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Synthesis and Self-Assembling of Amphiphilic Diblock Copolymers of 2,3,4,5,6-Pentafluorostyrene

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Abstract—Amphiphilic diblock copolymers (DC) of 2,3,4,5,6-pentafluorostyrene and 2-hydroxyethyl methacrylate were prepared for the first time by two-step reversible addition—fragmentation chain transfer (RAFT) polymerization. The morphology of films of diblock copolymers that have a composition close to equimolar was studied by transmission electron microscopy. The observed microphase separation and formation of spherical nanodomains is not typical for equimolar diblock copolymers and seems to result from hydrogen bonding between the hydroxyl and carbonyl groups (OH···OH and C=O···HO) in poly(2hydroxyethyl methacrylate) blocks. Obviously, it is the ability of diblock copolymers to self-organization is the cause of formation of fabric coatings with low surface energy ($\gamma = 11.9 \text{ mJ/m}^2$) and relatively large water contact angles ($\theta^{H_2O} = 120^\circ \pm 6^\circ$) and diiodomethane ($\theta^{CH_2I_2} = 93^\circ \pm 2^\circ$).

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Fluorine-containing polymers in recent time attract attention of researchers due to not only their thermal and chemical stability, and wear and ageing resistance but also poor wettability in aqueous and organic media [1-8]. The low surface energy and high water contact angles for fluorine-containing polymers make them promising for designing ultrahydrophobic coatings [2-8]. For example, ultrahydrophobic fabric coatings with high water contact angles above 150° were obtained from statistical copolymers of 2-(perfluorooctyl)ethyl methacrylate (PFOMA) and 2-(perfluorohexyl)ethyl methacrylate (PFHMA) with 2-(hydroxypropyl) methacrylate (HPMA) [7, 8]. PFOMA and PFHMA units impart ultrahydrophobic properties to coatings; however, on account of high toxicity of polymer degradation products, their manufacture and application are confined in certain countries. Therefore, it is an urgent problem to design hydrophobic coatings from polymers with a lower number of fluorine atoms. The hydroxy groups of HPMA units provide covalent binding of the copolymers with fabric, thus imparting to the coatings the ability not to be washed with water for a long time.

The adhesion of fluorinated copolymers to fabric can be considerably increased by using diblock copolymers (DCs) instead of statistical copolymers of the same composition. In contrast to irregular distribution of OH groups in a statistical copolymer, OH groups of hydroxyl-containing comonomers in DCs are arranged locally. One can expect that an increase in the local concentration of OH groups in DCs will increase the strength of coating binding to the fabric. Along with high adhesion to the support, amphiphilic DCs can undergo efficient self-organization due to microphase separation to form coatings with low surface energy and low hysteresis of contact angles with both polar and nonpolar liquids [6, 7]. Compounds with lower number of fluorine atoms can be used as fluorinated comonomers.

The aim of this work was to obtain amphiphilic fluorinated DCs by two-stage radical polymerization with reversible addition—fragmentation chain transfer (RAFT) mechanism of 2,3,4,5,6-pentafluorostyrene (PFS) and 2-hydroxyethyl methacrylate (HEMA), to study their ability to self-organization in thin films, and to compare the repellent properties of fabric coatings of poly(pentafluorostyrene) (PPFS), poly(hydroxyethyl methacrylate) (PHEMA), and DC from PFS and HEMA.

To find optimal conditions for DC synthesis, we initially studied RAFT polymerization of PFS in the presence of 2-cyano-2-propyl dithiobenzoate (CPDB) as a chain transfer agent (CTA). RAFT polymerization of PFS ([PFS] = 2.0 mol/L) initiated by AIBN ([AIBN] = 2.7×10^{-2} mol/L) was carried out in DMF at molar ratio [CPDB] / [AIBN] = 1.9 at 60°C (Table 1).

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Sample	[CPDB] [AIBN]	Time, h	$q,\%^1$		M/M^4		
				theor. ²	NMR ³	GPC ⁴	m _w /m n
	0	24	53	_	_	21	1.97
P1	1.9	8	12	9.0	11.0	11.9	1.17
P2	1.9	10	19	14.1	13.5	15.1	1.23
P3	1.9	18	33	24.3	19.6	25.4	1.33
P4	1.9	24	46.5	34.3	25.0	29.3	1.41

Table 1. Conditions of PFS polymerization and molecular-weight characteristics of PPFS

 1 q was determined by gravimetry.

² Theoretical values of M_n were calculated assuming that one CPDB molecule leads to controllable growth of one polymer chain according to the equation $M_n = M_{CPDB} + \frac{q[PFS]_0 M_{PFS}}{[CPDB]_0}$, where M_{CPDT} and M_{PFS} are molecular weights of CPDT and PFS, respec-

tively; [CPDB] and [PFS] are their initial concentrations, q is PFS conversion.

