

New Comb-Shaped Triblock Copolymers Containing a Liquid-Crystalline Block and Polyvinylpyridine Amorphous Blocks: Synthesis and Properties

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Abstract—New liquid-crystalline symmetric triblock copolymers ABA, in which central LC block B is poly(*p*-(6-acryloyloxypropoxyphenyl)-*p*-methoxybenzoate and blocks A are amorphous blocks of polyvinylpyridine, whose units are able to form various types of noncovalent chemical bonds, are synthesized. The phase behavior of the triblock copolymers is studied, and the type of their microphase-separated structure is ascertained. It is shown that the composition of the triblock copolymers affects the morphology of their thin films.

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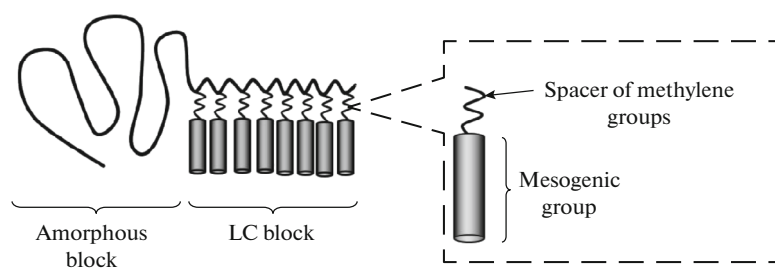
INTRODUCTION

In recent decades, various scientific schools have maintained their considerable interest in the synthesis and characterization of block copolymers of various chemical structures related to the search for novel innovative materials with a set of desired physico-chemical characteristics for their particular applications [1–3]. The combination of chemically different immiscible “building blocks” in the composition of a block-copolymer macromolecule entails formation of ordered microsegregated structures with the characteristic morphology (lamellar, cylindrical, spherical, gyroid) adjusted by a change in key parameters, such as the Flory–Huggins parameter of interaction between monomer units of different blocks, volume fractions of blocks, their degree of polymerization, and mutual arrangement [4, 5]. The spontaneous formation of spatially ordered periodic structures at a scale of 10–100 nm in block copolymer films makes them attractive for use in nanolithography [6, 7] and microelectronics [8], development of nanoporous membranes [9, 10] and photon crystals [11–13], and obtainment of effective templates for the targeted spatial orientation of metal nanoclusters [14–16].

Comb-shaped block copolymers composed of LC blocks containing mesogenic groups and amorphous blocks are of particular interest to researchers. These block copolymers feature two-level self-organization related to the tendency of mesogenic groups toward certain ordering within an LC block and thereby provide the anisotropy of physical properties (dielectric

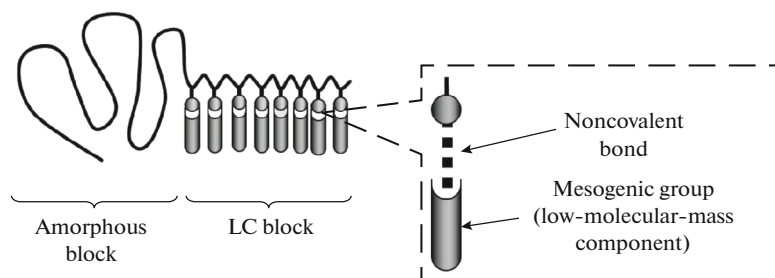
and diamagnetic susceptibility, birefringence) and microphase separation typical of block copolymers. Microphase separation in LC/amorphous block copolymers may affect the conformation of the LC block and its orientational ordering [17–22]. For example, as was shown for block copolymers with the typical cylindrical morphology, in which cylinders are formed by smectogenic LC blocks, there is the homogeneous orientation of mesogenic groups in parallel to cylinder walls (smectic layers are arranged perpendicularly) [19]. However, if LC blocks form the continuous phase, then smectic layers are arranged in parallel to cylinders formed by amorphous blocks [20]. At the same time, if the LC blocks form spheres, then the smectic mesophase in them is suppressed and the nematic ordering of mesogenic groups is observed [22].

To date, all of the synthesized comb-shaped LC/amorphous block copolymers may be divided into two families in terms of their organization mode. The first family includes block copolymers, in which the LC block consists of mesogenic groups (cyanobiphenyl, phenyl benzoate, cholesteryl, azobenzene-containing) covalently attached to the polymer chain through an aliphatic spacer and polystyrene, poly(methyl methacrylate), and poly(alkyl methacrylates) are frequently used as the amorphous block [23, 24]; their role is to form microphase-separated structures and to impart the desired mechanical properties to the system.



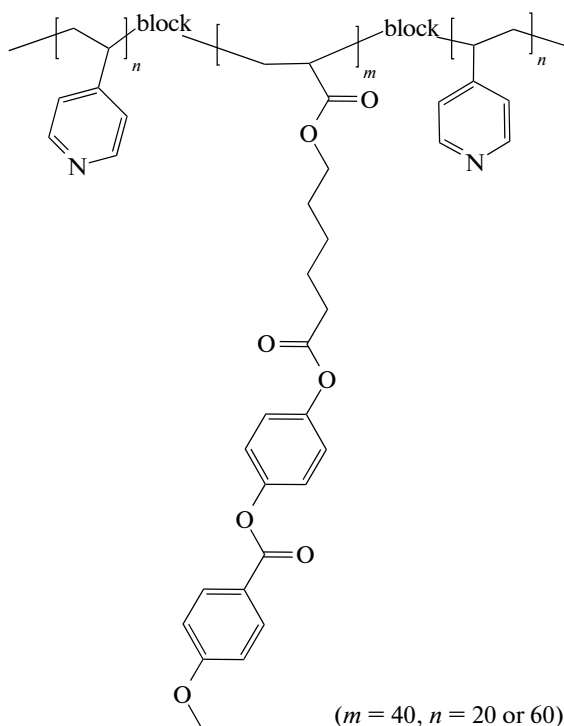
The second family of LC/amorphous block copolymers is assembled of amorphous blocks, one of which bears functional groups forming noncovalent bonds (i.e., hydrogen, ionic [25]) with low-molecular-

mass mesogen-containing compounds—supramolecular complexes. These functionalized blocks contain as a rule units of polyvinylpyridine [26] or poly(acrylic acid) [27].



