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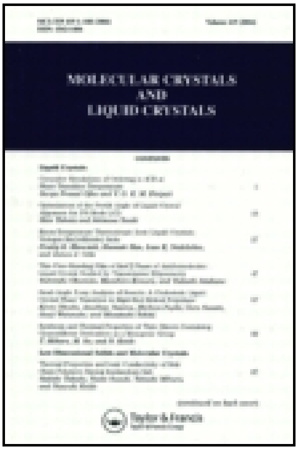

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Double-Hydrophilic Block Copolymers Forming Intramolecular Polycomplexes

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Double-Hydrophilic Block Copolymers Forming Intramolecular Polycomplexes

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Double-hydrophilic block copolymers containing the charged blocks of poly(acrylic acid) (PAAc) and the neutral blocks of monomethyl ether of poly(ethylene oxide) (MEPEO) are synthesized by a free radical block copolymerization of PAAc with monomethyl ether of poly(ethylene glycol) of various molecular weights ($M_{vMEPEG} = 1.1 \cdot 10^3 - 5 \cdot 10^3$)*. It is revealed that the block copolymerization has a matrix character because non-covalent interactions of propagating PAAc chains with MEPEG. This fact points out the formation of intramolecular polycomplexes in the given diblock copolymers. The MEPEO-b-PAAc copolymers obtained are characterized by* ^1H *NMR spectroscopy.*

Keywords: diblock copolymer; dynamic matrix effect; hydrogen bonds; intramolecular polycomplex; poly(acrylic acid)

INTRODUCTION

Double-hydrophilic block copolymers composed of two water-soluble polymers of different chemical nature are perspective polymer materials [1,2]. Their chemical structure may be tuned for a wide range of applications covering such different aspects as the stabilization of colloids, the micelle formation, and the complexation with drugs by electrostatic interactions and hydrogen bonds towards to novel drug delivery systems [1]. At the same time, the double-hydrophilic block copolymers with the system of cooperative hydrogen bonds between proton-donor blocks such as carboxylic polyacids and proton-accepting blocks such as poly(ethylene oxide) (PEO) or its monoethers are of

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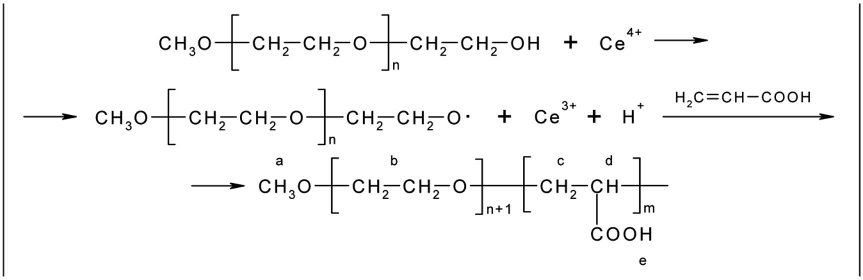
special interest [3,4,5]. Complex formation between individual poly(ethylene glycol) (PEG) and poly(acrylic acid) (PAAc) or poly (methacrylic acid) (PMAAc) in water is well known [6,7], but that between covalently linked PEO and polyacid chains is not adequately explored. In the present work, the peculiarities of the radical block copolymerization of PAAc with monomethyl ether of poly(ethylene glycol) (MEPEG) with different chain lengths and the main molecular parameters of the block copolymers, which form intramolecular polycomplexes (IntraPCs), are considered.

EXPERIMENTAL

Traditionally, PEO-*b*-PAAc or PEO-*b*-PMAAc diblock copolymers are prepared by the anionic polymerization [3,4]. In the given work, MEPEO-*b*-PAAc diblock copolymers were synthesized in water by the free radical block copolymerization, using ammonium cerium(IV) nitrate from "Aldrich" (USA), acrylic acid (AAc) from "Fluka" (USA), and monomethyl ethers of poly(ethylene glycol) with molecular weights $M_v = 1.1 \cdot 10^3$ (MEPEG1), $2 \cdot 10^3$ (MEPEG2), and $5 \cdot 10^3$ (MEPEG3) from the same firm. Block copolymerization was activated by Ce^{IV} ions according to the following scheme [8]:



