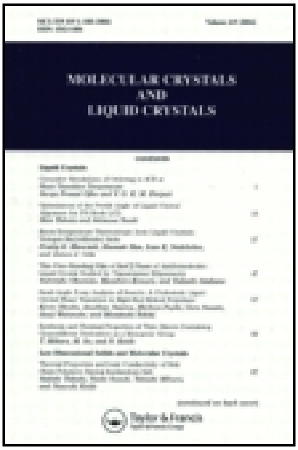

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Block-Copolymers of Polyacrylamide with Poly(Ethylene Oxide) Forming Intramolecular Polycomplexes

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Block-Copolymers of Polyacrylamide with Poly(Ethylene Oxide) Forming Intramolecular Polycomplexes

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Diblock-copolymers of polyacrylamide (PAA) and monomethyl ethers of poly(ethylene glycol) (MEPEG) of different molecular weights ($M_{v\ MEPEG} = 7.5 \cdot 10^2 - 5 \cdot 10^3$) *are obtained. The positive matrix effect depending on the length of MEPEG chains is revealed. The copolymerization kinetics is measured by dilatometry and compared with that of AA homopolymerization.*

Molecular parameters of synthesized copolymers are determined by size exclusion chromatography (SEC). Structural investigations are carried out by differential scanning calorimetry (DSC).

Keywords: acrylamide; diblock-copolymers; intramolecular polycomplex; matrix effect; monomethyl ether of poly(ethylene glycol)

INTRODUCTION

Heterogeneous polymers, in particular block-copolymers, are considered as perspective functional materials. These compounds are widely used as matrix binders in biotechnological processes, macromolecular therapeutic systems as semipermeable membranes, solid polymeric electrolytes, etc. Such heteropolymeric systems have attracted a growing interest in recent years owing to a great progress in developing the new nanoreactor catalytic processes and nanophase technologies. This is associated with considerable possibilities for controlling their structures and properties through variations in the chemical nature and a length of polymer components [1].

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The synthesis of diblock-copolymers with incompatible hydrophilic and hydrophobic blocks is one of the traditional approaches for creation of nanocontainers and nanoreactors. Self-assembly of such macromolecules in polar or non-polar solvents ensures the formation of "straight" or "reversible" micellar or vesicular structures which are functioning as nanocontainers and nanoreactors. Moreover, the amphiphilic block-copolymers of an absolutely new type have been developed recently [1]. They consist of hydrophilic blocks that are capable to cooperative interactions and form intramolecular polycomplexes (IntraPC). There are the hydrophobic areas of linking the active groups and hydrophobic fragments of unlinking polymer's segments on IntraPC.

One of the perspective directions of IntraPC application is the development of nanocontainers for the target delivery of drugs *in vivo* and nanoreactors for the growing of semiconductor's nanoparticles of a necessary size. To use the block- and graft copolymers forming IntraPC in such high nanotechnologies, the procedures of synthesis techniques should be improved. This is necessary for obtaining both the strictly controlled molecular mass and molecular architecture.

It is known that the matrix polymerization is widely used for the creation of IntraPC. The detailed study of a mechanism of the matrix process takes a considerable place in general investigations of macromolecular reactions [2].

As was shown, the graft copolymerization belongs to matrix processes, because the main chain and growing graft chains are chemically complementary and able to cooperative interactions.

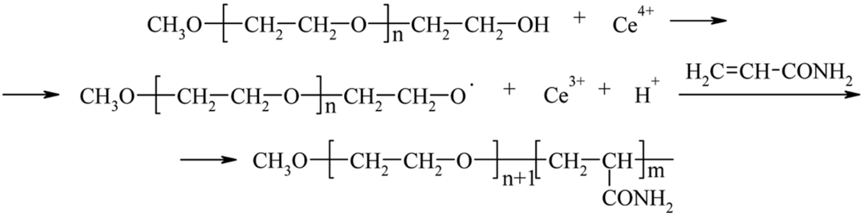
Particularly, the kinetic investigations of matrix graft copolymerization of polyarylamide (PAA) to polyvinyl alcohol (PVA) revealed the positive matrix effect since the growth rate of grafts was 2–4 times more than that of the homopolymerization of acrylamide (AA) under the same conditions [3].