It should be emphasized that very little information concerning this family of LC/amorphous block copolymers is available in the literature.

In this study, our tasks were to unite these two approaches and to synthesize triblock copolymers ABA containing phenyl benzoate mesogenic groups covalently bound to the polymer chain in the LC block (block B) and polyvinylpyridine units in amorphous blocks A:



The synthesis and characterization of these block copolymers are topical issues because, in addition to the anisotropy of physical properties specified by the LC block, vinylpyridine units can form hydrogen bonds with low-molecular-mass precursors imparting certain properties (e.g., light or thermal sensitivity) or coordination bonds with inorganic nanoparticles possessing a unique set of optical properties [28–31]. Using a limited set of these block copolymers with a certain microphase-separated structure, an array of polymeric materials possessing the whole spectrum of different physicochemical properties may be produced; moreover, they may be changed in the desired manner by varying the nature of an organic or inorganic precursor.

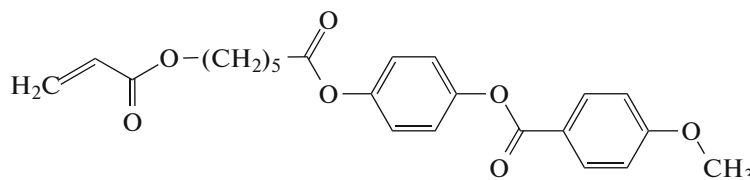
Block copolymers were synthesized through a variant of controlled radical polymerization, namely, reversible addition-fragmentation chain-transfer (RAFT) polymerization. As opposed to other methods of reversible-deactivation radical polymerization, RAFT polymerization is applicable to a wider scope of monomers and solvents and is implemented in a wide temperature range. Moreover, using this approach, we managed to synthesize liquid-crystalline triblock copolymers containing mesogenic groups in each block [32, 33].

EXPERIMENTAL

RAFT agent—*S,S'*-bis(methyl-2-isobutyrate) trithiocarbonate—was synthesized as described in [34] and identified by ^1H NMR spectroscopy. ^1H NMR spectrum (CDCl_3): singlets at 1.6 and 3.7 ppm. AIBN

was recrystallized from methanol and dried in vacuum to a constant weight. 4-Vinylpyridine (VP) was dis-

tilled in vacuum directly before use. *p*-(6-Acryloyloxy-caproyloxyphenyl)-*p*-methoxybenzoate



was synthesized as described in [35]; the purity of the product was ascertained by chromatography and NMR spectroscopy.

^1H NMR (CDCl_3 , trimethylsilane): 1.44–1.86 ($\text{CH}_2=\text{CHCOOCH}_2(\text{CH}_2)_3\text{CH}_2\text{COO}-$), 2.58 ($\text{CH}_2\text{CH}_2\text{COOAr}$), 3.84 ($-\text{PhOCH}_3$), 4.18 ($-\text{CH}_2\text{CH}_2\text{OOCCH}=\text{CH}_2$), 5.80 ($\text{CH}_2=\text{CH}-$, *trans*), 6.11 ($\text{CH}_2=\text{CH}-$, *cis*), 6.40 ($\text{CH}_2=\text{CH}-$), 6.97 (*ortho* to $-\text{OCH}_3$), 7.10–7.25 (ArH), 8.14 (*ortho* to $-\text{COO}-$) ppm.

DMF was dried over molecular sieves and distilled over the as-calcined magnesium sulfate; ethyl acetate was dried over molecular sieves and distilled over the as-calcined potassium carbonate; THF, diethyl ether, and petroleum ether were distilled over KOH; and chloroform was passed through a column packed with aluminum oxide and distilled.

Before the polymerization of 4-vinylpyridine, a solution of AIBN and *S,S'*-bis(methyl-2-isobutyrate) trithiocarbonate in the monomer or its mixture with DMF was prepared. The solution was poured in an ampoule and blown with argon for 20 min, and the ampoule was sealed. Polymerization was conducted for 24 h at 80°C. After completion of polymerization, the ampoule was cooled with liquid nitrogen and opened. If required, the reaction mixture was diluted with methanol, and the polymer was lyophilized.

Polymeric RAFT agents based on 4-vinylpyridine were synthesized as follows. In the first case (polyRAFT agent PVP-1), 1 g (9.53 mmol) of the as-distilled monomer, 25 mg (79 μmol) of RAFT agent, and 2.7 mg (16.3 μmol) of AIBN were placed in the ampoule; the molar ratio monomer : RAFT agent : initiator was 620 : 5 : 1. In the second case (polyRAFT agent PVP-2), a solution of RAFT agent (74 mg, 239 μmol) and AIBN (5 mg, 30.5 μmol) in a mixture of DMF (1 mL) and the monomer (1 g, 9.53 mmol) was prepared; the molar ratio monomer : RAFT agent : initiator was 307 : 8 : 1. The reaction mixtures were prepared and polymerized as described above. The yield of the polymer in both cases was ~95%. According to the GPC data, $M_n = 5.4 \times 10^3$ and $M_w/M_n = 1.23$ for PVP-1 and $M_n = 2.9 \times 10^3$ and $M_w/M_n = 1.11$ for PVP-2.

The polymerization of 4-vinylpyridine mediated by polyRAFT agents PVP-1 and PVP-2 was performed as

follows. The ampoule was loaded with 25 mg (0.24 mmol) of 4-vinylpyridine, 60 mg (4.8 μmol) of PVP-1 or 22 mg (4.8 μmol) of PVP-2, 0.1 mL of DMF, and 0.2 mg (1.2 μmol) of AIBN; in both cases, the molar ratio monomer : RAFT agent : initiator was 200 : 4 : 1 (concentrations, 1.2, 2.5×10^{-2} , and 6×10^{-3} mol/L, respectively). Upon dissolution and mixing of all of the components, the resultant homogeneous solution was purged with a flow of argon and the ampoules were sealed. Polymerization was performed for 24 h at 80°C. After completion of polymerization, the ampoule was cooled and opened. The polymer was precipitated from methanol solution into diethyl ether. The yields of the products were 92 and 76% for PVP-1 and PVP-2, respectively.