Syntheses of MEPEO-*b*-PAAc copolymers were performed for 24 h in an inert atmosphere at $T = 20^{\circ}C$, the constant molar ratios $[Ce^{1V}]/[MEPEG] = 1$ and $[MEPEG]/[AAc] = 1$, and variable molar ratios $[Ce^{1V}]/[AAc] = 0.9 \cdot 10^{-2}$, $2.2 \cdot 10^{-2}$, and $4 \cdot 10^{-2}$. Diblock copolymers were precipitated from reaction mixtures by centrifugation for 15 min at $\omega = 6000$ rot/min. All the sediments were cleansed by deionized water and dissolved in 0.2 N NaOH. Further, the MEPEO-*b*-PAAc samples in the Na-form of a polyacid block were transferred to those in the H-form of a PAAc block by the addition of HCl up to pH = 2. Additionally, PAAc samples were obtained by the free radical homopolymerization of AAc in the presence of C_2H_5OH instead of MEPEG using Ce^{IV} ions for the initiation under the same experimental

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conditions. All the samples were purified analogously to MEPEO-*b*-PAAc samples.

Kinetic studies of the block copolymerization processes compared to the homopolymerization of acrylic acid under the same experimental conditions were carried out using dilatometry [9], spectrophotometry, and potentiometric titration. Changes in the turbidity of the reaction mixtures during the polymerization were recorded by a photoelectrocalorimeter LMF-69 (Russia) at the wavelength $\lambda = 620\,\text{nm}$. The polymerization rate and the monomer conversion in the block copolymerization and the homopolymerization were controlled by means of potentiometric titration. The certain volumes of a reaction mixture (10 ml) were taken away through a definite time of the polymerization process. The diblock copolymer sediment was selected of every taken volume by centrifugation at $\omega = 6000\,\text{rot/min}$. Potentiometric titration of supernatants containing no reacted AAc were performed using a digital pH-meter 1–160 M (Belarus) calibrated with standard buffer solutions. Every titration was carried out with 0.2 N NaOH in an argon flow at $T = 25^\circ\text{C}$, allowing the 2 min equilibrium time for each point. Majority of the potentiometric titration curves demonstrated a sharp jump of the electric potential at a certain equivalent NaOH volume that is characteristic for the low-molecular-weight acids.

NMR spectroscopy was applied to confirm a chemical structure of the diblock copolymers and to determine the molecular weights of PAAc blocks and the whole copolymer chains [2,10]. ^{1}H NMR spectra of MEPEO-*b*-PAAc and also MEPEG and PAAc samples in DMSO-d_6 were recorded at 20°C using a Mercury-400 spectrometer from "Varian" (USA). The ratios between PAAc and MEPEO units in the diblock copolymers (base-mole PAAc/base-mole MEPEO) were calculated from the ratios of the integral intensities of corresponding ^{1}H NMR signals [10].

RESULTS AND DISCUSSION

The initiation reaction of the block copolymerization and the homopolymerization proceeded by the same mechanism; therefore, the comparison of the kinetic parameters of both processes was possible. The results of dilatometry researches turned out to be not quite correct due to the appearance a significant turbidity in reaction mixtures followed by the precipitation of polymer aggregates in the cases of the AAc homopolymerization (Fig. 1).

The last effect was attributed to the formation of badly solvable complexes of PAAc chains with Ce$^{\text{III}}$ ions [11]. The turbidity of a

FIGURE 1 The photography of dilatometers with reaction mixtures obtained in the processes of block copolymerization of PAAc with MEPEG3-*1* and AAc homopolymerization-*2*.

reaction mixture in the block copolymerization, especially in the case of the highest molecular weight of the initial MEPEG sample (MEPEG3), was found to be essentially more intensive and stable in time (Fig. 1, the first dilatometer) than that in the process of AAc homopolymerization (the second dilatometer). Spectrophotometry measurements of the turbidity changes during the block copolymerization and the homopolymerization confirmed this fact (Fig. 2):

The significant increase in the turbidity of a reaction mixture in the block copolymerization of PAAc with MEPEG3 indicated strong intramolecular interactions between different polymer blocks in MEPEO-*b*-PAAc3 as compared with the AAc homopolymerization, i.e., the formation of IntraPC by hydrogen bonds in its macromolecules [4,5]. We note that changes in the reaction mixture turbidity during the block copolymerization of PAAc with lower-molecular-weight MEPEG samples (MEPEG1 and MEPEG2) differ slightly from those at the AAc homopolymerization (Fig. 2a, b).

