



Synthesis and properties of N-isopropylacrylamide and benzylmethacrylate-based amphiphilic block copolymers on different interphase surfaces

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Abstract

New amphiphilic block copolymers on based benzylmethacrylates or 2,3,4,5,6-pentafluorobenzyl methacrylate and N-isopropylacrylamide with high yields (89–94%) and MM $1.2 \cdot 10^5$ and $1.63 \cdot 10^5$ were synthesized. The relative constants of chain transfer to *tris*-(pentafluorophenyl)germanium during the radical polymerization of 2,3,4,5,6-pentafluorobenzyl methacrylate and benzylmethacrylate were 1.26 and 0.45, respectively. The structure of the copolymers was confirmed by IR and NMR spectroscopy. By the method of TGA analysis, the temperature of the beginning of decomposition of polymers was established, which amounted to 228.2 °C and 150 °C for the fluorinated and non-fluorinated block copolymer, respectively. The properties of polymers in solutions were studied by GPC, molecular hydrodynamics and optics. For both fluorinated and non-fluorinated samples, only macromolecules were observed in dilute solutions. The behavior of a non-fluorinated sample was well described as a coil in a good solvent, while fluorinated macromolecules were characterized by a compressed coil conformation, due to the presence of fluorine in the polymer structure. It was shown that the block copolymers formed stable Langmuir monolayers with high surface pressures (50–58 mN/m), and the transferred Langmuir–Blodgett films on silicon wafers were hydrophilic (water contact angles are 68–73 °C). A large hysteresis loop on the surface pressure isotherm obtained under compression-expansion conditions for a fluorinated block copolymer indicates significant inter- and intramolecular interactions at the water–air interface.

Keywords Fluorinated block copolymers · Synthesis · Structure · Solution properties · Benzyl methacrylate · Monolayer · Langmuir–Blodgett films

Introduction

Block copolymers (BCP) form the basis of the most ubiquitous materials such as thermoplastic elastomers, bridge interfaces in polymer blends, and are fundamental for the development of high-performance materials. Important advance of these materials is the accessibility of block copolymers, their wide variety in composition and functional group content, and ability to tune their properties [1–3].

Fluorinated polymers are well known for their thermal, chemical, and physical stability. For this reason, they can be used for sensors and cable insulation, membranes, packaging, sealing materials or chemical resistant components [4]. Moreover, fluorinated polymers belong to the category of low surface energy materials, due to their relatively low attraction to other molecules. Therefore, their interfacial energy is low, which causes their easy segregation [5]. Due

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to the advantages of fluorinated polymers, they are widely used to synthesis block copolymers.

Bosson et al. have reported on the successful synthesis of poly(pentafluorostyrene)-block-poly(butylacrylate) (PPFS-*block*-PBuA) block copolymers. Regulated radical polymerization of BCPs using poly(pentafluorostyrene) have already been reported, however, generally by ATRP. Click-chemistry for para-fluorine substitutions with azide and thiol have already been proposed for PPFS. Additionally, the self-assembly of the prepared BCPs before and after modification with 1-hexanethiol was studied by AFM and SAXS [6].

Polyvinyl ethers have attracted significant interest due to their applications in gas-selective permeable membranes, transparent materials for optical lenses [7], bioinert interfaces and hydrogen generation [8]. Block copolymers composed of vinyl ethers were prepared by living cationic polymerization technique [9, 10], for application as polymer surfactants [11], stimuli-responsive gels [12], and thermo-plastic elastomers [13].

Block polymers prepared via cationic polymerization still show some possible applications despite the recent scarcity of researches respectively other branches of fundamental science. Since the breakthrough in 1980s, the conventional living cationic polymerization (LCP) has made remarkable progress and has become one of the most important pathways to synthesize well-defined polymers. Investigations and expansions of Lewis acid/base pairs have greatly promoted the development of LCP, and have inspired lots of subsequent developments. Tailored polymers with desirable chemical structures, molar masses, and functional groups have benefitted numerous studies and applications [14].

The study by Blagodatskikh et al. exploited several methods and was aimed to investigate the influence of the lengths of both fluorinated and anchor blocks of amphiphilic fluorinated diblock copolymers (DBCP) based on 2,3,4,5,6- pentafluorostyrene (PFS) and 2-hydroxyethyl methacrylate (HEMA) on repellent properties of the DBCP coatings applied on cotton/polyester fabrics. PFS was chosen as comonomer because it is commercially-available and its homopolymer is more soluble in most organic solvents than other fluorinated polymers [15]. Hydroxyl groups of hydroxyethyl methacrylate (HEMA) units were used to covalently attach DBCPs to hydroxyl groups of cotton/polyester fibers using hexamethylene diisocyanate (HMDI) as a crosslinking agent [16] and to form intradomain crosslinking between poly(2-hydroxyethyl methacrylate) (PHEMA) blocks. The amphiphilic fluorinated DBCPs were synthesized by two-stage radical polymerization with reversible addition-fragmentation chain transfer (RAFT) mechanism of PFS and HEMA. The resulting DBCP were characterized by GPC and FTIR. The repellent properties of cotton/polyester fabric

DBCP coatings were estimated by water and diiodomethane (DI) contact angles (WCA and DICA) measurements. The chemical composition and morphology of the DBCP coatings on smooth (silicon slides) and rough (cotton/polyester fabric) surfaces were investigated using FTIR, energy dispersive spectroscopy (EDS) and SEM [16].

