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SURFACE PROPERTIES OF THIN FILMS OF POLY(2,3,4,5,6-PENTAFLUOROSTYRENE) AND DIBLOCK COPOLYMERS BASED ON 2,3,4,5,6-PENTAFLUOROSTYRENE AND 2-HYDROXYETHYL METHACRYLATE

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Abstract: The surface properties of thin films obtained by applying poly(2,3,4,5,6-pentafluorostyrene) (PPFS) and amphiphilic diblock copolymers (DC) of 2,3,4,5,6-pentafluorostyrene (PFS) and 2-hydroxyethylmethacrylate (HEMA) on smooth substrates (silicone plates) from solutions in THF and DMF, respectively, in the presence and absence of a cross-linking agent– hexamethylenediisocyanate (HMDI) were studied. Comparative testing of the DC films obtained in the presence and in the absence of HMDI showed that the DC films have the higher water and diiodomethane (DI) contact angles: $\theta^{\text{H}_2\text{O}} = 108 \pm 2^\circ$ and $\theta^{\text{CH}_2\text{I}_2} = 83 \pm 1^\circ$, than a film of PPFS ($\theta^{\text{H}_2\text{O}} = 98 \pm 1^\circ$ and $\theta^{\text{CH}_2\text{I}_2} = 74 \pm 1^\circ$). The energy characteristics of the thin films surface were determined by the results of measuring the water and DI contact angles. It was established that DC films have a lower specific free surface energy than films based on PPFS.

Keywords: 2,3,4,5,6-pentafluorostyrene, amphiphilic diblock copolymers, surface properties.

Introduction

For creating omniphobic coatings the compounds containing long-chain fluorinated alkyl fragments with terminal $-\text{CF}_3$ groups, capable of self-assembly with close packing of $-\text{CF}_3$ groups, are usually used. The dense packing provides low values of the specific free surface energy of coatings ($\gamma_{\text{SV}} = 6-7 \text{ mJ/m}^2$) [1] and makes them resistant to wetting by both polar and non-polar liquids. However, long fluorinated fragments do not decompose in nature, and the destruction of coatings is accompanied by the release of toxic perfluorooctane sulfonic and perfluorooctanoic acids [2]. In this regard, an urgent task is to create omniphobic coatings without the use of compounds with long-chain fluorinated alkyl fragments.

The solution of this problem is the coating of amphiphilic fluorine-containing block copolymers [3]–[9]. As a result of microphase separation, amphiphilic block copolymers create a nanoscaled rough surface with a low surface energy due to a high content of fluorine atoms on the surface, which leads to the realization of the Cassie state and an improvement in the repellent properties of coatings [3]–[9].

Previously, our group proposed to use amphiphilic diblock copolymers (DC), consisting of poly(2,3,4,5,6-pentafluorostyrene) (PPFS) and poly(2-hexaethyl methacrylate) blocks, to create omniphobic coatings on cotton-polyester fabrics. The application to the fabric of the DC consisting of 32 HEMA-units and 197 PFS-units ($H_{32}-F_{197}$), creates a nanoscaled rough surface with a rather high content of fluorine atoms on the surface ($[F] = 19.7\%$), which has superhydrophobic and oleophobic properties with water and diiodomethane (DI) contact angles (CA) $\theta^{H_2O} = 158 \pm 4^\circ$ and $\theta^{CH_2I_2} = 107 \pm 3^\circ$ ($> 90^\circ$ for PPFS), and hysteresis CA (CAH) = $5 \pm 2^\circ$ [3]–[5].

This work continues these investigations, and its purpose is to comparatively study the surface properties and energy characteristics of thin films made of PPFS and $H_{32}-F_{197}$, copolymerapplied from organic solvents (THF and DMF) in the presence and absence of a crosslinking agent - hexamethylenediisocyanate (HMDI) on smooth silicon wafers.