It was established that polyacrylamide (PAA) and poly(ethylene oxide) (PEO) can interact with each other in water solutions via hydrogen bonds and can form intramolecular polycomplexes [4]. Macromolecules of PAA and polyethylene glycol (PEG) can interact with each other by hydrogen bonds as well. It is confirmed by the spontaneous formation of intermolecular polycomplexes (InterPC) between PAA and PEG in their water mixtures. Owing to this fact, it was suggested that the block-copolymerization of PAA and PEG have the matrix nature. This suggestion was validated by kinetic investigations of the synthesis of three-block-copolymers PAA-b-PEO-b-PAA [5].

It is reasonable to suppose that the process of formation of diblock-copolymers PAA-b-PEO belongs to matrix processes as well. In order to recognize the presence or absence of the matrix phenomenon in the mentioned diblock-copolymers, the free-radical copolymerization of PAA with monomethyl ethers of poly(ethylene glycol) (MEPEG) of various molecular weights was carried out.

EXPERIMENTAL

Diblock-copolymers (DBC) MEPEG-b-PAA were obtained by the conversion of end OH-groups of MEPEG into macroradicals which then initiated the radical copolymerization:



$$CH_3O{-}[CH_2{-}CH_2{-}O]_n{-}CH_2{-}CH_2{-}OH + Ce^{4+} \longrightarrow$$

$$\longrightarrow CH_3O{-}[CH_2{-}CH_2{-}O]_n{-}CH_2{-}CH_2{-}O^{\cdot} + Ce^{3+} + H^{+} \xrightarrow{H_2C=CH{-}CONH_2}$$

$$\longrightarrow CH_3O{-}[CH_2{-}CH_2{-}O]_{n+1}{-}[CH_2{-}\underset{CONH_2}{CH}]_m{-}$$

Diammoniumhexanenitrocerate performed the function of an oxidant. Four samples of MEPEG with $M_v = 7.5{\cdot}10^2$ (MEPEG1), $1.1{\cdot}10^3$ (MEPEG2), $2.0{\cdot}10^3$ (MEPEG3), and $5 \cdot 10^3$ (MEPEG4) from “Fluka” (Germany) were used. The reaction was carried out at $T = 20°C$ in argon atmosphere during 24 h at the permanent equimolar ratio $[Ce^{IV}]/[MEPEG]$ and a constant concentration of AA in the reaction mixture. Molecular characteristics of diblock copolymers and corresponding individual polymers are shown in Table 1.

Molecular parameters of synthesized DBC1-4 samples were determined by size exclusion chromatography (SEC) that was performed on a ≪Du Pont≫ Liquid Chromatograph with refractive index detector, by using dimethyl formamide as an eluent at 50°C with an elution rate of $0.7\,cm^3/min$ and at a working pressure of 44–45 bar. ≪Zorbax≫

