3/kg, Q_{lim} = 90–95%, and for CP-OFD-10/P-1, η_{red} = 0.038–0.070 m^3/kg, Q_{lim} = 95–97%.

The glass transition temperature T_g is determined by DSC method. The DSC measurements are carried out on differential scanning calorimeter Perkin–Elmer-DSC-4 at a heating rate of 5 K/min. The sample mass makes up 4 mg.

The formal content C_{form} is expressed in OFD-10M percents in the studied copolymers composition.

RESULTS AND DISCUSSION

In Figure 1 the dependences of glass transition temperature T_g, determined by thermomechanical method, on formal contents C_{form} for indicated copolymers are shown. As one can see, the course of dependencies $T_g(C_{\text{form}})$ is different for these copolymers. For APESF, the T_g values are located above the additive glass transition temperature T_g^{ad}, for CP-OFD-10/P-1 lower than T_g^{ad}, and for diblock copolymer of CP-OFD-10/OSF-10 the dependence $T_g(C_{\text{form}})$ has a sigmoid character. Such course of dependencies $T_g(C_{\text{form}})$ for indicated copolymers assumes different change of K_M with copolymer composition. The value K_M can be estimated according to the well-known Gordon-Tailor-Wood equation:[10]

$$T_g = K_M\left[(T_{g2} - T_{g1})\left(\frac{W}{1-W}\right)\right] + T_{g1} \qquad (1)$$

where T_{g1} and T_{g2} are homopolymer glass transition temperatures, W is the molar fraction of comonomer.

Let us consider now the reasons of K_M change within the framework of irreversible aggregation models. As a model for copolycondensation processes description, a generalized model of diffusion-limited aggregation (DLA) was selected.[11] The reason of such a choice is as follows: experimentally determined values D_f (measured for those solvents in which synthesis was carried out) are equal to 1.69–1.83, which corresponds to universality class of DLA cluster–cluster.[5] The authors of Ref. 11

Figure 1 The dependence of glass transition temperature T_g on formal contents C_{form} for APESF (1), CP-OFD-10/OSF-10 (2), and CP-OFD-10/P-1 (3).

proposed the following relationship for determination of value D_f for generalized DLA:

$$D_f = \frac{d^2 + \eta(d_w - 1)}{d + \eta(d_w - 1)} \quad (2)$$

where d is dimension of Euclidean space in which a fractal is considered (in our case $d = 3$), η is a physical parameter, the significance of which will be considered low, d_w is the dimension of trajectories of the particles forming aggregate (macromolecule).

Aharony and Stauffer offered the following relationship for value d_w estimation:[12]

$$d_w = D_f + 1 \quad (3)$$

As it was shown,[12] the relation (3) is an approximation precise enough for aggregation processes, limited by diffusion, which assumes the possibility to use this relationship for d_w estimation in the case of generalized DLA.

Matsushita and others[11] interpreted in general case the parameter η as the ratio n/m (n, m are integral positive numbers), characterizing "chemical" reaction of n particles, making random walk, with m aggregate perimeter sites. It is obvious that in the considered case the value n characterizes a number of small (oligomeric or monomeric) molecules (or their intermediate aggregates), and the value m is the number of growing macromolecule perimeter sites accessible (nonscreened) for adding small molecules determined by n value. If one assumes, that m value in copolymerization process remains non-changed, then the parameter η change is due to n variation, and it is necessary to assume that the change (or, more precisely, decrease) in n is defined by an intermediate aggregation process. In its turn, microheterogeneity coefficient K_M characterizes the copolymer type: for strictly alternating copolymer $K_M = 2$, for fully statistical $K_M = 1$, and for two homopolymers blend $K_M = 0$. According to the absolute value of K_M derivation from the unit, it is possible to judge about ordering the degree of links distribution in copolymer and then, to which direction this derivation is observed, on the monomer's (oligomers) tendency either to alternation in chains ($K_M > 1$) or to formation of long blocks of both comonomers ($K_M < 1$).[1,2] In Figure 2, the relationship between K_M and η for considered copolymers is shown, which proved to be linear, and K_M growth at η reduction (n decrease) is observed. As it was noted earlier, n decrease can be connected with the intermediate aggregation process. If a pair of monomers (oligomers) forms intermediate aggregate, and it is included in this form to the growing macromolecule, then it will mean twice decrease of n (one molecule is formed instead of two). At $K_M = 2.0$, copolymer with a strict alternation of blocks is formed,
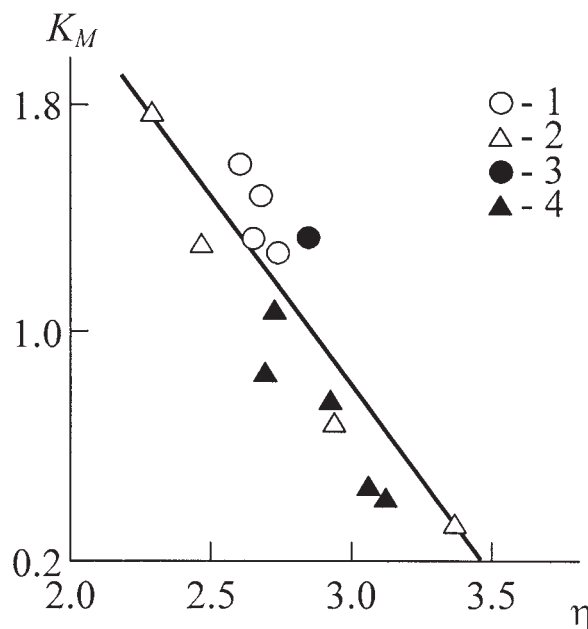