Fedorczyk, Krzywicka et al. have reported a new synthetic approach for the block copolymers of polyN-isopropylacrylamide-*block*-polystyrene (PNIPAM-*b*-PS) via the ATRP technique. The proposed method relies on application of 2-chloro-N-(2-hydroxyethyl)propanamide (NCPAE) acting as bifunctional initiator. Functional groups in NCPAE opens up the opportunity to perform ATRP of two monomers differing in activity in a sequential manner. Based on this protocol, copolymers with molecules containing two well-defined polymer chains linked by the proposed initiator were synthesized. To the best of our knowledge, NCPAE has not been used as an initiator in ATRP; and the synthesis of block copolymers via the ATRP technique with a sequence wherein PNIPAM is the first block and PS is the second one has not been reported yet. Importantly, the developed synthetic way allows to build macromolecules with required lengths of their hydrophobic blocks. Due to the sequence of the blocks, the synthesized molecules have an active end group on the hydrophobic side. Therefore, a hydrophobic block can be easily extended, modified and attached to the surface. The last possibility makes the synthesized materials especially promising for the preparation of modified surfaces with hydrophobic inside layer and hydrophilic as well as thermosensitive outside layer. Such surfaces are highly desirable in tissue engineering and construction of smart membranes [17, 18]. Consequently, it is proved that physical properties of block copolymers provide and even guarantee their future application in both industry and science despite of the difficulty of their synthesis [19–21].

A thermo- and pH-responsive copolymer of N-isopropylacrylamide (NIPAM) with maleic acid was studied by the light scattering and turbidimetry [22, 23]. Aqueous solutions with different pH and concentration were investigated. The temperatures of the onset of the phase separation and the width of this interval increased with decrease in copolymer concentration and increase in pH. Copolymers of NIPAM with fluorine-containing comonomers are of particular interest. The need to create methods for the synthesis of block copolymers based on fluorine-containing compounds is primarily due to the surface properties of these materials, which are characterized by low values of surface energy [24–26].

Moreover, the presence of fluorinated groups with a strong cohesive potential in the composition of block copolymers causes increased propensity of macromolecules for self-organization in solutions [27–29].

In previous study we investigated linear-dendritic block copolymers based on NIPAM and perfluorinated polyphenylengermane with different molar masses of hydrophilic blocks. These copolymers were studied in solutions and in Langmuir–Blodgett (LB) films. It was found that the macromolecules are capable of forming stable monolayer films at the water–air interface, regardless of the subphase acidity. For solutions of PNIPAM containing terminal a *bis*-pentafluorophenyl germanium group at the end of the chain, no low critical solution temperature behavior was found. In addition, the introduction of pentafluorophenylgermanium groups into PNIPAM significantly changes its properties at various interface boundaries [30]. The amphiphilic block copolymer PNIPAM–Ge(C₆F₅)₂–poly(2,2,3,3-tetrafluoropropyl methacrylate) was prepared by the reaction of chain transfer to *bis*-(pentafluorophenyl)germane during the polymerization of N-isopropylacrylamide and the subsequent postpolymerization of isolated functional polymers in 2,2,3,3-tetrafluoropropyl methacrylate. The colloidal chemical properties of Langmuir monolayers and LB films of synthesized block copolymer have been studied. It was shown that regardless of the acidity of the subphase, high pressure of fracture of films are characteristic of monolayers of collapse pressures $\pi_{\text{coll}} = (48–61)$ mN/m. The morphology of the LB films of functional polymer exhibit isolated elongated micelles with high densities in the “octopus” shape on the periphery of which there are terminal hydrophobic groups. For the LB film of block copolymer, a comb-like structure is observed with characteristic protrusions.

The technology for producing LB films has recently become a tool for studying various intermolecular interactions under conditions where the distance between molecules and their mutual orientation are strictly fixed. LB films are three-dimensional assemblies with predetermined and controllable properties at the molecular level. Analysis of the behavior of macromolecules in LB films will make it possible to determine the nature of intramolecular interactions and predict the properties of polymer materials in order to determine their potential area of use.

Amphiphilic fluorinated block copolymer films are promising materials for the creation of biosensors, artificial endoprotheses, heart valves and other implants for which the adhesion of blood clots is unacceptable. The thromboresistance of their surface is based on the formation of a thin organized layer of blood components due to the irreversible adsorption of proteins on the surface of the implant or biosensor, with the formation of a uniform hydrophilic layer with increased biocompatibility.

The aims of this work are synthesis, characterization analysis of possibility of formation and thin and stable monolayers and LB films of the new amphiphilic block-copolymers on based benzylmethacrylates и N-isopropylacrylamide.

Experimental

Materials

Tris-(pentafluorophenyl)germanium had been recrystallized from hexane and dried in vacuum. *Bis*-(pentafluorophenyl)germanium was used without any additional purification. The monomers, 2,3,4,5,6-pentafluorobenzylmethacrylate (BMA(F)) (boil temperature $T_{\text{boil}} = 205$ °C) and benzylmethacrylate (BMA) ($T_{\text{boil}} = 250$ °C) were distilled in vacuum with 4-methoxyphenol as their inhibitor. The initiator, AIBN, was recrystallized twice from ethanol, and then it was dried in vacuum at room temperature. Structure of the studied monomers and organic compounds is shown in Scheme 1.

Before the polymerization, NIPAM was recrystallized twice from hexane, the crystals were dried in vacuum at room temperature (melt temperature $T_{\text{melt}} = 62–63$ °C). Chain transfer constants C_s were determined by Mayo equation [31]:

$$\frac{1}{\bar{p}} = \frac{k_o}{k_p^2} \frac{V}{[M]^2} + C_s \frac{[S]}{[M]} \quad (1)$$

where \bar{p} —degree of polymerization, V —polymerization rate, k_p —chain growth constant, k_o – open circuit constant, $[S]$ – chain transfer concentration, $[M]$ – monomer concentration, C_s —chain transfer constants.