Triblock copolymers were synthesized according to two methods. In the first case, 18 μmol of PVP-1 (225 mg) or PVP-2 (81 mg) and *p*-(6-acryloyloxy-caproyloxyphenyl)-*p*-methoxybenzoate (300 mg, 0.73 mmol) were dissolved in 0.35 mL of DMF. Afterwards, the calculated amount of AIBN solution in DMF was added so that the concentration of the initiator in the reaction mixture was 8×10^{-3} mol/L. In the second case, 57 μL (38 μmol) of 4-vinylpyridine solution in DMF (70 mg/mL) and the calculated amount of AIBN solution in DMF were added to the analogous solution of polymeric RAFT agent based on PVP and the monomer in DMF. The reaction mixtures were poured in ampoules and purged with argon. Afterwards, the ampoules were sealed. Polymerization was conducted at 80°C for a day. The block copolymers were isolated by precipitating the reaction mixture into excess diethyl ether. The polymerization product was purified via reprecipitation of the block copolymer from ethyl acetate solution into petroleum ether. The as-purified block copolymers were dried in vacuum at 70°C and characterized by GPC and ^1H NMR spectroscopy.

NMR spectra were recorded on a Bruker DRX500 NMR spectrometer. The analyte solution with a concentration of 3% was prepared in CDCl_3 , which was preliminarily passed through aluminum oxide to remove phosgene and HCl admixtures.

The molecular-mass characteristics of the polymers were analyzed by GPC in DMF containing 0.1 wt % LiBr at 50°C on a PolymerLabs GPC-120 chromatograph equipped with two columns PLgel

5 μm MIXED B ($M = (5 \times 10^2) - (1 \times 10^7)$) and a differential refractometer. Narrowly dispersed PMMA standards were used for calibration.

Samples for TEM studies were prepared as follows. A film of the test block copolymer was cast from 2% chloroform solution on a PET substrate. The films were annealed in vacuum at 140°C for 3 h. Then with the aid of a Reichert-Jung ultramicrotome, the cross sections of block copolymer films with a thickness of 50–60 nm were obtained using a Diatome diamond knife at a cutting speed of 2 mm/s, transferred on a copper grid, and contrasted with iodine vapor for 50 min. Afterwards, the samples were studied on a LEO 912 AB Omega (Carl Zeiss) transmission electron microscope with an accelerating voltage of 100 kV.

The optical textures and phase-transition temperatures were studied in crossed polaroids using a Lomo P-112 polarization microscope equipped with a Mettler FP-84 hot stage and a Mettler FP-800 microprocessor temperature control unit.

The heat and phase-transitions temperatures of the polymers were estimated by differential scanning calorimetry on a PerkinElmer DSC-7 instrument. The heating rate was 10 K/min, and the sample weight was 10–20 mg. Before measurements the polymer samples were annealed to avoid influence of the thermal prehistory.

RESULTS AND DISCUSSION

Synthesis of Triblock Copolymers ABA

Homopolymerization of 4-vinylpyridine. The controlled synthesis of PVP and related block copolymers is traditionally conducted by anionic living polymerization [36] and group-transfer anionic polymerization [37]. In recent years, reversible-deactivation radical polymerization has actively been used for the synthesis of PVP with the desired MM and narrow molecular-mass distribution [38–43]. Our previous studies have shown that symmetric trithiocarbonates $\text{R}-\text{SC}(=\text{S})\text{S}-\text{R}$ make it possible to implement the controlled synthesis of PVP with a high yield. Among the examined trithiocarbonates, PVP with the narrowest MMD is formed in the presence of *S,S'*-bis(methyl-2-isobutyrate) trithiocarbonate ($\text{R} = \text{C}(\text{CH}_3)_2(\text{COOCH}_3)$) [42]. Therefore, this RAFT agent was chosen for the synthesis of block copolymers.

The mechanism of RAFT polymerization mediated by symmetric trithiocarbonates was described in detail in [44, 45]. In a general case, when symmetric trithiocarbonates are used for the controlled synthesis of poly-

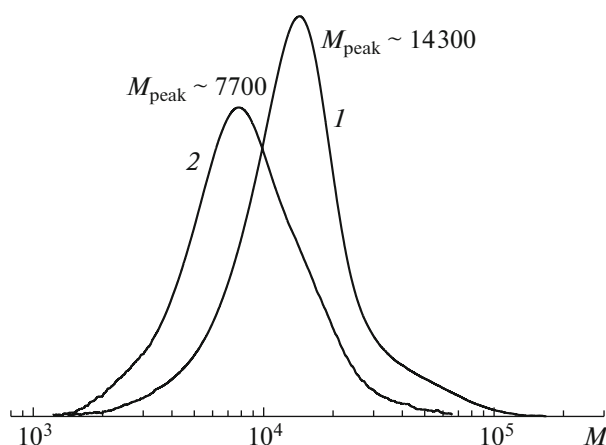
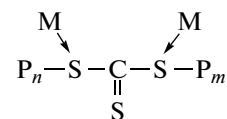


Fig. 1. MMD curves of polyvinylpyridine synthesized in the presence of *S,S'*-bis(methyl-2-isobutyrate) trithiocarbonate (*I*) before and (*2*) after heating with the 100-fold molar excess of AIBN in benzene at 80°C for 24 h.

mers, a monomer inserts into a chain occurs via two ends relative to the trithiocarbonate group [44, 45]:



However, from the viewpoint of synthesis of symmetric triblock copolymers ABA, it is important that the lengths of polymeric substituents P_n and P_m in the polymer structure be similar. Note that the structure of a macromolecule in this case is determined by the nature of the monomer and leaving group in the RAFT agent. Therefore, at the initial step, the synthesis of PVP was mediated by *S,S'*-bis(methyl-2-isobutyrate) trithiocarbonate and the position of the trithiocarbonate group in a chain was investigated. For this purpose, the technique described in [46] was applied. According to this technique, a polymer solution in an inert solvent was heated with the 100-fold molar excess of AIBN at 80°C for 24 h and the MMD of the polymer was analyzed [46]. Figure 1 shows the chromatograms of PVP synthesized using the chosen RAFT agent (curve *I*) and heated with excess AIBN (curve *2*). The MMD of the polymer after heating with excess AIBN remains unchanged: the curve remains unimodal but shifts to low molecular masses; its M_{peak} is ~ 2 times lower than that of the initial PVP. Hence, according to the known scheme of this experiment [45, 46], it may be inferred that chain growth evenly occurs via two ends and the trithiocarbonate group occurs near the chain center.