Figure 2 The dependence of microheterogeneity coefficient K_M on parameter η for APESF (1), CP-OFD-10/OSF-10 (2), regular CP-OFD-10/OSF-10 with $C_{form} = 30$ mol % (3), and CP-OFD-10/P-1 (4).

and this assumes that all 100% of monomeric (oligomeric) molecules form intermediate aggregates.

Let us consider possible reasons of intermediate aggregate formation. As it is known,[13] at various chemical reactions carrying essential role plays the so-called steric factor p ($p \leq 1$), showing that not all collisions occur with proper orientation of these molecules for chemical bond formation. It is obvious that this factor of orientation is important for molecules with complicated shape and large sizes, which are the molecules of the used copolymers monomers and the more so oligomers at synthesis. In Ref. 14, it was shown that at a constant reaction duration $t = 60$ min, the value p can be expressed as follows:

$$p = \frac{1.6}{10800^{(D_f - 1)/2}} \quad (4)$$

In Figure 3, the dependence of η value from p calculated according to the eq. (4) is shown. As follows from Figure 3, p increase results to η growth and, consequently, to D_f decrease, which follows from eq. (2). Such character of D_f change with p fully corresponds to the theory of aggregate formation by aggregation mechanism cluster–cluster.[15]

Hence, the results stated earlier allow to offer the following mechanism of copolymers formation within the framework of irreversible aggregation models. The steric factor p decrease means the increase of monomers (oligomers) molecules fraction that did not form chemical bond at the contact with
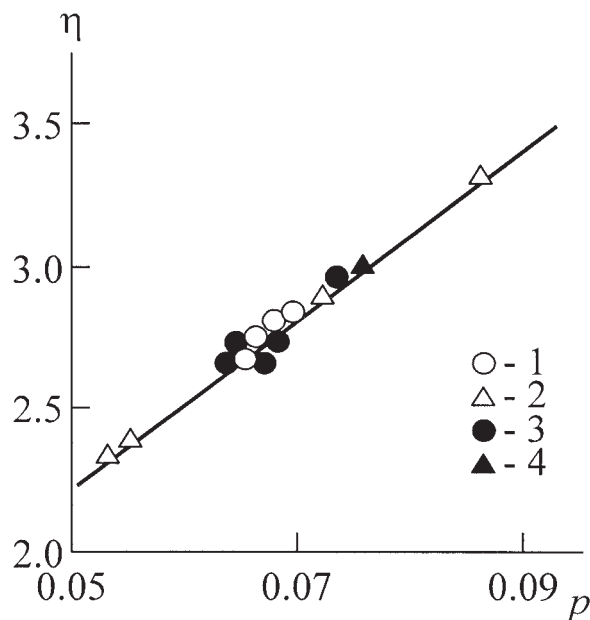
Figure 3 The dependence of parameter η on steric factor p for APESF (1), CP-OFD-10/OSF-10 (2), CP-OFD-10/P-1 (3), and regular CP-OFD-10/OSF-10 with $C_{form} = 30$ mol % (4).

the growing macromolecule and owing to processes of diffusion returning back into solution. The increase of such molecules fraction means raising of formation probability of chemical bonds between them and, consequently, formation probability of intermediate aggregates. Formation of such aggregates results in the increase of regularly alternating block fraction and accordingly K_M growth. From the data of Figure 3, we can estimate the limiting (at $p = 0$ and 1) η values and according to the eq. (2), calculate the limiting values D_f (D_f^{min} and D_f^{max}). At $p = 0$, the value $\eta \approx 0.76$ and $D_f^{max} \approx 2.35$, which corresponds excellently with fractal dimension in the point of physical formation of gel.[16] At $p = 1$, $\eta \approx 30.76$ and $D_f^{min} \approx 1.15$. Such D_f value is typical of rigid-chain polymers. For example, using formula:[17]

$$D_f = \frac{3}{1+a} \qquad (5)$$

where a is the exponent in Kuhn-Mark-Houwink equation, it gives for poly-n-benzamide the value $D_f = 1.11$ ($a = 1.7$[18]).

Let us note that values η [the eq. (2)] and p [the eq. (4)] are defined mainly by D_f value. As it is known,[19] the D_f value for macromolecular coil in

interactions is defined by two interaction groups, interactions between elements of coil itself and interactions of polymer–solvent. Therefore, by solvent variation, it is possible to change the D_f value and, consequently, copolymer type, synthesized from the same monomers (oligomers). The D_f increase means raising of coil compactness, the p decrease and K_M increase.

CONCLUSIONS

Therefore, the results obtained in the present article showed that the application of fractal analysis and irreversible aggregation models allows to obtain a clear physical picture of copolycondensation process and to estimate its quantitative characteristics. The basic characteristic, controlling this process, is fractal dimension D_f of macromolecular coil in solution.

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