TABLE 1 Molecular Parameters of Diblock Copolymers PAA-b-MEPEG

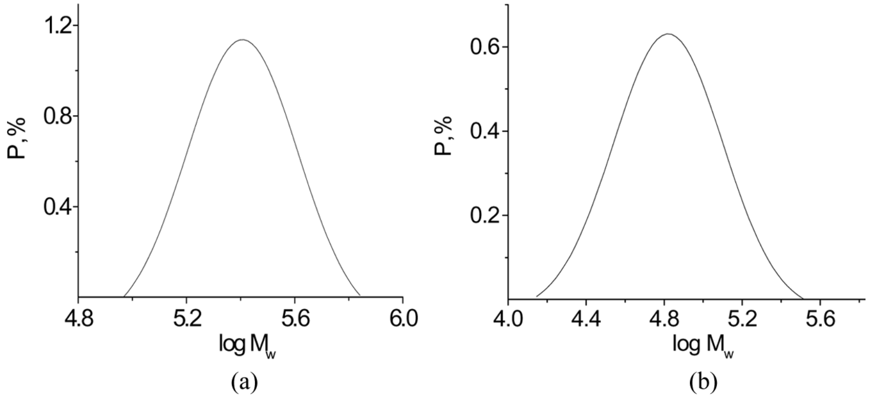
Polymer	$M_{v\ MEPEG}$	$M_w{}^a$	$M_n{}^a$	$M_w/M_n{}^a$	M PAA[b]
PAA	–	81000	59000	1.38	–
DBC1	750	248000	182000	1.36	247250
DBC2	1100	195000	96000	2.03	193900
DBC3	2000	159000	149000	1.06	157000
DBC4	5000	77000	64000	1.19	72000

PSM-100 and 1000 bimodal columns were calibrated by polystyrene standard samples with $M_w = 100000$ and 50000 (M_w/M_n, $n = 1.01$). Unimodal curves of the chain-length distribution were observed for all samples of DBC. Some examples are shown in Figure 1.

As seen from Table 1, the DBC of this series are nonsymmetric, since the PAA polymerization degree is much more than the MEPEG polymerization degree. All samples of DBC have narrow chain-length distribution. All these facts are confirmed that the side reactions of AA homopolymerization are absent.

The copolymerization kinetics was measured by dilatometry and compared with that of AA homopolymerization. For the homopolymerization of AA, the redox system Ce^{IV}-ethyl alcohol was used. All reactions were carried out under the same experimental conditions. The value of the limit conversion of a monomer through 24 h was used for the calibration of a dilatometer. To determine the limit conversion, we have found the bromine value in the initial and final reaction mixtures by the known method [4].

Structural investigations of MEPEG-b-PAA and individual polymer components were carried out by the differential scanning calorimetry (DSC) with the use of a thermoanalyzer 1090 "Du Pont" and a microcalorimeter DSC-210 that was calibrated by indium and zinc. There were studied the thermal transitions that have been observed in copolymers before the beginning of thermal-oxidative degradation. For these purposes, the polymer samples were heated from $T = -150°C$ to 200°C, instantly cooled, and heated again with the same rate of heating (16 degrees per min). To determine the nature of a structural



(a) (b)

FIGURE 1 Plots of MMS were obtained by SEC for DBC1 (a) and DBC4; (b) in DMF.

transition, the repeated scanning for the same samples was done. Heat flow changes were measured comparative to those in a sapphire crystal as the standard. According to the results of these measurements, the dependence of heat capacity on the temperature was calculated as

$$C_P(T) = C_P^0 \cdot \frac{l}{l^0} \cdot \frac{m_0}{m},$$

where C_{p0} – sapphire heat capacity at a current temperature, l_0 and l are, respectively, the distances of the sapphire thermogram and the polymer thermogram at a current temperature from the base line, m^0 and m – the sapphire crystal mass (61.66 mg) and the sample mass.

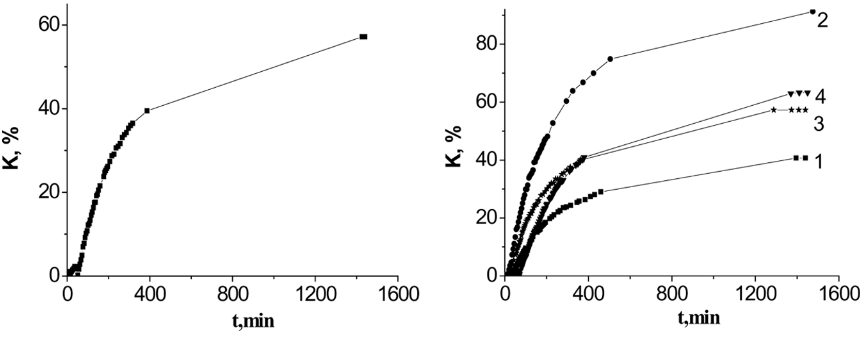
RESULTS AND DISCUSSION

It was pointed above that the kinetics of block-copolymerization was investigated in comparison with that of homopolymerization of AA. The results of investigations by dilatometry are shown in Figure 2.