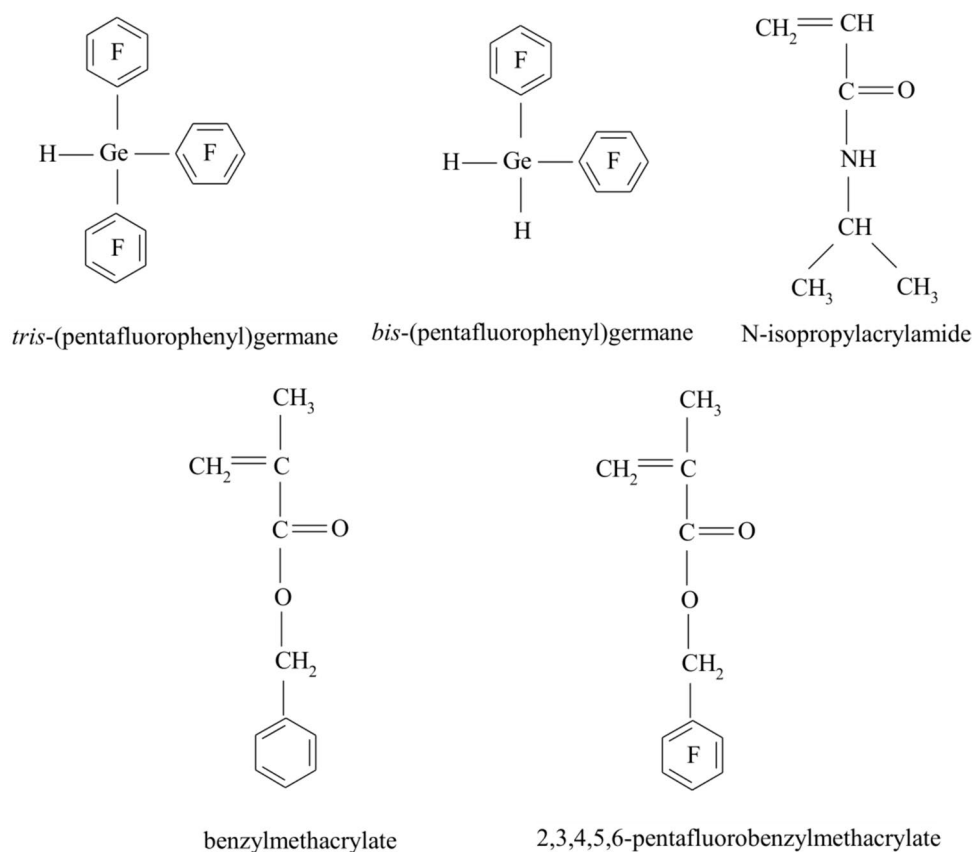
The radical polymerization of NIPAM was carried out with AIBN qua the initiator in the mixture of solvents benzene-acetone (volume ratio 1:1) with an addition of [*bis*-(pentafluorophenyl)germane] = $2 \cdot 10^{-2}$ mol/L in dilatometer ampoules. The ampoule was degassed in vacuum thrice, after that it was sealed off and polymerization was carried out at 60 °C for 24 h.

PNIPAM synthesis conditions: [AIBN] = $9.1 \cdot 10^{-3}$ mol/L, benzene-acetone solvent, $t = 24$ h, $T = 60$ °C, [NIPAA] = 1.3 mol/L [32].

The obtained PNIPAM samples were purified from the monomer by threefold reprecipitation using the solvent, the acetone-hexane precipitant system, and dried in vacuum at room temperature until their stable weights. Thus, a functional polymer containing *bis*-(pentafluorophenyl) germanium groups was obtained.

Postpolymerization of PNIPAM-GeH(C₆F₅)₂ in BMA(F) and BMA

Conditions of polymerization PNIPAM-GeH(C₆F₅)₂ in BMA(F) were: (PNIPAM + BMA(F)) = 4% + 96%, [AIBN] = $5 \cdot 10^{-3}$ mol/L, conversion 12%, acetone:

Scheme 1 Structure of monomers and organic compounds

BMA(F) = 2:1, [BMA(F)] = 2.08 mol/L. The same conditions were applied for the polymerization in BMA.

During the postpolymerization of functional PNIPAM-GeH(C₆F₅)₂ in BMA(F) and BMA, not all macromolecules having active *bis*-pentafluorophenylgermanium groups participate in the chain transfer reaction. Thus, the postpolymerization product contained, in addition to the block copolymers PNIPAM-Ge(C₆F₅)₂-PBMA(F) and PNIPAM-Ge(C₆F₅)₂-PBMA, also PNIPAM-GeH(C₆H₅)₂H, as well as homopolymers PBMA(F) and PBMA. For their separation, the hot extraction method was used in a Soxhlet apparatus in specially selected solvents: ethyl alcohol and benzene. In the case of the PNIPAM-Ge(C₆F₅)₂-PBMA(F), the yield was 94 wt % of block copolymer and 1.2 wt % of PNIPAM-HGe(C₆F₅)₂ homopolymer. For PNIPAM-Ge(C₆F₅)₂-PBMA, the yield 89 wt % of copolymer and 2.0 wt % of PNIPAM-HGe(C₆F₅)₂ homopolymer.