³ $M_{\rm n}$ was determined from the integrated intensity ratio of signals of the CH group of the polymer backbone at 2.35 and 2.80 ppm and the proton signals of the phenyl group of CPDB at 7.35 and 7.75 ppm. $M_{\rm n} = \frac{H_C M_{\rm PFS}}{5H_F}$, where H_C and H_F are integrated intensities of signals from CH group of the main polymer chain of PPFS and the proton signals of phenyl group of CPDB; $M_{\rm PFS}$ is the molecular weight of PFS. It was assumed that all polymer chains contain terminal phenyl groups of the CTA.

⁴ Experimental conditions: an Agilent 1200 instrument with a refractometric detector, a PLmixC column, THF as an eluent, 25°C, flow rate 1.0 mL/min. The column was calibrated using polystyrene standards.

The obtained PPFSs are characterized by the symmetrical unimodal molecular weight distribution (MWD) curves (Fig. 1). The shift of MWD curves of PPFS with an increase in monomer conversion q to higher molecular weights (MW) and M_w/M_n values close to unity indicate the controlled character of PFS polymerization under the conditions used. Thus, the RCT polymerization of PFS in the presence of CPDB in DMF affords rather high-molecular-weight PPFSs with a narrow MWD.

The amphiphilic PFS-HEMA diblock copolymers were obtained for the first time by two-stage



Fig. 1. Comparison of MWD curves for PPFS: (1) P1, (2) P2, (3) P3, (4) P4.

RAFT polymerization in DMF. At the first stage, we obtained hydrophilic PHEMA-CTA with $M_n(GPC) =$ 23.5×10^3 and $M_w/M_n = 1.23$ by the RAFT polymerization of HEMA in DMF in the presence of AIBN $([AIBN] = 8.0 \times 10^{-3} \text{ mol/L})$ at molar ratio [CPDB]/[AIBN] = 2.5 at 60°C. At the second stage, we obtained diblock copolymers by RAFT polymerization of PFS ([PFS] = 2 mol/L) in the presence of PHEMA-CTA with a terminal dithiobenzoate group and AIBN ([AIBN] = 1×10^{-3} mol/L) at constant molar ratio [PHEMA]/[AIBN] = 4 in DMF at 60°C (Table 2). Figure 2 shows the MWD curves of initial PHEMA-CTA and diblock copolymer whose composition, according to elemental analysis (EA), is close to equimolar. The MWD curves for diblock copolymers are unimodal and shifted toward higher molecular weights. The experimental values of $M_{\rm p}({\rm EA})$ are close to theoretical values. The discrepancy in $M_{\rm p}({\rm GPC})$ and $M_{\rm p}({\rm EA})$ values is caused by that GPC is not absolute method and obtained relative molecular weights reflect the hydrodynamic size of macromolecules depending on their conformation. The polydispersity of diblock copolymers of $M_{\rm w}/M_{\rm n} \leq 1.30$ is typical for RAFT polymerization.

Since the obtained diblock copolymers consist of polymer blocks of different nature, hydrophobic PPFS block and hydrophilic PHEMA block, they can undergo self-organization in solutions and melts to form nanometer-sized microphases. The morphology of diblock copolymer films 700 μ m thick containing 52 and 54 mol % of PFS units obtained by application from 5 wt % solutions of copolymers in DMF to a

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Sample	Time, h	$q, \%^1$	$M_{\rm n} imes 10^{-3}$			M/M^3	DC composition, mol % ⁴	
Sample			theor. ²	GPC ³	EA ⁵	M _W / M n	HEMA	PFS
C1 PHEMA ₁₈₀ PPFS ₁₉₅	24	28.6	51.2	36.6	61.3	1.30	48	52
C2 PHEMA ₁₈₀ PPFS ₂₁₁	28	33.2	55.7	39.3	64.4	1.26	46	54

Table 2. Conditions of PFS polymerization and molecular-weight characteristics of diblock copolymers

 1 *q* was determined by gravimetry. ² Theoretical values of $M_{\rm n}$ were calculated assuming that one molecule of the PHEMA-CTA leads to controllable growth of one diblock

copolymer molecule according to the equation $M_n = M_{PHEMA} + \frac{q[PFS]_0 M_{PFS}}{[PHEMA]_0}$, where M_{PHEMA} and M_{PFS} are the molecular weights of PHEMA and PFS, $[PHEMA]_0$ and $[PFS]_0$ are their initial concentrations, q is PFS conversion.