Most of the kinetic curves have S-shaped form that is caused by some inductive period. A nonmonotonic increase of the monomer conversion depending on MM MEPEG is observed as well.

For a more detailed analysis of the kinetic regularities of block-copolymerization of PAA with MEPEG, the rates of polymerization at the different fractional conversions of the monomer have been calculated ($K = 10$, 20, and 30%) and shown in Table 2.

As seen from Table 2, there is the initial inductive period for all samples. This is due to the formation of a complex between OH-groups



(a) (b)

FIGURE 2 Plot of the monomer conversion versus the reaction times of AA homopolymerization (a) and block-copolymerization (b) of AA with MEPEG1 – 1, MEPEG2 – 2, MEPEG3 – 3, MEPEG4 – 4. T = 20°C.

TABLE 2 Kinetic parameters of the block-copolymerization of acrylamide and monomethyl ethers of poly(ethyleneglycol) with various M_v

Polymer	$M_{v\ \mathrm{MEPEG}} \cdot 10^{-}$	τ_0, min[b]	$\upsilon_{10} \cdot 10^5$, mole·dm^{-3}·s^{-1}[a]	$\upsilon_{20} \cdot 10^5$, mole·dm^{-3}·s^{-1}	$\upsilon_{30} \cdot 10^5$, mole·dm^{-3}·s^{-1}	K,[c]%
PAA	-	57	3.8	2.4	1.6	57.2
DBC1	0.75	33	1.7	1.0	0.4	40.7
DBC2	1.10	15	6.2	5.3	4.4	91.3
DBC3	2.00	33	4.3	2.4	1.3	57.3
DBC4	5.00	70	3.2	2.7	1.8	63.3

[a] The rate of homopolymerization and block-copolymerization of the monomer at 10, 20, and 30% conversion.

[b] Inductive period.

[c] Conversion of the monomer in 24 h.

of MEPEG and Ce^{IV} ions. It is known that the lifetime of such complexes can vary from several minutes till several hours depending on the hydrocarbon radical structure in alcohol [5]. In accordance with Table 2, the rate of block-copolymerization passes over the maximum with increase in MM MEPEG and is different from the rate of AA homopolymerization.

Thus, at $M_{v\ \mathrm{MEPEG}}$ equal to $7.5 \cdot 10^2$, the rate of block-polymerization is less by a factor of 2 as compared with the rate of AA homopolymerization. At $M_{v\ \mathrm{MEPEG}}$ equal to $1.1 \cdot 10^3$, the sharp increase in the block-polymerization rate (by 7.6 times) is observed. It is 3.5 times greater than the rate of AA homopolymerization. The minimal inductive period is observed in this case as well. When $M_{v\ \mathrm{MEPEG}}$ increases to $2 \cdot 10^3$ and then to $5 \cdot 10^3$, the rate of block-polymerization decreases and became less than the rate of AA homopolymerization. One can see that the inductive period rises.