Experimental methods

IR spectroscopy

The IR spectra of polymers were recorded on an Infracum-FT801 IR-Fourier spectrometer (Russia, Novosibirsk) in the wavelength range from 400 to 4000 cm⁻¹. For this

purpose, tablets of polymers with KBr were prepared by pressing. The obtained absorption ranges were assigned to the respective groups using the table of characteristic frequencies.

NMR spectroscopy

Analysis of the structure of polymers was performed with aid of ¹H NMR by spectrometer Agilent DD2 400 NB (USA, United Kingdom). NMR spectra were recorded using a solution in CDCl₃. The reference combination was tetramethylsilane. The spectra were processed and interpreted by program MestReNova.

Gel-penetration chromatography (GPC)

The molar mass characteristics of the polymers were determined by GPC in high performance liquid chromatograph LC-20AD (Shimadzu, Japan). The analysis conditions: THF as an eluent, flow rate 1.0 cm³/min; the temperature level of the column oven and the refractometric detector cells equaled 40 °C. Polymethyl methacrylate was used as standads.

Differential scanning Calorimetry (DSC)

Thermal analysis of the studied copolymers was performed using DSC 204 F1 Phoenix (NETZSCH-Geratebau, Germany). The measurement instrumentation and technique allow to measure phase transformations temperatures with an error of ± 1 °C enthalpy of transformation $\pm 2\%$. During the differential scanning calorimetry, the samples were held at constant temperature (25 °C) for 30 min under argon, followed with cooling to -70 °C and then heating with a rate of 5 °C/min up to 300 °C.

Thermogravimetric analysis (TGA)

Thermogravimetric analysis was performed with NETZSCH TG 209 F1 Phoenix (NETZSCH-Geratebau, Germany). During the thermogravimetric analysis, the samples were heating with a rate of 10 °C/min from 25 °C up to 300 °C.

CHN(S)—analysis

The fraction of the hydrophilic block in the block copolymers was determined using a Elementar Vario EL cube for simultaneous CHN(S) determination (Elementar Analysensysteme GmbH, Germany).

Methods molecular hydrodynamics and optics

The absolute molar masses (MM) and the hydrodynamic radii R_{h-D} of macromolecules are determined by static (SLS) and dynamic light scattering (DLS) methods in solutions in chloroform (density $\rho_0 = 1.486$ g/cm³, dynamic viscosity $\eta_0 = 0.57$ cP, and refractive index $n_0 = 1.4443$). The experiments were performed using Photocor Complex instrument (Photocor Instruments Inc., Moscow Russia). For investigated solutions in chloroform, the distribution of the light scattering intensity I over the hydrodynamic radii $R_{h-D}(c)$ of scattering objects was unimodal. The values of translation diffusion coefficient $D(c)$ were determined in the wide concentration range and extrapolated to zero concentration to obtain the diffusion constant D_0 . As is well known, the constant D_0 are related to value of hydrodynamic radius R_{h-D} of macromolecules, which is defined using Stokes–Einstein equations [33, 34]:

$$D_0 = k_B T / 6\pi\eta_0 R_{h-D} \quad (2)$$

where k_B is Boltzmann's constant and T is the absolute temperature. SLS measurements were performed at the angle of 90° since no angular dependence of the scattered light was observed [35, 36]. The obtained results were analyzed according to the Debye method, and the values of the

weight-average molar masses M_w and the second virial coefficient A_2 were calculated using the following formula [36]:

$$\frac{cH}{I_{90}} = \frac{1}{M_w} + 2A_2c \quad (3)$$

where H is the optical constant [36].

$$H = \frac{4\pi^2 n_0^2 (dn/dc)^2}{N_A \lambda_0^4} \quad (4)$$

Here, I_{90} is the excessive intensity of light scattered at an angle of 90°, N_A is Avogadro's number, and dn/dc is the refractive index increment, which was determined using an RA-620 refractometer (Shimadzu, Kyoto, Japan) with a wavelength $\lambda_0 = 589.3$ nm. The dn/dc values were calculated from the slope of concentration dependences of the difference $\Delta n = n - n_0$ between refractive indexes of the solution n and the solvent n_0 . Note that the second virial coefficient A_2 for solutions for both copolymers was positive and high enough: $A_2 \cdot 10^4 = 2.4$ and 4.1 cm³ mole/g² PNIPAM-Ge(C₆F₅)₂-PBMA(F) and PNIPAM-Ge(C₆F₅)₂-PBMA. Therefore chloroform is thermodynamically good for investigated samples.

The viscometry experiments were performed using an Ostwald-type Cannon–Manning capillary viscometer (Cannon Instrument Company Inc., PA, USA). The dependencies of the reduced viscosity η_{sp}/c on the concentration were analyzed using the Huggins equation [35]:

$$\eta_{sp}/c = [\eta] + k_H [\eta]^2 c \quad (5)$$

where $[\eta]$ is the intrinsic viscosity, and k_H is the Huggins constant. The Huggins constant k_H characterizes the polymer–solvent hydrodynamic interaction and the hydrodynamic behavior of macromolecules copolymers in solutions. For the highest molar mass samples, the Huggins constants for linear polymers are close in magnitude and lie in the range of values typical for polymers in thermodynamically good solvents ($0.3 < k_H < 0.5$).

Light scattering, viscometry, and refractometry experiments were carried out at 21 °C. Millipore filters (Millipore Corp., Billerica, MA, USA) with a PTFE membrane with a pore size of 0.20 nm were used.