Experimental part

Monomers 2,3,4,5,6-pentafluorostyrene (PFS) (98%, PIM-INVEST, Russia) and 2-hydroxyethyl methacrylate (HEMA) (98%, ZL Chemical, China) were distilled under vacuum before use ($P = 0.1$ mbar, $T = 63^\circ C$ and $105^\circ C$ for PFS and HEMA, respectively). The polymerization initiator α -bis-isobutyric acid dinitrile (AIBN) (98%, Sigma-Aldrich, Germany) was twice recrystallized from methanol. Chain transfer agent (or RAFT-agent) 2-cyano-2-propyl-dithiobenzoate (CPDB) ($>97\%$, Sigma-Aldrich, Germany) and crosslinker hexamethylenediisocyanate (HMDI) ($> 99\%$, Sigma-Aldrich, Germany) were used as received. The solvents were purified according to conventional techniques.

PPFS was synthesized by polymerization of PFS via reversible addition-fragmentation chain-transfer polymerization (RAFT polymerization) according to the procedure described in [3]–[5]. Polymerization of PPFS at $[PFS] = 2$ mol/l in *N,N*-dimethylformamide (DMF) at $60^\circ C$ at a molar ratio of $[CPDB]/[AIBN]=1.9$ and an initiator concentration $[AIBN] = 2.7 \times 10^{-3}$ mol/l. The resulting PPFS was precipitated in excess of methanol, followed by centrifugation for 10 min at 11000 rpm (Rotina R38, Germany). The polymers obtained were dried at room temperature under vacuum up to constant weight.

DCs were synthesized by two-stage RAFT polymerization. At the first stage, the PHEMA-RAFT-agent was obtained by polymerization of HEMA ($[HEMA] = 2 \text{ mol / l}$) at $[CPDB] = 2 \times 10^{-2} \text{ mol / l}$ and $[AIBN] = 8 \times 10^{-3} \text{ mol / l}$ in DMF at 60° C . The PHEMA-RAFT-agent was precipitated in excess of chloroform, followed by centrifugation for 10 min at 11000 rpm (Rotina R38, Germany). At the second stage, DCs were synthesized by polymerization of PFS ($[PFS] = 2 \text{ mol / L}$) in the presence of PHEMA-RAFT-agent at $[PHEMA] / [AIBN] = 5$ in DMF at 60° C . At the end of the reaction, the product was precipitated in a 10-15 fold excess of chloroform, then centrifuged for 10 min at 11000 rpm (Rotina R38, Germany) and dried in a vacuum to constant weight. Conversion was determined gravimetrically. The composition was determined by elemental analysis (Table 1).

Molar masses (M_n and M_w) and polydispersity indexes (M_w/M_n) of PPFS, PHEMA and DCs (Table 1) were determined by gel permeation chromatography (GPC) using Agilent 1200 liquid chromatograph equipped with a refractometric detector and data processing system ChemStation 1200 (Agilent). PLmixC (Agilent) column was used for analysis of PPFS a temperature of 30° C and eluent flow rate of 1 ml / min . G-gel column (spherical macroporous sorbent based on a hydrolyzed glycidyl methacrylate copolymer with ethylene dimethacrylate [10], [11]) was used at a temperature of 30° C and eluent flow rate of 0.5 ml / min . 0.03 M LiBr in DMF was used as an eluent for PHEMA; a mixture of THF : 0.03 M LiBr in DMF (50:50 vol.%) was used for analysis of DCs and for comparison with the initial PHEMA-RAFT-agent. The instrument was calibrated according to Waters and Merck polystyrene (PS) standards.