The conversion–time kinetic curve which were calculated from the data of potentiometric titration for the processes of block copolymerization of PAAc with MEPEG of different molecular weights and the AAc homopolymerization are represented in Figure 3.

Solubility of the diblock copolymers in water was essentially less than that of PAAc (because of the IntraPC formation). That is why they can be well separated from the corresponding reaction mixtures by centrifugation. Unlike this, PAAc samples were partially dissolved in a reaction mixture in 40 h after the beginning of the polymerization

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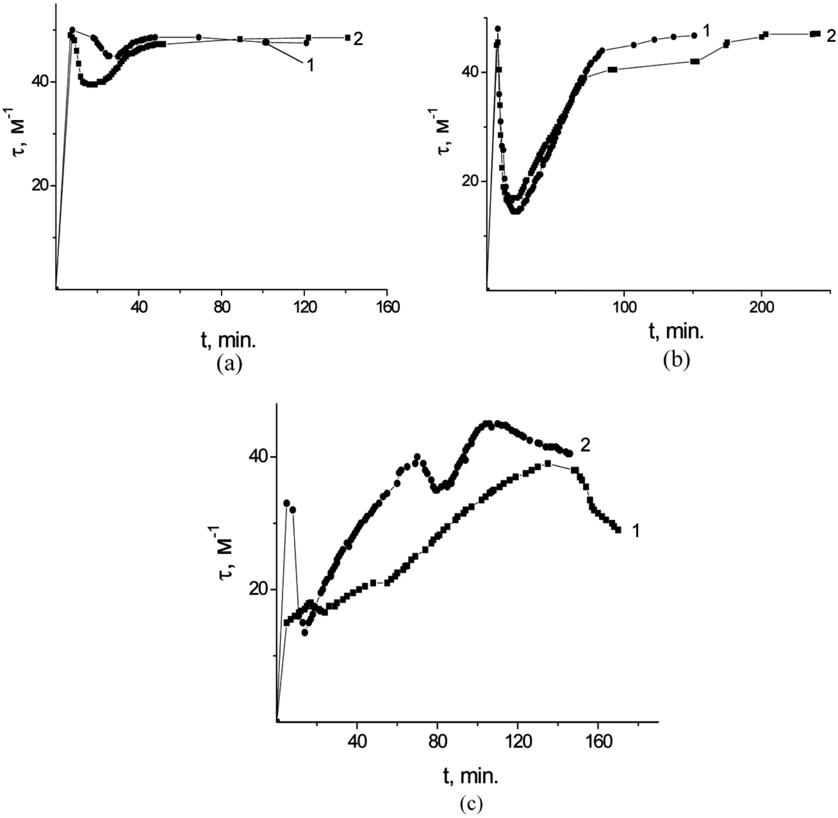

FIGURE 2 The reaction mixture turbidity *vs* time for the AAc homopolymerization – *1* (a–c) and the block copolymerization of PAAc with MEPEG1 – *2* (a), MEPEG2 – *2* (b), and MEPEG3 – *2* (c). $\lambda = 620\,\text{nm}$.

process. So, the kinetic investigations for the block copolymerization could be carrying out for a longer time (up to the higher conversion values) than that for the homopolymerization (Fig. 3). It was shown that the polymerization rate and the monomer conversion were higher at the block copolymerization of PAAc with all MEPEG samples as compared with the AAc homopolymerization carried out under the same experimental conditions. This situation is reflected by Table 1, whose data were defined from the kinetic curves in Figure 3.

The essential increase in the polymerization rate and the monomer conversion in the block copolymerization processes as compared with those at the AAc homopolymerization indicates the positive dynamic matrix effect [12]. The value of this effect grew with increase in the