Receiving isotherms of surface pressures

Surface pressure isotherms were obtained by an installation KSVMini (Finland, Helsinki). Registration of π -A compression isotherms of monolayers was carried out using an automated Langmuir balance using the Wilhelmy plate method. Solutions of polymers in chloroform were being added to the surface of the aqueous subphase with a microsyringe for uniform distribution of the substance (volume of spreading solution $V_{s.sol.} = 30$

μL). The time for dissolving and evaporation of the solvent was 30 min during every experiment. After evaporation of the solvent from the surface of the subphase, the monolayer compressed with velocity 10 mm/min. The instrument was operated with deionized water (deionizer Chromatech (Russia, Dzerzhinsk) calculated electroconductivity less than $0.1 \mu\Omega/\text{cm}$).

The effective molecular area A_0 of polymers in a monolayer was determined graphically by extrapolating the descending part of the isotherm $\pi=f(A)$ to the abscissa axis ($\pi=0$).

Receiving surface pressure isotherms under compression-expansion conditions was carried out under compression rate was 10 mm/min, expansion rate was 2 mm/min until surface pressure reached 45 mN/m.

Preparation of langmuir–blodgett films

The transfer of monomolecular films from the water–air interface was carried out by LB method. Silicon plates were used as transfer substrates (JSC "Telecom-STV", Russia, Moscow). Substrate parameters: width 1 cm, length 2.5 cm, thickness 0.014 cm. Before testing, the substrates were degreased with ethyl alcohol.

The purity of the substrates was controlled by the contact angle of deionized water on a silicon plate ($\theta=56^\circ$). The levels of the surface pressure during the transfer of LB films equaled 45 mN/m, the volume of spreading solution was 30 μL , the transfer coefficients varied from 0.9 to 1.0.

Wetting contact angles

The wetting contact angles of the LB films were determined under leakage conditions by the "sitting drop" method with aid of a setup consisting of a microscope with a light source (Digital Microscope Model 500X, China), a lift table for a plate, and the CoolingTech program. To do this, a drop of deionized water (3 μL) was applied to the films with a microsyringe. The value of the contact angle θ was calculated from the size of the liquid droplets deposited on the solid surface, i.e., the height h and the base diameter d . Wetting kinetics was studied for all the copolymer films. It was found that there is no change for the contact angle while any timespan.

The value of the cosine of the wetting angle was calculated by the formula [33]:

$$\cos\theta = \frac{(d/2)^2 - h^2}{(d/2)^2 + h^2} \quad (6)$$

AFM

The surface topography of the LB films was studied in the semi-contact mode by such an AFM as Solver P47 (NT-MDT) (Zelenograd, Russia) at room temperature.

Results and discussion

Synthesis and description of the block copolymers

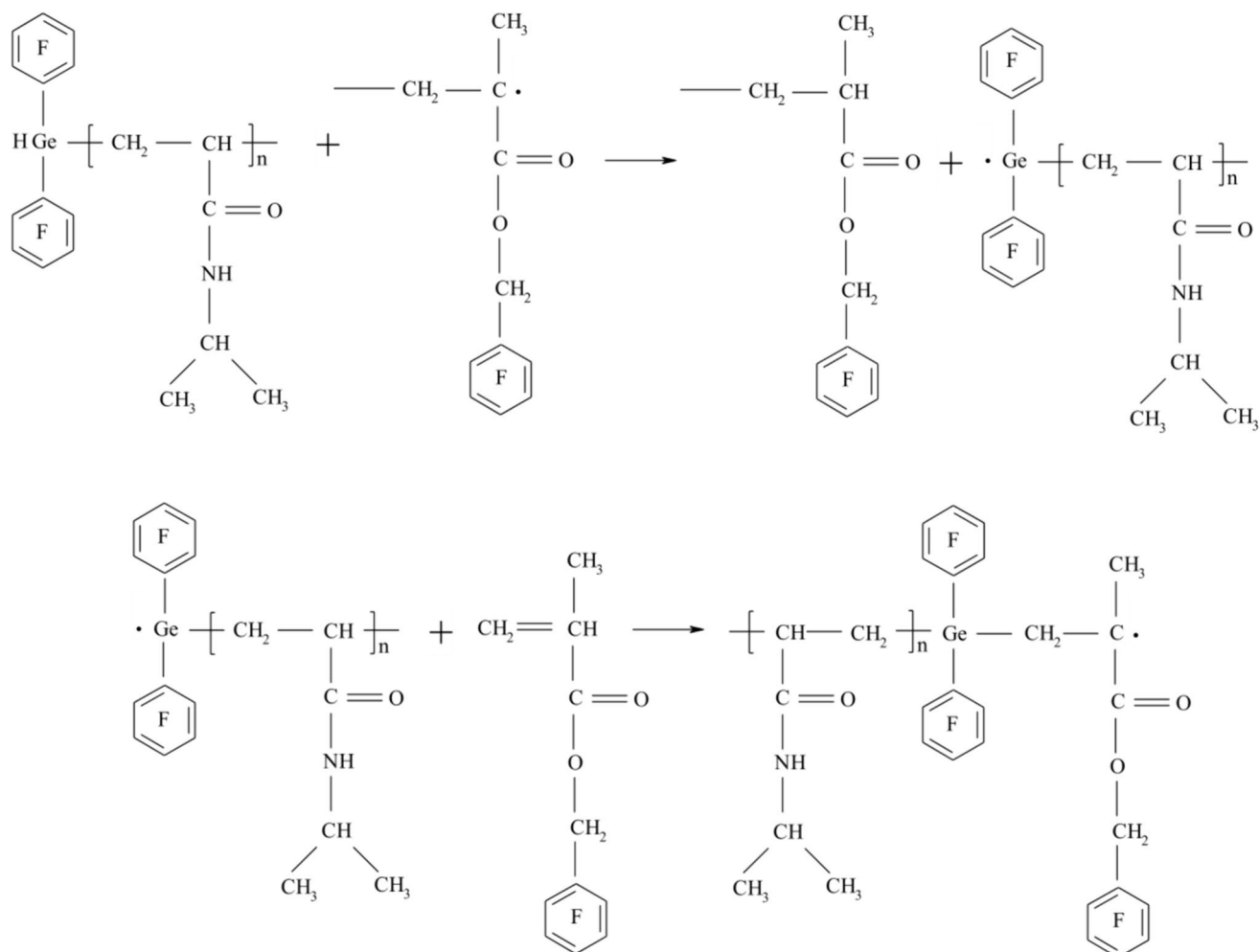
The relative chain transfer constants C_s of radical polymerization of 2,3,4,5,6-pentafluorobenzyl methacrylate and benzyl methacrylate on tris-(pentafluorophenyl)germanium were equaled 1.26 and 0.45, respectively. Identically with the case of ST, NIPAM, and FMA, tris-(pentafluorophenyl)germanium proved to be an active chain transmitter [27, 30]. At the initial stage, N-isopropylacrylamide was radically polymerized in presence of bis(pentafluorophenyl)germanium to synthesized the PNIPAM-GeH(C₆F₅)₂ functional polymer.