For further studies, PVP-1 and PVP-2 were synthesized and their ability to function as polymeric RAFT agents upon addition to a new portion of its monomer and initiator was probed. Figure 2 shows the MMD curves of the polymers before and after postpo-

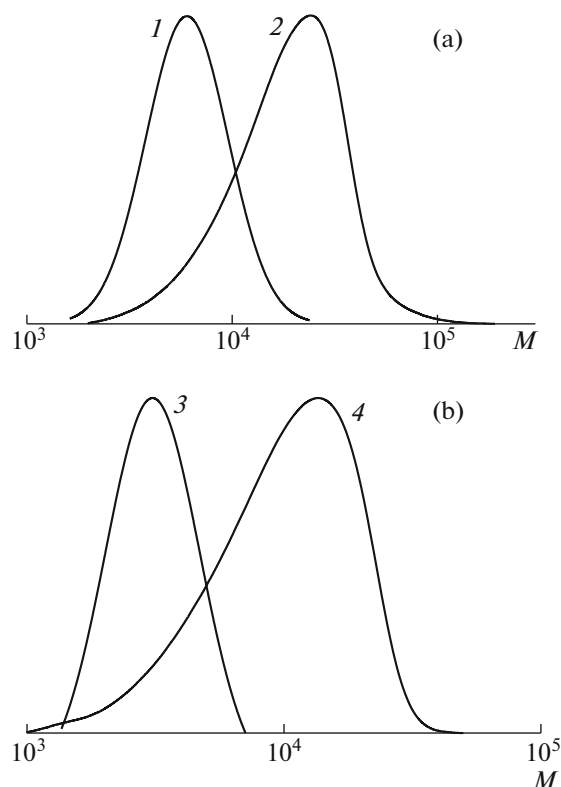


Fig. 2. MMD curves of polyRAFT agents (1) PVP-1 and (3) PVP-2 and (2, 4) the products of polymerization mediated by these agents. $[M] = 1.2$, $[\text{polyRAFT agent}] = 2.5 \times 10^{-2}$, and $[\text{AIBN}] = 6 \times 10^{-3}$ mol/L.

lymerization. It is seen that, regardless of the MM of the initial polymeric RAFT agent, the MMD curves of the postpolymerization product are unimodal and shift to high molecular masses. If the polymeric RAFT agent is in the 4-fold molecular excess with respect to AIBN, the polymer with $M_w/M_n = 1.4\text{--}1.6$ is produced. Thus, the majority of chains in the above poly-

meric RAFT agents are living. This finding makes it possible to expect that the synthesis of triblock copolymers via polymerization with the acrylate monomer containing mesogenic groups will be efficient.

As is known, GPC is a relative method of molecular mass determination. Therefore, NMR spectroscopy was applied to determine the number-average MM of polymeric RAFT agents. These data are required for the correct calculation of concentrations in the synthesis of block copolymers. The ^1H NMR spectrum of polyRAFT agent PVP-2 (Fig. 3) shows the following characteristic signals due to protons of the polymer: signals at 8.2–8.6 and 6.2–6.9 ppm correspond to protons of the pyridine ring, signals at 1.3–2.2 ppm are due to methylene and methine protons of the backbone, and signals at 3.24 and 1.00 ppm are due to methyl protons of the leaving group in the RAFT agent.

The quantitative analysis of the spectrum allows the M_n of the polymer to be estimated under the assumption that, under the chosen synthesis conditions (molar ratio $[\text{RAFT agent}] : [\text{initiator}] = 5\text{--}8$), macromolecules predominantly contain ends groups of the initial RAFT agent. The number-average molecular mass of polyRAFT agents was calculated from the ratio of integrals of peaks at 6.2–6.9 and 3.24 ppm normalized to the number of protons according to the following formula:

$$M_n(\text{PVP}) = \frac{I_{6.2-6.9}/2}{I_{3.24}/6} M,$$

where M is the molecular mass of the polyvinylpyridine unit equal to 105.

PVP-2 has $P_n = 40$ and $M_n = 4.5 \times 10^3$, and PVP-1 has $P_n = 120$ and $M_n = 12.9 \times 10^3$. According to the GPC data (Fig. 2, curves 1, 3), the values of M_w/M_n are 1.11 and 1.23 for PVP-2 and PVP-1, respectively. The experimentally measured degrees of polymeriza-

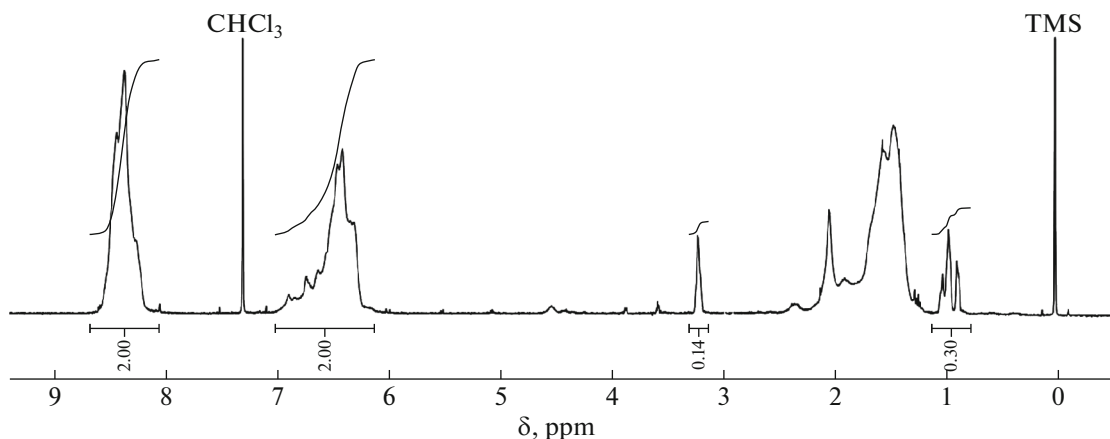


Fig. 3. ^1H NMR spectrum of polyRAFT agent PVP-2 (CDCl_3).