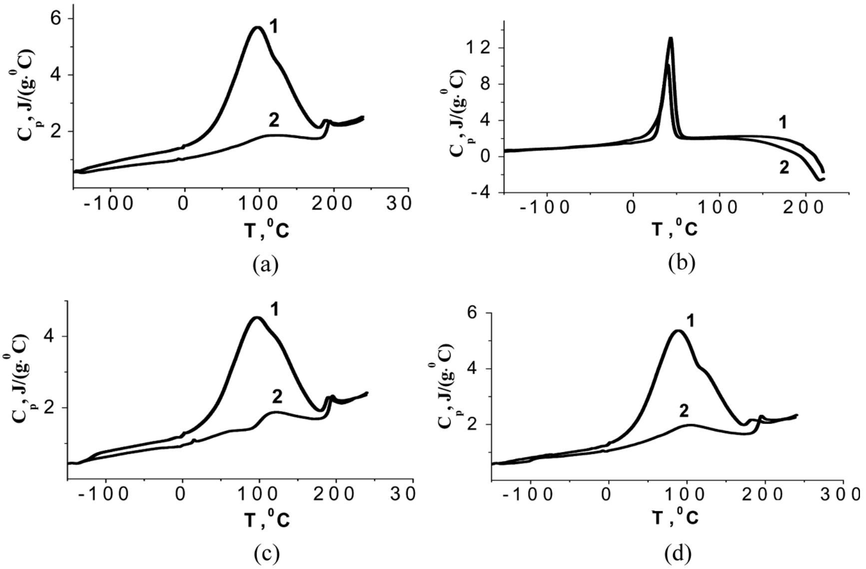
The change of the block-copolymerization rate in comparison with the rate of AA homopolymerization and the influence of the MEPEG block length on this process are the factors that show the dynamic matrix effect [6]. In case where the growing chain is not covalently bound with the matrix, both the increasing and decreasing copolymerization rates indicate the presence of the dynamic matrix effect [7,8]. Increasing the PAA and MEPEG2 block-copolymerization rates in comparison with the rate of AA homopolymerization and a decrease of the inductive period testify to the positive matrix effect. It can be explained by the complexation of growing chains of PAA with the chemically complementary matrix MEPEG.

It is significant that a decrease of the block-copolymerization rate for more long chains of MEPEG3 and MEPEG4 is contrary to the effect of an increase of the positive matrix effect in three-block copolymers PAA-bPEO-b-PAA [9]. Probably, it depends on different hydrophilic-hydrophobic balances in macromolecules of diblock- and three-block-copolymers. It is well known that an increase of the matrix length leads to a strengthening of interactions with the growing chain [10,11]. This can be explained by the existence of the exponential dependence between the equilibrium constant of complexation K_ν and the polymerization degree of the polymer component [10]:

$$K_{\mathrm{v}} = K_{l\mathrm{v}} = \exp(-\nu\cdot\Delta G^\circ/RT),$$

where $K_{1\nu}$ and ΔG°– equilibrium constant and standard free energy of the formation of a hydrogen bond, and ν – polymerization degree of the component. Considerable hydrophobization and compactization of InterPC particles in a water solution can be a consequence of an increase in the matrix length and a strengthening of interactions with the growing chain. The active centers became inaccessible for molecules of a monomer, and the polymerization rate decreases [7]. Just this effect is typical of the synthesis of DBC PAA-b-MEPEG in contrast to three-block-copolymers PAA-b-PEO-b-PAA.

Thermograms of DBC are shown in Figure 3. The DSC of amorphous PAA with $M_{\mathrm{v}} = 6.3\cdot 10^5$ (Fig. 3a) have the endothermic peak of



(a) (b)

(c) (d)

FIGURE 3 DSC thermograms of PAA (a), MEPEG4; (b), DBC1; (c), DBC4; (d). The first scanning 1; the second scanning 2.

water evaporation at $T \sim 100°C$ and the heat capacity race that reflects the process of devitrification of the polymer (α-relax transition).

Parameters of the structural transition in PAA, MEPEG, and DBC are shown in Table 3.

On the thermograms of all MEPEG (Fig. 3), the only intensive endothermic peak of the melting of crystalline regions is observed. Such a type of thermograms completely agrees with the fact that PEG and its ethers are crystalline polymers [6,8].