As a result of further postpolymerization of the functional polymer with 2,3,4,5,6-pentafluorobenzyl methacrylate and benzyl methacrylate, after separation of homopolymers by hot extraction, PNIPAM-Ge(C₆F₅)₂-PBMA(F) and PNIPAM-Ge(C₆F₅)₂-PBMA were prepared (Scheme 2). Scheme 3 shows the structure formulas of the studied copolymers.

In Fig. 1 (a, b), IR ranges of BCP(F) (2) and BCP (3) are shown. Evidence of the formation of polymers is the presence bands characteristic of units of the functional polymer PNIPAM-GeH(C₆F₅)₂ and PBMA(F) or PBMA homopolymers in the IR spectra of absorption. Typical stretching vibrations of the C–H bonds of the PBMA benzene ring appears in the range from 2953 to 3077 cm^{-1} (a). The bending vibrations of the C–H bonds and the stretching vibrations of the –C₆H₅ group of the aromatic ring are observed in the ranges of 696–750 cm^{-1} and 1454 cm^{-1} , respectively (Fig. 1b). There are spectra related to vibrations of the carbonyl of the functional polymer PNIPAM-GeH(C₆F₅)₂, PBMA(F) 1650 cm^{-1} (a), –NH group of chains PNIPAM 1644 cm^{-1} (a,b) and the –NH group (a wide band 3304 cm^{-1} and 3306 cm^{-1}). There is also some growth in the intensity of the absorption band corresponding to the –C₆F₅ group (963 cm^{-1}) [37] in Fig. 1a, representing the presence of PBMA(F) blocks in the copolymer.

Another confirmation of the block copolymer formation are the results obtained by NMR spectroscopy. Figure 2 shows ¹H NMR spectra of 3 and 2 BCPs. The block copolymer spectra present chemical shifts characteristic of both units (Table 1). The chemical shifts characteristic of a functional polymer in the block copolymers (Fig. 2a) shifted to a lower area: –CH₃ (0.96 ppm) and >CH- (2.00 ppm). In fluorinated BCP (Fig. 2b), compared to PNIPAM-Ge(C₆F₅)₂H, the chemical shifts of the –CH₃ group to a lower area (0.86 ppm), the >CH-NH- group to a higher area (4.03 ppm).

In Fig. 3 presents data from DSC analysis of the obtained polymers. The melting point of the PNIPAM homopolymer depends on the production conditions and can vary over a



Scheme 2 Postpolymerization of PNIPAM-GeH(C₆F₅)₂ in PBMA(F) (or PBMA)