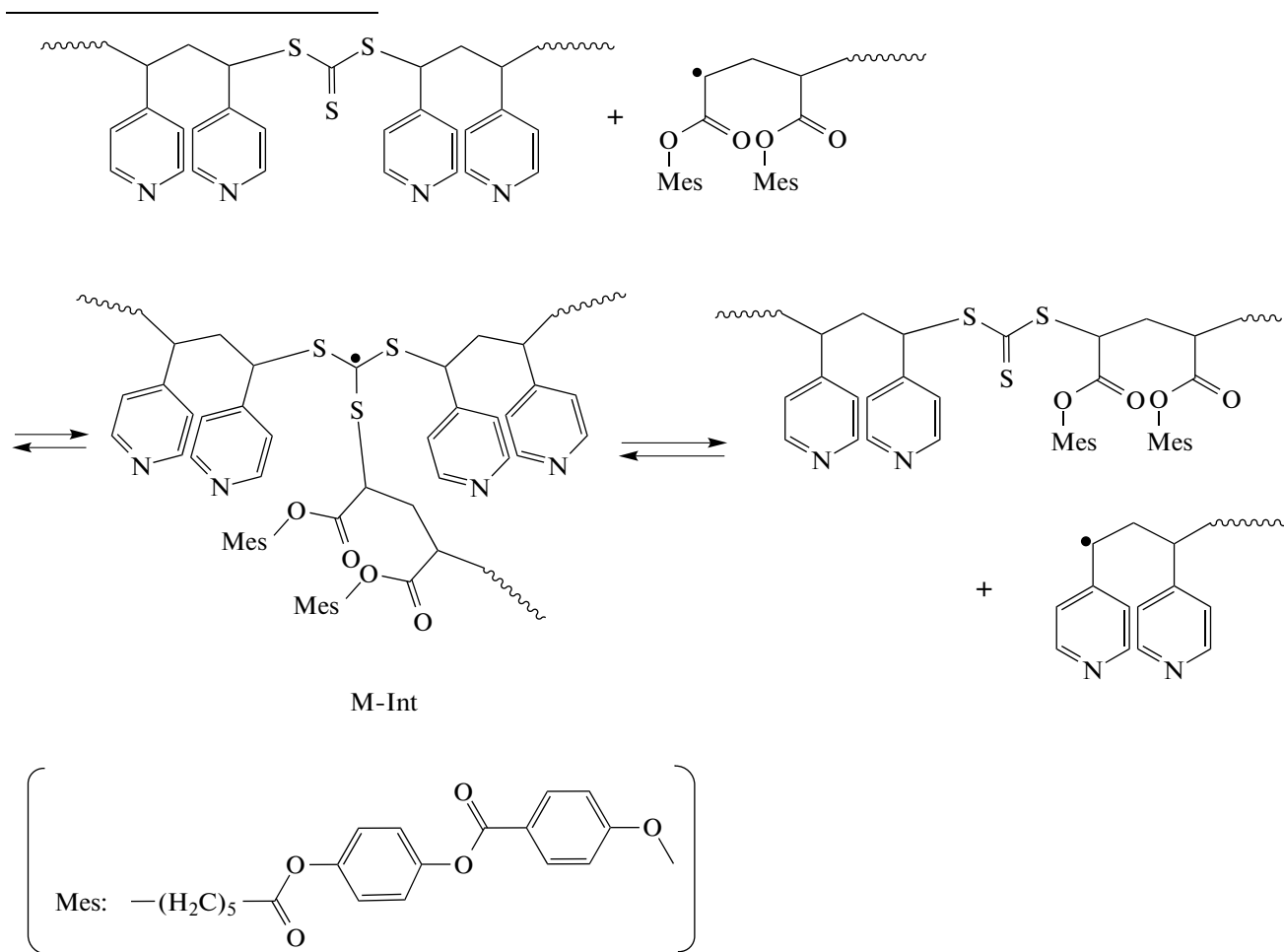
tion are close to the theoretically calculated values—36 and 110 for PVP-2 and PVP-1, respectively. This fact indicates that the chosen RAFT agent shows a fairly high efficiency in the polymerization of 4-vinylpyridine.

Thus, the structures of the synthesized polymeric RAFT agents may be outlined as $\text{PVP}_{60}\text{-SC(=S)S-PVP}_{60}$ (PVP-1) and $\text{PVP}_{20}\text{-SC(=S)S-PVP}_{20}$ (PVP-2).

Synthesis of triblock copolymers. Preliminary experiments showed that the polymerization of *p*-(6-acryloyloxycaproyloxyphenyl)-*p*-methoxybenzoate mediated by polymeric RAFT agents PVP-1 (1.5×10^{-2} mol/L) and PVP-2 (2.2×10^{-2} mol/L) (concentrations of the monomer and AIBN are 0.60 and

10^{-3} mol/L for PVP-1 and 0.86 and 10^{-3} mol/L for PVP-2, respectively) leads to a low yield of the products (no more than 30%) and the resulting triblock copolymers feature moderate values of $M_w/M_n \sim 1.5$. As the concentration of the radical initiator was increased to 8×10^{-3} mol/L, the yield of the polymerization product was raised to 70%, but simultaneously the MMD of the polymer widened abruptly ($M_w/M_n = 1.9$, Fig. 4).