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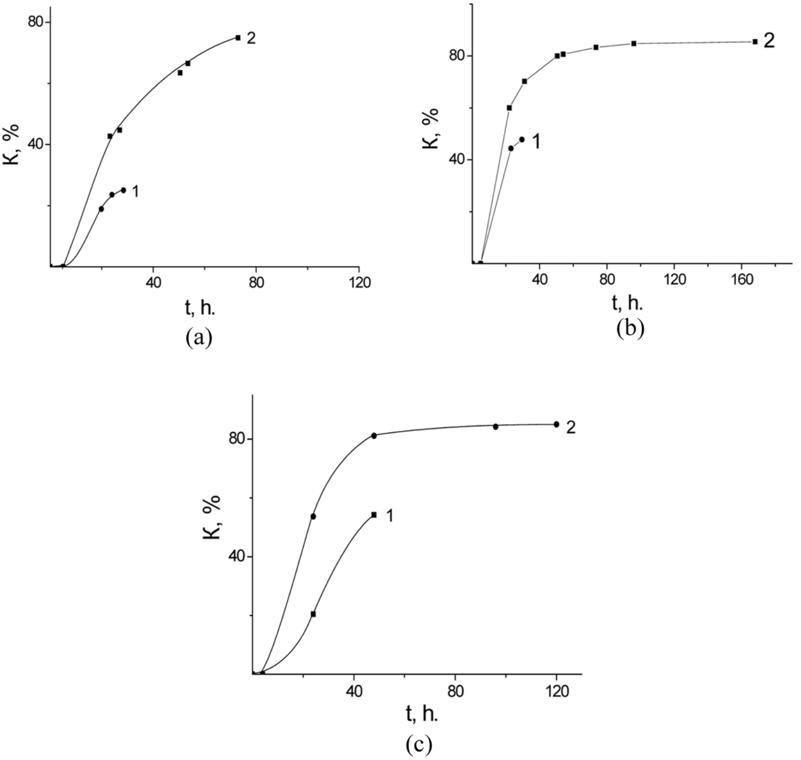

FIGURE 3 The monomer conversion *vs* time for the AAc homopolymerization – *1* (a–b) and the block copolymerization of PAAc with MEPEG1 – *2* (a), MEPEG2 – *2* (b), and MEPEG3 – *2* (c). T = 20°C.

TABLE 1 Kinetic Parameters of the Block Copolymerization of PAAc with MEPEG and the AAc Homopolymerization

Polymer	$M_{v\text{MEPEG}} \cdot 10^{-3}$	$\alpha \cdot 10^{2}$ [a]	$V_r^{20} \cdot 10^6$ [b] mole · dm^{-3}·c^{-1}	$V_r^{40} \cdot 10^6$ mole · dm^{-3} · c^{-1}	$\mathcal{K}$,[c] %
MEPEO-*b*-PAAc1	1.1	4	4.93	5.08	49
PAAc1	–	4	2.78	–	25
MEPEO-*b*-PAAc2	2.0	2.2	6.59	7.22	67
PAAc2	–	2.2	4.81	5.02	47
MEPEO-*b*-PAAc3	5.0	0.9	5.56	6.50	64
PAAc3	–	0.9	2.40	3.08	29

[a] The molar ratio between Ce^{1V} and AAc.

[b] The polymerization rate at the 20% and 40% monomer conversion.

[c] The monomer conversion in 28.5 hours after the polymerization beginning.

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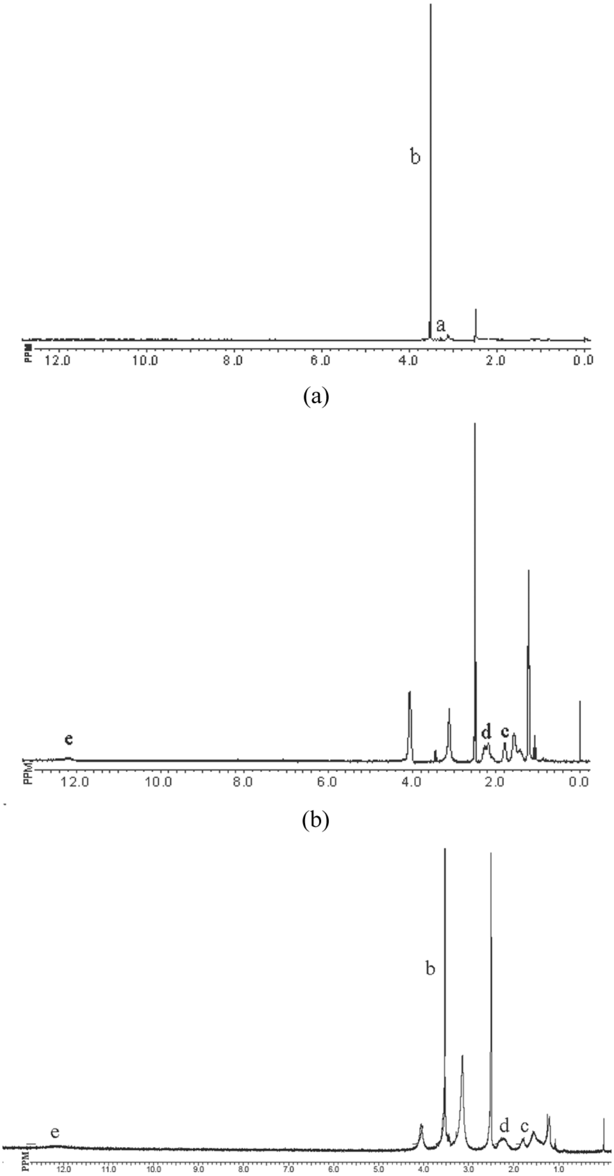