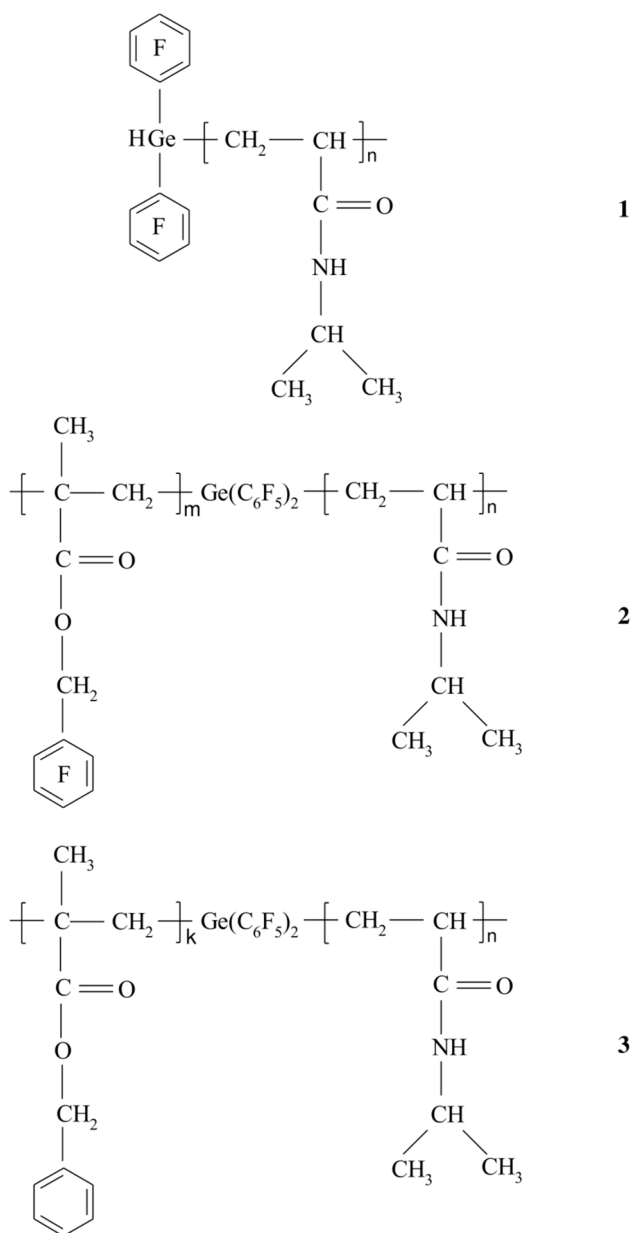
wide temperature range. In the case of the functional polymer PNIPAM-Ge(C₆F₅)₂H, which has a bispentafluorophenylgermanium group at the end of the chain, the melting point is 76.6 °C. The thermodynamic characteristics of fluorinated and non-fluorinated block copolymers differ significantly; in the case of BCP(F), a completely amorphous polymer with $T_g = 76$ °C is obtained, while for block copolymer 3, in addition to the amorphous phase, there is also an ordered phase, as evidenced by the DSC curve, where areas of both melting and devitrification are present. Moreover, in the latter case, the presence of the amorphous phase slightly disorders the system, lowering the melting temperature (T_{melt}) by 7 °C, compared to the original polymer 1, while the glass transition temperature of the amorphous block (T_g) increases compared to BCP(F) by 12.8 °C.

One can be seen that transfer from the functional polymer to the block copolymer induces by growth of molar mass not breaking the single mode of molar mass distribution (Fig. 4), which means formation of BCPs, while which M_w of the

block copolymers overcomes M_w of the functional polymer in many times (Table 2).

Molar masses and hydrodynamic characteristics of amphiphilic copolymers on based N-isopropylacrylamide and benzylmethacrylate

Analyzing experimental data obtained by SLS for multicomponent polymer systems, it is necessary to take into account the possible effect of compositional inhomogeneity on the determined values of MM. The compositional inhomogeneity of the polymer, that is, the inhomogeneity of its molecules in chemical composition, manifests itself in the fact that the components of the copolymer, scattering light independently, make different contributions to the total measured light scattering intensity. Therefore, the scattering intensity can be intensive even when the refractive index increment dn/dc of the block copolymer is close to zero. Accordingly,



Scheme 3 Structure formules copolymers: functional PNIPAM-GeH(C₆F₅)₂ (**1**), block copolymers PNIPAM-Ge(C₆F₅)₂-PBMA(F) (**2**) and PNIPAM-Ge(C₆F₅)₂-PBMA (**3**)

the measured molar mass will be apparent M_a , which may differ from the real M_w [38].

As shown in theoretical and experimental studies [39, 40], the compositional inhomogeneity leads to strongly overestimated values of the determined MM in cases where the refractive index increment dn/dc of the copolymer is low (generally $dn/dc \leq 0.03$), while the refractive index increments components $(dn/dc)_1$ and $(dn/dc)_2$ are large and differ in meanings. For such systems, the apparent MM is described by the ratio [39, 40]:

$$M_a = \frac{(dn/dc)_1(dn/dc)_2}{(dn/dc)^2} M_w + \frac{(dn/dc)_1}{(dn/dc)} \phi_{12} x M_{w-1} - \frac{(dn/dc)_2}{(dn/dc)} \phi_{12} (1-x) M_{w-2} \quad (7)$$

where $\phi_{12} = [(dn/dc)_1 - (dn/dc)_2]/(dn/dc)$, M_{w-1} and M_{w-2} are weight-average molar mass of components 1 and 2, respectively, x is the mass fraction of component 1 in the sample. It can be seen from the above ratio that the magnitude of the apparent molar mass M_a varies from solvent to solvent. It can be shown that if the value of the parameter ϕ_{12} is in the range from -1 to 1 then the value of the measured M_a differs from the real molar mass by no more than 10%. In the case of a non-fluorinated polymer, where $dn/dc = 0.11 \text{ cm}^3/\text{g}$, this information is redundant, because the refractive index increment is high. For a linear copolymer, dn/dc was determined, but for its fluorinated copolymer, it was less, which is explained by the presence of fluorine in the units of the polymer chain, namely, by the fact that fluorine reduces the refractive index. Molar mass and hydrodynamic parameters are presented in Table 3.

Molar masses determined by SLS are higher than MM determined by GPC (Table 2). When comparing these MM values, the following circumstances must be taken into account. As is known, GPC is not an absolute method, and in this case, the polystyrene standard was used to determine the M_w . This single fact can lead to a systematic experimental error in the measurement of MM. In addition, the studied block copolymers, which contain components that differ greatly in chemical nature. Consequently, the hydrodynamic volumes of block copolymers can differ significantly from those of homopolymers of the same M_w , which can lead to an incorrect value of M_w according to GPC data.