Because, as was shown above, the majority of macromolecules in the polymeric RAFT agents are living, a poor control of MMD makes it possible to suggest that either PVP is a low-efficiency RAFT agent in the polymerization of *p*-(6-acryloyloxycaproyloxyphenyl)-*p*-methoxybenzoate and equilibrium in the reaction



shifts to the left to initial products or the formed intermediate is more active in the reaction of chain termination with a macroradical than in the fragmentation reaction. The latter assumption is confirmed by the following facts: PVP is an efficient polymeric RAFT agent in the polymerization of *tert*-butyl acrylate [47]; the yield of the polymer is low which indicates the retardation of polymerization; and acrylate intermediates show a higher tendency toward participation in

termination reactions than styryl or vinylpyridyl intermediates [48].

Therefore, we used the following trick. In the reaction mixture containing the polymeric RAFT agent, acrylate monomer, AIBN, and DMF, 5 mol % (with respect to acrylate) of 4-vinylpyridine was added. The activity of 4-vinylpyridine in copolymerization with alkyl acrylates is higher by more than an order of magnitude [43, 49, 50]. Therefore, it may be expected that

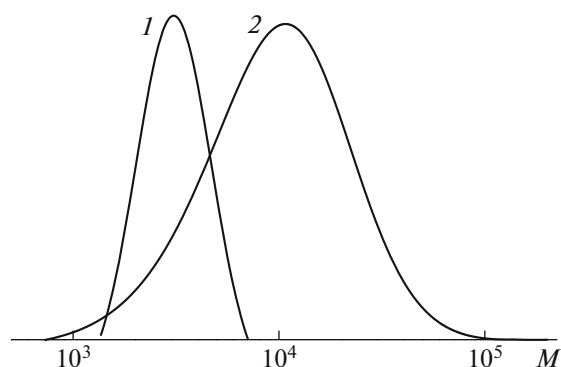


Fig. 4. MMD curves of (1) polyRAFT agent PVP-2 and (2) the product of its block copolymerization with *p*-(6-acryloyloxycaproyloxyphenyl)-*p*-methoxybenzoate. $[M] = 0.82$, $[\text{polyRAFT agent}] = 2.2 \times 10^{-2}$, and $[\text{AIBN}] = 8 \times 10^{-3}$ mol/L.

4-vinylpyridine-end-capped propagating radicals will appear in the reaction mixture. These radicals can interact with the polymeric RAFT agent to give rise to the radical intermediate containing three polymeric substituents end capped with the 4-vinylpyridine unit linked to sulfur atoms. This intermediate, as follows from the above data, undergoes fragmentation at a higher rate and, hence, its tendency to participate in termination reactions is lower. Indeed, our expectations were met, and thus two triblock copolymers—PVP₆₀-*block*-poly(*p*-(6-acryloyloxycaproyloxyphenyl)-*p*-methoxybenzoate)₄₀-*block*-PVP₆₀ (B-1) and PVP₂₀-*block*-poly(*p*-(6-acryloyloxycaproyloxyphenyl)-*p*-methoxybenzoate)₄₀-*block*-PVP₂₀ (B-2)—were synthesized. In both cases, the triblock copolymers are unimodal and their MMD is fairly narrow (Fig. 5). According to GPC, for B-1 synthesized in the presence of PVP-1, M_w/M_n is 1.45; for B-2 prepared in the presence of PVP-2, 1.40. Our estimates show that with allowance for difference in the activity of monomers and a low content of 4-vinylpyridine in the monomer mixture (5 mol %), 4-vinylpyridine is fully consumed when the monomer conversion reaches 15–20% and its single units in a growing block will be arranged near the end PVP blocks.

The composition of the triblock copolymers and their M_n values were determined by NMR spectroscopy. The ¹H NMR spectrum of triblock copolymer B-1 (Fig. 6) shows peaks of both aromatic protons of poly(*p*-(6-acryloyloxycaproyloxyphenyl)-*p*-methoxybenzoate) units and polyvinylpyridine units (at 8.2–8.5 and 6.1–6.7 ppm and 8.08, 7.15, 7.09, and 6.92 ppm, respectively). Peaks corresponding to the mesogen-containing fragment are as follows: the peak at 3.83 ppm corresponds to the methyl group and peaks at 4.04 and 2.53 ppm correspond to methylene protons arranged nearby the main-chain ester group and the ester group of the aliphatic spacer. A multiplet

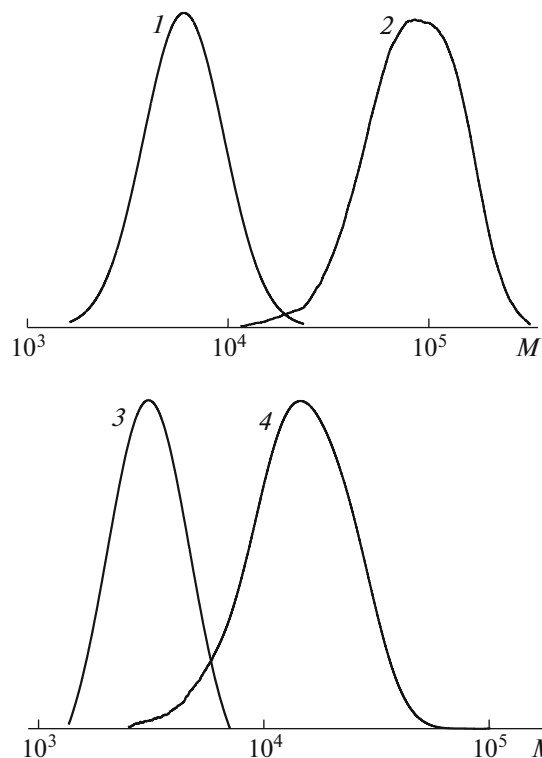


Fig. 5. MMD curves of polyRAFT agents (1) PVP-1 and (3) PVP-2 and (2, 4) triblock copolymers synthesized in their presence (2) B-1 and (4) B-2. $[M] = 0.85$, $[\text{polyRAFT agent}] = 2 \times 10^{-2}$, and $[\text{AIBN}] = 1 \times 10^{-3}$ mol/L.

in the range of 1.0–2.3 ppm corresponds to methylene protons of the aliphatic spacer and methylene and methine protons of the polymer backbone. In addition, this region shows the peak of water that is always present in the solvent.