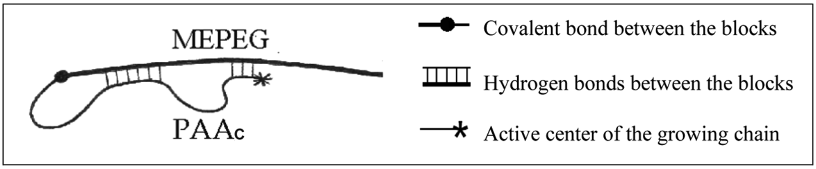
(a)

(b)

(c)

FIGURE 4 ^{1}H NMR spectra for MEPEG3 (a), PAAc (b), and MEPEO-*b*-PAAc3 (c) recorded in DMSO-d_6.

MEPEO block (matrix) length (Fig. 3, Table 1). The matrix character of the block copolymerization (at least in the initial stage) was caused by the formation of the H-bond system between different polymer chains [9,12]:



One of the diblock copolymers synthesized was characterized by NMR spectroscopy. The ^{1}H NMR spectra for MEPEG3, PAAc3, and MEPEO-*b*-PAAc3 in DMSO-d$_6$ are represented in Figure 4.

The ^{1}H NMR spectrum of MEPEG3 (Fig. 4a) shows a weak signal with $\delta = 3.28$ p.m. and an intense signal with $\delta = 3.53$ p.m., which belong to methyl (a) and methylene protons (b), respectively [2]. In the ^{1}H NMR spectrum of PAAc3 (Fig. 4b), the multiple signals with $\delta = 1.59$–1.81 p.m. (c) and $\delta = 2.18$–2.27 p.m. (d) correspond to methylene and methyne protons. In addition, a weak signal of the protons of -COOH groups with $\delta = 12.05$ p.m. (e) [13] was observed. The ^{1}H NMR spectrum of MEPEO-*b*-PAAc3 (Fig. 4c) demonstrates all proton signals for methylene, methyne, and $-$COOH groups of PAAc chains. Moreover, the signal of methylene protons of a MEPEO block was revealed in this spectrum. Thus, the presence of PAAc and MEPEO units in MEPEO-*b*-PAAc3 was confirmed. The units' ratio of both blocks in the diblock copolymer was calculated using the integral intensities (A) of the corresponding signals [2,10]:

$$\frac{n_{PAAc}}{n_{MEPEG}} = \frac{A_{CH(PAAc)}}{A_{CH_2(MEPEO)}/4} = 0.73, \text{ base-mole PAAc/base-mole MEPEO}$$

According to these data, the number-averaged molecular weights of a PAAc block and the whole MEPEO-*b*-PAAc3 diblock copolymer are equal to $6 \cdot 10^3$ and $1.1 \cdot 10^4$, respectively.

CONCLUSION

It is shown that the process of radical block copolymerization of PAAc with MEPEG initiated by Ce^{IV} ions has a pronounced matrix character because of the non-covalent interactions of propagating polyacid (daughter's) chains with polyethers (matrices). The positive dynamic

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matrix effects observed in the MEPEO-*b*-PAAc syntheses are caused by: i) the formation of IntraPCs by hydrogen bonds in diblock copolymer macromolecules and ii) their stability in a solution that ensures the accessibility of the active centers of propagation to monomer molecules. The characterization of one of the diblock copolymer samples carried out by ^{1}H NMR spectroscopy fully confirmed its chemical structure and allowed finding the number-averaged molecular weights of PAAc blocks and the whole copolymer macromolecules.

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