Table 1. Molecular weight characteristics of PPFS, PHEMA and DC

Sample	Composition, mol. %		$M_n \cdot 10^{-3}$	M_w/M_n
	PFS	HEMA		
PPFS	100	0	29.3	1.17
H ₃₂ ¹⁾	0	100	6.6	1.23
H ₃₂ -F ₁₉₇ ²⁾	86	14	40	1.05

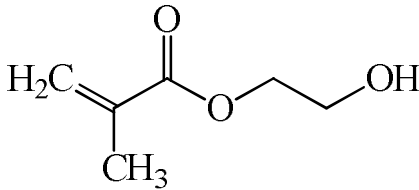
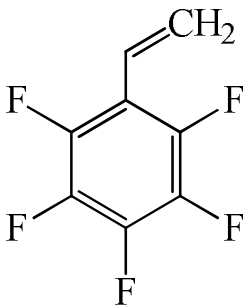
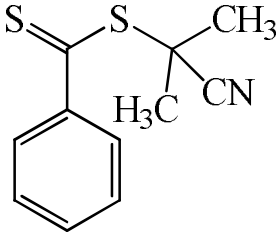
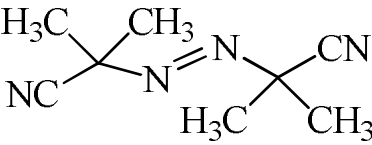
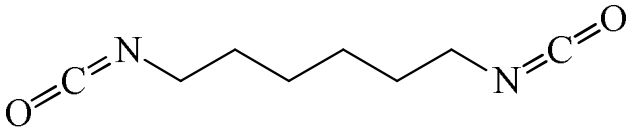
¹⁾ The letter "H" designates HEMA units. The subscripts associated with the H letter correspond to the degree of polymerization of PHEMA P_n^{HEMA} (or n) which was defined as $M_n/130$, where M_n – is the number average molecular weight of PHEMA as determined by GPC and 130 is the molar mass of HEMA; ²⁾The letters "H" and "F" designate HEMA and PFS units, respectively. The subscripts associated with the letters correspond to the degree of polymerization P_n of each polymer blocks. The degree of polymerization (P_n^{PFS}) of PPFS was calculated taking into account the content of PFS units in copolymer as follows: $P_n^{\text{PFS}} = P_n^{\text{PHEMA}} \times m_{\text{PFS}} / m_{\text{HEMA}}$, where m_{PFS} and m_{HEMA} are the content of PFS and HEMA units in DC according to element analysis data.

The films were deposited onto silicon wafers from 50 mg/ml solution of PPFS in THF and DC in DMF in the presence and absence of HMDI by *spin-coating* in the operating mode for 15 sec at 1000 rpm and 60 sec at 3000 rpm. Before films deposition, silicon wafers were treated by boiling

in 30% H₂O₂ solution (T = 107°C) for 50 min to form silanol SiOH groups on their surface [12]. The prepared samples were dried in vacuum (P = 6 × 10⁻²Pa) at 40°C for 24 h.

The hydrophobic and oleophobic properties of polymer films on the surface of silicon wafers were determined from the static water (θ^{H_2O}) and DI ($\theta^{CH_2I_2}$) CAs by the sessile drop method (volumes were 1.5 μ L) using Kruss DSA 25 (Germany) device with the accuracy of 1°. The average of six readings was used as the data.

The chemical formulas of the compounds used are shown below:

Monomers	HEMA	
	PFS	
RAFT-agent	CPDB	
Initiator	AIBN	
Crosslinker	HMDI	

Chemical structures of the monomers, RAFT-agent, initiator and crosslinker for the preparation of thin films

Results and discussion

The wetting method was used to determine the energy characteristics of the surface of PPFS and DCs films deposited in the presence and absence of HMDI [13]. The values of the

specific free surface energy (γ_{SV}), polar (γ_{SV}^p) and dispersion (γ_{SV}^d) components were calculated using the Owens-Wendt equation [13]:

$$1 + \cos \theta = \frac{2\sqrt{\gamma_{SV}^d} \cdot \sqrt{\gamma_{LV}^d}}{\gamma_{LV}} + \frac{2\sqrt{\gamma_{SV}^p} \cdot \sqrt{\gamma_{LV}^p}}{\gamma_{LV}}$$

where θ – water and DI CAs, γ_{LV}^p and γ_{LV}^d – polar and dispersion components of liquid surface tension γ_{LV} . The accuracy of determining the γ_{SV} values is 1 mJ/m². The values of polar and dispersive components of surface tension for test liquids (water and DI) are shown in Table 2.