The composition of the block copolymers was determined from the ratio of the total integral of peaks at 8.0–8.5 ppm which includes two protons of each type of monomer units and from the integral of the peak at 6.1–6.7 ppm containing the signal due to two protons of polyvinylpyridine units. Calculations were performed using the formula

$$v(\text{PVP}) = \frac{I_{6.2-6.9}/2}{I_{8.0-8.5}/2},$$

where $v(\text{PVP})$ is the molar fraction of polyvinylpyridine units.

The data on the composition and molecular-mass characteristics of the synthesized triblock copolymers are summarized in Table 1.

Phase Behavior and Morphology of Triblock Copolymers

As evidenced by polarization optical microscopy and DSC, homopolymer poly(*p*-(6-acryloyloxycaproyloxyphenyl)-*p*-methoxybenzoate) is character-

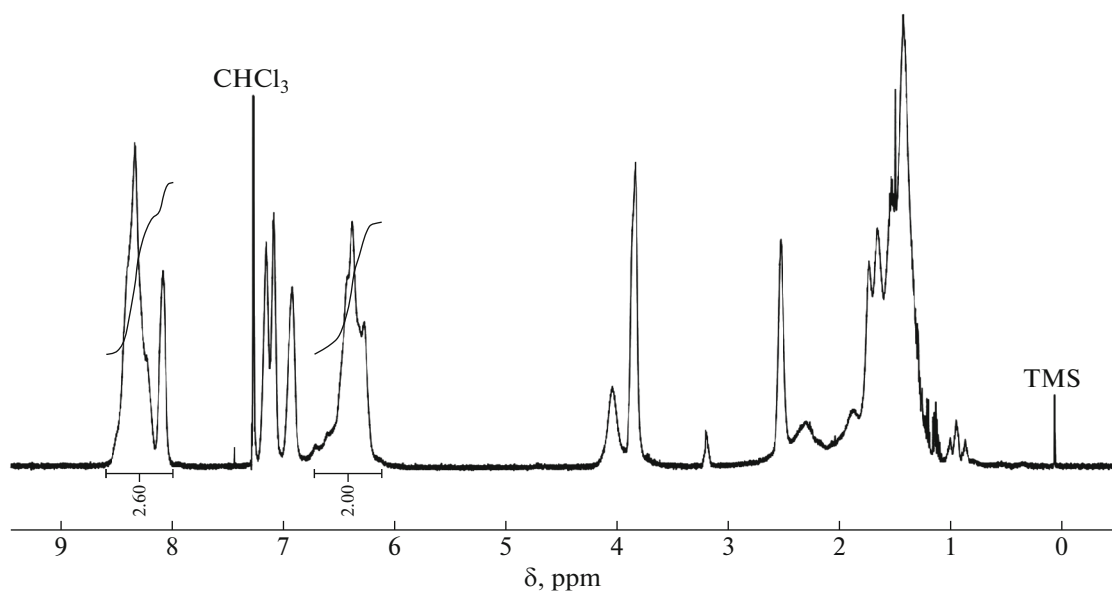


Fig. 6. ^1H NMR spectrum of triblock copolymer B-1 (CDCl_3).

ized by formation of the nematic LC phase with a melting temperature of 120°C ; PVP is the amorphous polymer with a glass-transition temperature of 110°C .

In accordance with the DSC data, triblock copolymers B-1 and B-2 feature a single glass-transition temperature and a single first-order phase transition (Table 2). According to the phase behavior of model homopolymers, it may be inferred that the observed glass-transition temperature corresponds to the phenyl benzoate block. At the same time, the glass transition of the polyvinylpyridine block is absent on the DSC curves.

Both triblock copolymers B-1 and B-2 formed the nematic LC phase, as confirmed by POM images (Fig. 7). The micrographs display the marble texture typical of the nematic LC phase. Formation of this phase may be attributed to the presence of nematogenic phenyl benzoate units in the central block of the triblock copolymers.

The morphological study of samples of B-1 and B-2 was performed using TEM. For this purpose, thin (40–50 nm) cross sections of triblock copolymer films

were prepared. Because both blocks of the triblock copolymers contain only light chemical elements, which almost equally scatter electrons, microphase separation was probed by the contrasting technique. For block copolymers containing vinylpyridine units, a suitable contrasting technique involves the exposure of polymer samples in the vapor of elementary iodine, which is selectively adsorbed by vinylpyridine units [51]. Iodine atoms scatter electrons well; therefore, the microphases adsorbing iodine will be much darker than those observed on the TEM images. The contrasted samples of triblock copolymer B-1 exhibit a well-defined lamellar microphase-separated structure well-ordered on a micron scale near the substrate–block copolymer boundary, which most probably facilitates the ordering of layers (Fig. 8a). Dark regions correspond to microphases containing polyvinylpyridine blocks and light regions correspond to microphases containing the LC block. The periodicity of the detected structure is 14 nm. Upon going away from the substrate–block copolymer boundary, the orientation of the layers becomes chaotic.