Parameters of the melting, T_m and ΔT_m, as well as the melting enthalpy ΔH_m and the crystallinity degree X_C for MEPEG, are shown in Table 3 as well. It is worth to note the high crystallinity degree of MEPEG (almost 100% for MEPEG4). Therefore, the α-relax transition is absent. The values of T_m, ΔH_m , and X_C for the second scanning are reduced. It is stipulated by a sharp (about 300 degree/min) cooling of the samples after the first scanning. So, the formation of a crystalline structure is too complicated.

In contrast to the above-mentioned, the thermograms of DBC contain no endothermic peak of melting (Figs. 3c, d). That is, regions of MEPEG are totally absent in the structure of a DBC crystal.

TABLE 3 Parameters of Structural Transitions in PAA, MEPEG, and DBC

Polymer	Scanning	T_v, °C	ΔT_v, °C	$\Delta C_P{}^a$, J/(g· °C)	T_m, °C	ΔT_m, °C	ΔH_m, J/g	$X_c{}^b$, %
PAA	1	184.4	8.9	0.28	–	–	–	–
	2	190.6	9.4	0.76	–	–	–	–
MEPEG1	1	–	–	–	21.3	64.1	132.4	67
	2	–	–	–	23.5	64.1	117.8	60
MEPEG2	1	–	–	–	43.4	47.0	168.6	86
	2	–	–	–	40.0	88.0	142.5	72
MEPEG3	1	–	–	–	53.0	39.0	194.8	99
	2	–	–	–	50.6	85.0	167.2	85
MEPEG4	1	–	–	–	61.5	48.9	200.8	100
	2	–	–	–	59.5	56.7	175.9	89
DBC1	1	184.9	11.1	0.38	–	–	–	
	2	190.2	9.7	0.65	–	–	–	
DBC2	1	184.1	5.9	0.17	–	–	–	–
	2	189.0	10.2	0.81	–	–	–	–
DBC3	1	180.9	8.9	0.23	–	–	–	–
	2	189.6	9.4	0.63	–	–	–	
DBC4	1	177.8	10.8	0.20	–	–	–	–
	2	190.3	8.9	0.65	–	–	–	–

[a] The heat capacity jump.

[b] The range of crystallinity $Xc = \Delta Hm/\Delta H°m$, where $\Delta H°m$–enthalpy of melting for 100% crystalline polymer (196.8 J/g).

The lack of the crystalline phase on the DSC thermograms of DB? and the comparative analysis of glass transition parameters in copolymers and individual PAA show the total compatibility of the polymer components in the samples, i.e., the homogeneous structure of diblock-copolymers.

Destruction of crystalline regions of MEPEG in the DBC structure indicates the interaction between MEPEG and PAA blocks. There is one peak of heat capacity appeared both in DBC thermograms and the PAA thermogram. The value of T_m on the middle of the peak for DBC1,2 is practically the same as that for PAA, but T_m for the samples of DBC3,4 is lower than T_m for individual PAA. The reduction of T_m for samples DBC with long blocks of MEPEG ($M_\mathrm{v} \geqslant 2\cdot 10^3$) in comparison with T_m for PAA points to the intramolecular interaction between PAA and MEPEG segments which increases with the growth of MM MEPEG.

CONCLUSION

We have established that the block-copolymerization of PAA with MEPEG belongs to the matrix processes. The positive dynamic matrix effect has maximum value at $M_{\mathrm{v\ MEPEG}} = 1.1\cdot 10^3$. The reduction of that at $M_{\mathrm{v\ MEPEG}} > 1.1\cdot 10^3$ can be explained by the strengthening of interblock interactions with increase in $M_{\mathrm{v\ MEPEG}}$ and by the following macrocoil compactization in the aqueous medium. The destruction of crystalline ranges of MEPEG in the PAA-b-MEPEG structure proves that the interaction between MEPEG and PAA blocks takes place.

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