Water and DI CAs θ^{H_2O} and DI $\theta^{CH_2I_2}$ on the surface of the films were determined by the sessile drop method. Drops of water and DI spread on the hydrophilic surface of the treated silicon wafers due to complete wetting. After applying PPFS and DCs, the plates become hydrophobic (Fig.1), and the value of θ^{H_2O} of film coated with DC in presence of HMDI, is $108 \pm 2^\circ$, which is 10° higher than θ^{H_2O} for a thin film of PPFS ($\theta^{H_2O} = 98 \pm 1^\circ$), despite the fact that the DC contains only 86 mol.% of hydrophobic PFS units. The static CA versus DI (droplet volume 1.5 μ L) for PPFS and DC films are $74 \pm 1^\circ$ and $83 \pm 1^\circ$, respectively (Table 2). Similar CA values are also observed for films from DC prepared without crosslinker HMDI: $\theta^{H_2O} = 106 \pm 1^\circ$ and $\theta^{CH_2I_2} = 82 \pm 1^\circ$.

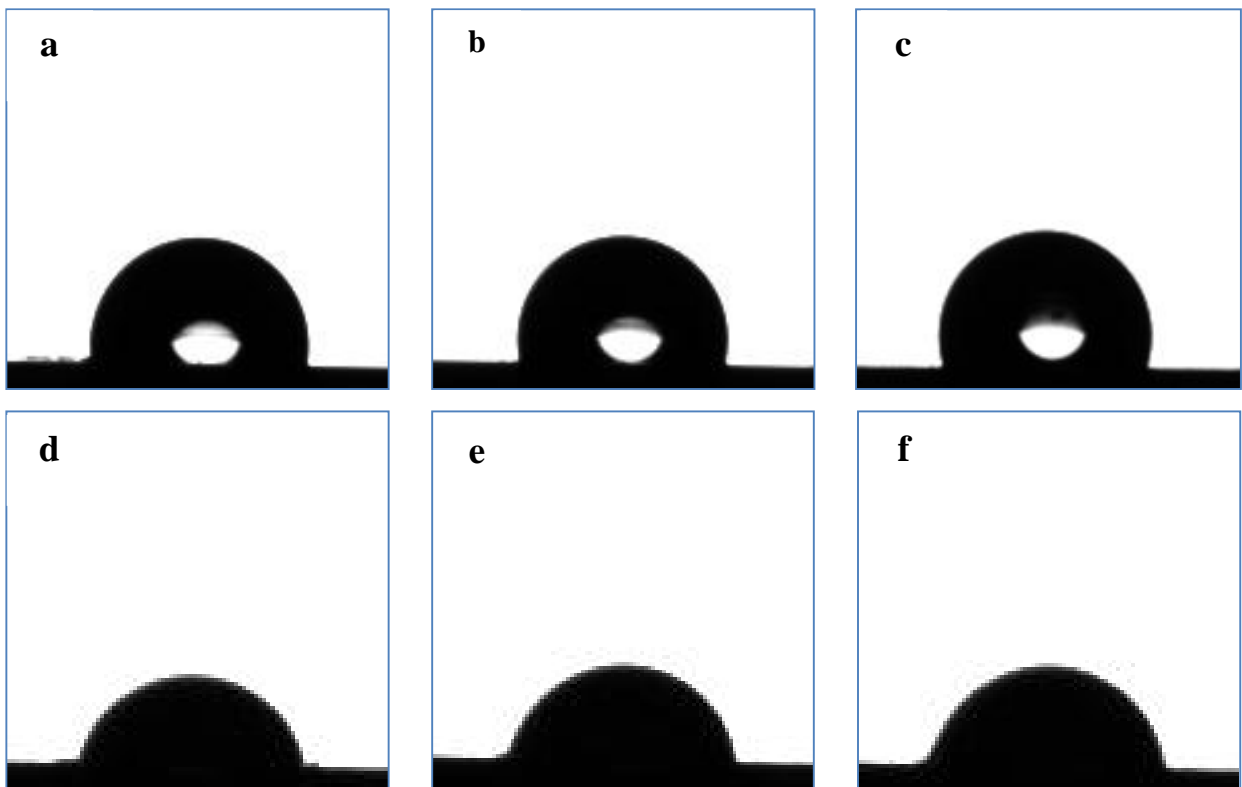


Figure 1. Instantaneous images of water and DI droplets ($V = 1.5 \mu\text{L}$) on the surface of PPFS (a, d) and $\text{H}_{32}\text{-F}_{197}$ films without HMDI (b, e) and with HMDI (c, f) on silicon wafers.

The observed improvement in the repellent properties of films from DC in comparison with the corresponding parameters for PPFS films can be associated with higher adhesion of the $\text{H}_{32}\text{-F}_{197}$ to the substrate surface [3]–[5]. In PPFS, there are no functional groups that are reactive with respect to SiOH groups on the surface of silicon wafers, which leads to low polymer adhesion and, as a consequence, to the formation of defective film. Due to the presence of OH-groups in the PHEMA blocks, DC binds to the substrate due to formation of weak hydrogen (in the absence of HMDI) or strong covalent (in presence of HMDI) bonds, and this leads to the formation of homogeneous defect-free coatings.

The values of the polar and dispersion components of the surface tension for water and DI, as well as the free surface energy, calculated from the data of the CA measurements for water and DI $\theta^{\text{H}_2\text{O}}$ and $\theta^{\text{CH}_2\text{I}_2}$, are given in Table 2.

Table 2. Water and DI CAs and the values of the surface energy, as well as the dispersion and polar components of the surface energy of the PPFS and DC films, and test liquids, used in calculating the free surface energy of thin polymer films.