³ Experimental conditions: an Agilent 1200 instrument with a refractometric detector, a G-gel column [12, 13], THF : 0.03 M LiBr in DMF (50 : 50 v/v) as an eluent, 30° C, flow rate 0.5 mL/min. The column was calibrated using polystyrene standards.

⁴ Diblock copolymer composition was determined by elemental analysis.

 5 $M_{\rm n}$ was determined from $M_{\rm n}$ of PHEMA-CTA ($M_{\rm n} = 23.5 \times 10^{3}$) and diblock copolymer composition by equation: $M_{\rm n} = M_{\rm PHEMA} + 10^{3}$

N_{PFS} $- \times M_{PFS}$, where M_{PHEMA} and M_{PFS} are molecular weights of PHEMA and PFS, N_{PFS} and N_{HEMA} are the numbers $N_{\rm PFS} + N_{\rm HEMA}$

of PFS and PHEMA units in diblock copolymer.

hydrophobized support followed by annealing in vacuum was studied by transmission electron microscopy (TEM). The films have nearly the same morphology: TEM images show domains of almost spherical shape with a sphere diameter from 24 to 40 nm. Figure 3 displays the TEM image of film of C2.

It should be noted that the morphology with spherical domains is not typical of the films of equimolar diblock copolymers, and additional studies are neces-



Fig. 2. Comparison of MWD curves for (1) PHEMA $(M_n = 23.5 \times 10^3, M_w/M_n = 1.23)$ and the products of PFS polymerization in the presence of PHEMA: (2) C1 $(M_n =$ 36.6×10^3 , $M_w/M_n = 1.30$) and (3) C2 ($M_n = 39.3 \times 10^3$, $M_{\rm w}/M_{\rm n} = 1.26$).

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sary to reveal the reasons of emergence of such a structure. One can suppose that hydrogen bonding between hydroxyl and carbonyl groups (OH…OH and $C=O\cdots HO$ [9, 10] in the microphase formed by PHEMA blocks plays the decisive role in this phenomenon. The existence of hydrogen bonds between two hydroxyl groups (OH…OH) and between hydroxyl and carbonyl groups (C=O···HO) of PHEMA blocks of diblock copolymers is confirmed by the data of IR



Fig. 3. TEM image of C2 film. Dark regions correspond to PPFS phase, light regions correspond to PHEMA phase.



Fig. 4. A fragment of IR spectra of (1) PHEMA and (2) C2 in the region of stretching vibrations of O=C and OH groups.

spectroscopy (Fig. 4). Figure 4 shows the fragments of the IR spectra of PHEMA and C2 in the region of HO and O=C stretching vibrations. Two overlapping bands at 1730 and 1704 cm⁻¹ refer to the stretching vibrations of free C=O groups (not involved in hydrogen bonding) and C=O groups bound to OH groups (C=O···HO), respectively [9, 10]. The wide band of stretching vibrations of OH groups is observed in the range from 3536 to 3325 cm⁻¹ for both PHEMA and C2 and characterizes the stretching vibrations of OH groups hydrogen bonded to carbonyl group (3536 cm⁻¹), overtone of C=O stretching vibrations (3432 cm⁻¹), and aggregates of OH groups (···HO···HO···HO···) (3325 cm⁻¹).

The repellent properties of nylon fabric samples treated with PPFS, PHEMA, and C2 prepared by the procedure described in [7, 8] were assessed by the static contact angle of water (θ^{H_2O}) and diiodomethane $(\theta^{CH_2I_2})$ on a Kruss DSA 25 instrument. The samples of non-treated fabric and a fabric coated by PHEMA excellently absorb water and DI due to capillary effects. After application of PPFS and C2, the samples become hydrophobic: θ^{H_2O} value for the fabric treated with C2 is $120^{\circ} \pm 6^{\circ}$, which is almost 20° higher than θ^{H_2O} for the fabric impregnated with PPFS (θ^{H_2O} = $102^{\circ} \pm 2^{\circ}$), in spite of the fact that diblock copolymer contains 50 mol % of hydrophilic HEMA units. The static contact angles for DI (drop volume is $1.5 \,\mu$ L) for the fabric treated with PPFS and C2 are $80^{\circ} \pm 2^{\circ}$ and $93^{\circ} \pm 2^{\circ}$, respectively. The values of specific free surface energy γ calculated by the Owens–Wendt equation [11] are 18.1 and 11.9 mJ/m² for PPFS and C2, respectively. The observed improvement of energetic characteristics for the surface of DC films as compared with the corresponding parameters for PPFS films can be related to both the induced surface curvature and perpendicular orientation of PPFS blocks toward the support surface owing to the self-organization of amphiphilic diblock copolymers [5, 6].

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