On one hand, this finding may be attributed to structural defects in the film bulk, and, on the other

Table 1. Characteristics of triblock copolymers based on 4-vinylpyridine and *p*-(6-acryloyloxypropoxyphenyl)-*p*-methoxybenzoate

Sample	PolyRAFT agent	$M_n \times 10^{-3}$	M_w/M_n	Content of PVP in block copolymer, mol %
B-1	PVP-1	31.4	1.45	75
B-2	PVP-2	20.9	1.40	50

Table 2. Temperature and heat of phase transitions for liquid-crystalline triblock copolymers

Sample	T_g , $^\circ\text{C}$	Melting temperature of the LC phase, $^\circ\text{C}$	Heat of melting, J/g
B-1	34	110	0.4
B-2	36	111	0.5

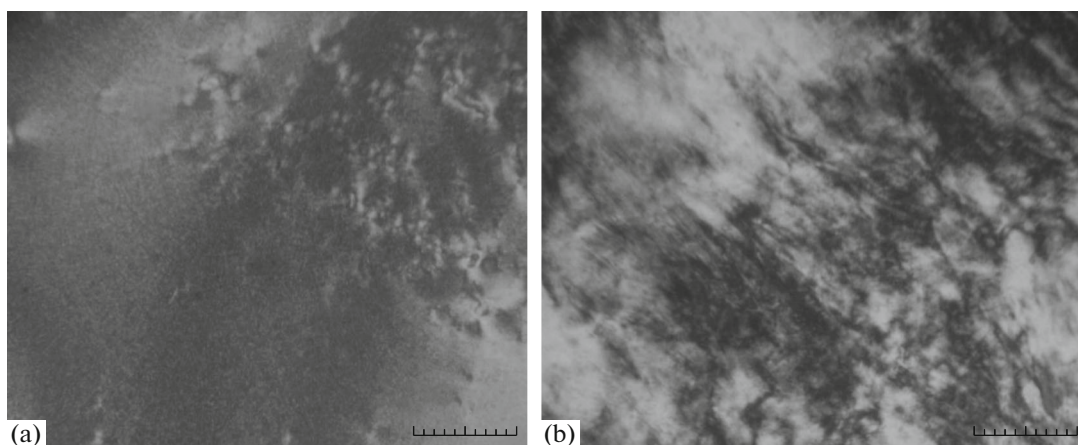


Fig. 7. POM micrographs of textured triblock copolymers (a) B-2 and (b) B-1. The scale division is 10 μm .

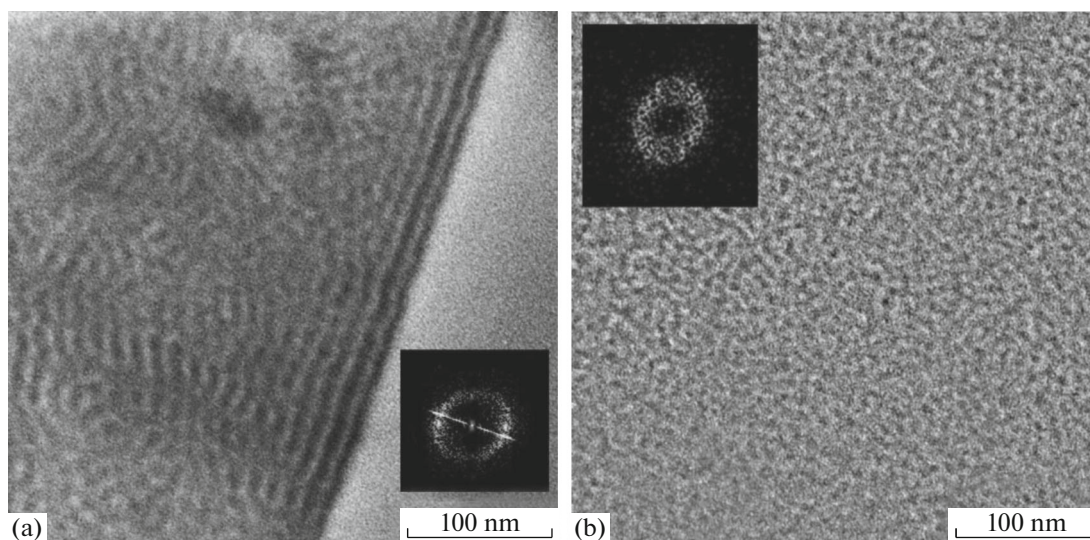


Fig. 8. TEM micrographs of cross sections for contrasted films of triblock copolymers (a) B-1 and (b) B-2 annealed at 140°C for 3 h. The insets show images calculated from TEM images using the fast Fourier transform algorithm.

hand, it must not be ruled out that disordering is caused by the method of sample preparation (its cutting with the aid of the diamond knife); as a consequence, the film may be deformed.

The micrographs of triblock copolymer B-2, as opposed to triblock copolymer B-1, exhibit a disordered microphase-separated structure (Fig. 8b). On the basis of the image calculated by the fast Fourier transform algorithm, the period of the observed disordered structure was estimated to be nearly 10 nm. The volume fraction of the LC block in triblock copolymer B-2 is about 80%; hence, it may be assumed that polyvinylpyridine blocks should form discrete cylindrical or spherical microphases. This micrograph exhibits a great number of dark circular microphases. This observation provide evidence for the hypothesis about

discrete microphases containing polyvinylpyridine blocks surrounded by the matrix composed of LC units. The presence of a weakly pronounced microphase-separated structure in triblock copolymer B-2 is associated with a low degree of polymerization of this triblock copolymer. As is known, for microphase separation to be implemented, product $N\chi$ (N is the degree of polymerization of the block copolymer, and χ is the Flory–Huggins parameter) should be above the threshold value, which for symmetric triblock copolymers is 9.5 [52]. Then for the typical value $\chi = 0.1$, $N\chi = \sim 8$ for B-2, i.e., lower than the threshold value. As a result, a disordered and weakly pronounced microphase-separated structure is formed in triblock copolymer B-2.

CONCLUSIONS

The symmetric triblock copolymers consisting of the polyacrylate LC block with phenyl benzoate mesogenic groups covalently bound to the polymer chain and the amorphous polyvinylpyridine blocks have been synthesized for the first time through the reversible addition-fragmentation chain-transfer radical polymerization. The chosen synthesis conditions made it possible to prepare two triblock copolymers, in which the length of the LC block was constant (40 monomer units) and the degrees of polymerization of the amorphous blocks were 20 and 60. It is shown that the block copolymers form the nematogenic mesophase and depending on the composition feature a microphase-separated lamellar or cylindrical structure. Owing to the ability of polyvinylpyridine to form coordination bonds with inorganic nanoparticles, the synthesized block copolymers show promise for the production of anisotropic materials with a certain organization of nanoparticles set by the morphology of block copolymers.

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