Sample	$\theta^{\text{H}_2\text{O}}$	$\theta^{\text{CH}_2\text{I}_2}$	$\gamma_{SV}^p, \text{mJ/m}^2$	$\gamma_{SV}^d, \text{mJ/m}^2$	$\gamma_{SV}, \text{mJ/m}^2$
PPFS	98	74	2.4	18.6	21.0
$\text{H}_{32}\text{-F}_{197}$	106	82	1.3	15.3	16.6
$\text{H}_{32}\text{-F}_{197}$ + HMDI	108	83	1.0	15.0	16.0
Water	-	-	50.8	21.8	72.6
DI	-	-	2.3	48.5	50.8

Table 2 shows that on the surface of films based on PPFS and $\text{H}_{32}\text{-F}_{197}$, prepared both in the presence and in the absence of HMDI, fluorinated fragments are predominantly concentrated. Indeed, the calculated values of the free surface energy below $\gamma_{SV} = 25.6 \text{ mJ/m}^2$, characteristic of polytetrafluoroethylene (PTFE) [14] and above $\gamma_{SV} = 6 - 7 \text{ mJ/m}^2$, typical for close packing of $-\text{CF}_3$ -groups [1]. It is important to note that the presence of hydrophilic PHEMA block in the composition of the DC did not lead to an increase in the surface energy, but, on the contrary, reduced its values in comparison with the values obtained for the PPFS films. This is probably due to the microphase separation of DCs in the films and the formation of nanosized domains with a predominant content of one of the polymer blocks. The investigation of the $\text{H}_{32}\text{-F}_{197}$ coating on

smooth surface using transmission electron microscopy showed that it is characterized by a spherical morphology with a sphere diameter of 30 nm [5].

The films based on H₃₂-F₁₉₇ prepared with HMDI have lower values of both the total surface energy and its dispersion and polar components than films from PPFs and DC prepared without HMDI. This may be due to the fact that a DC covalently bonded to a smooth surface, completely covers it, thereby creating a more energetically homogeneous surface.

Conclusion

Thus, the introduction of hydrophilic PHEMA block into PPFs provides uniform and homogeneous deposition of the copolymer on the hydrophilic surface of silicon wafers, reduces the specific free surface energy of the resulting coating, and improves its repellent properties with respect to water and DI.

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