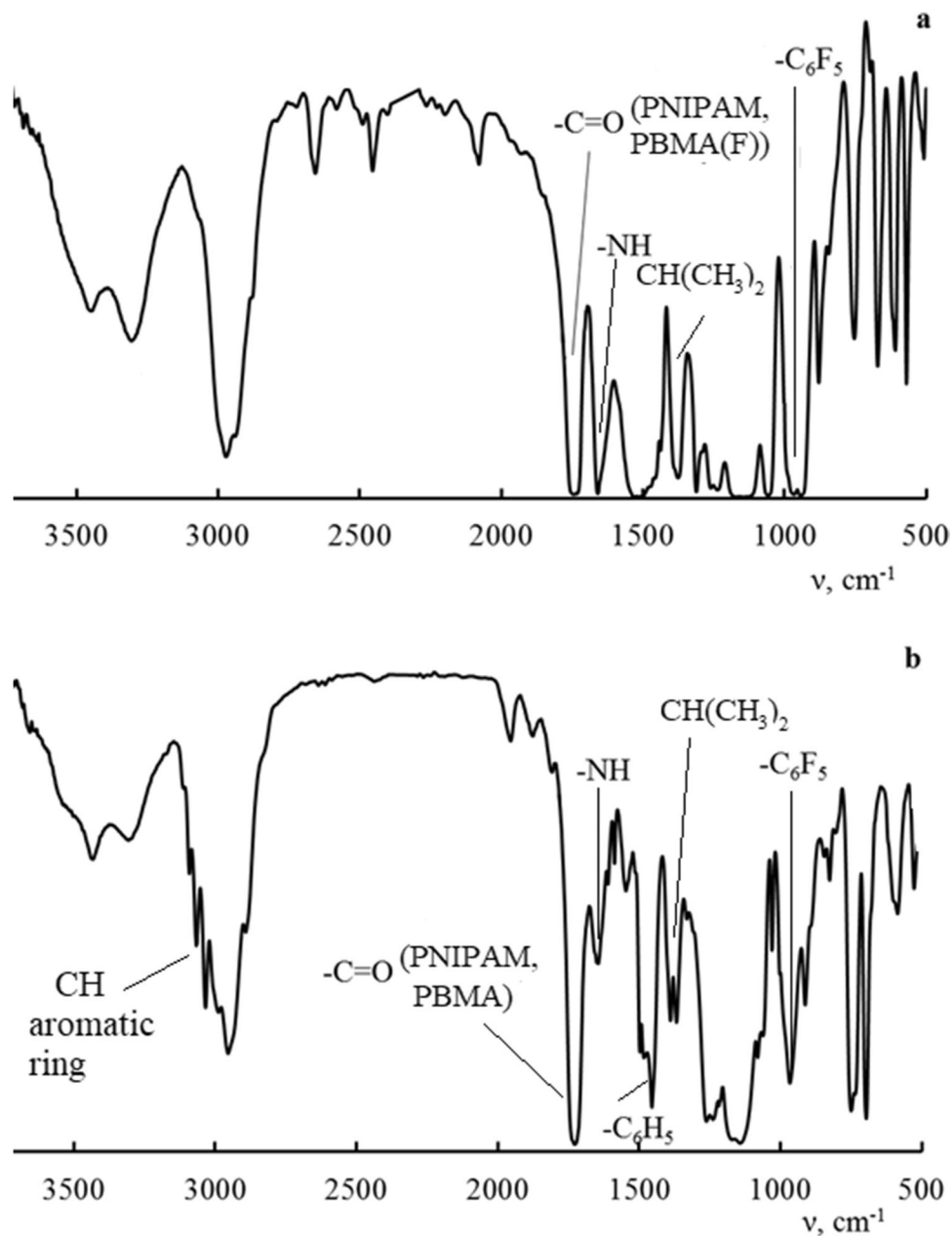
The first value is obtained using the molar masses determined by the SLS method; the second value is the value determined using the molar masses determined by the SEC method.

The correctness of the MM values determined by SLS and GPC can be judged by the values of the hydrodynamic invariant A_{0-hd} , which is calculated by the formula [41–43]:

$$A_{0-hd} = \eta_0 D_0 \left(\frac{M[\eta]}{100} \right)^{1/3} / T \quad (8)$$

with using the experimental values of molar mass M , intrinsic viscosity $[\eta]$, and translation diffusion coefficient D_0 . The use of MM determined by SLS leads to A_{0-hd} typical for flexible chain polymers ($A_{0-hd} = (3.2 \pm 0.2) 10^{-10} \text{ erg/K mol}^{1/3}$ [38, 43, 44]). The values A_{0-hd} obtained by MM from GPC data, much less than the given value. These facts indicate that the MM measured using the GPC is most likely underestimated. Accordingly, in further discussion we will use MM determined by the SLS method.

Fig. 1 IR ranges of **2** (a) and **3** (b) BCPs



The difference in MM determined by different methods is also observed for the functionalized polymer PNIPAM- $\text{GeH}(\text{C}_6\text{F}_5)_2$. In the same way, the values of the hydrodynamic invariant calculated using SLS and GPC differ for

this sample (Table 3). The low MM value determined by GPC may be due to the conformation of its macromolecules. Actually functional group is high enough; its MM is eight percent of MM of functionalized polymer.

Table 1 ^1H NMR data for functional polymer (1), BCP(F) (2) and BCP (3)

Polymers	Chemical shift of protons					
	$-\text{CH}_3$	$-\text{CH}_2-$	$>\text{CH}-$	$>\text{CH}-\text{NH}-$	$-\text{C}_6\text{H}_5$	$-\text{CH}_2-\text{O}-\text{CO}-$
1	1.08	1.59	2.11	3.93	-	-
2	0.86	-	-	4.03	-	5.04
3	0.96	-	2.00	-	7.32	4.93

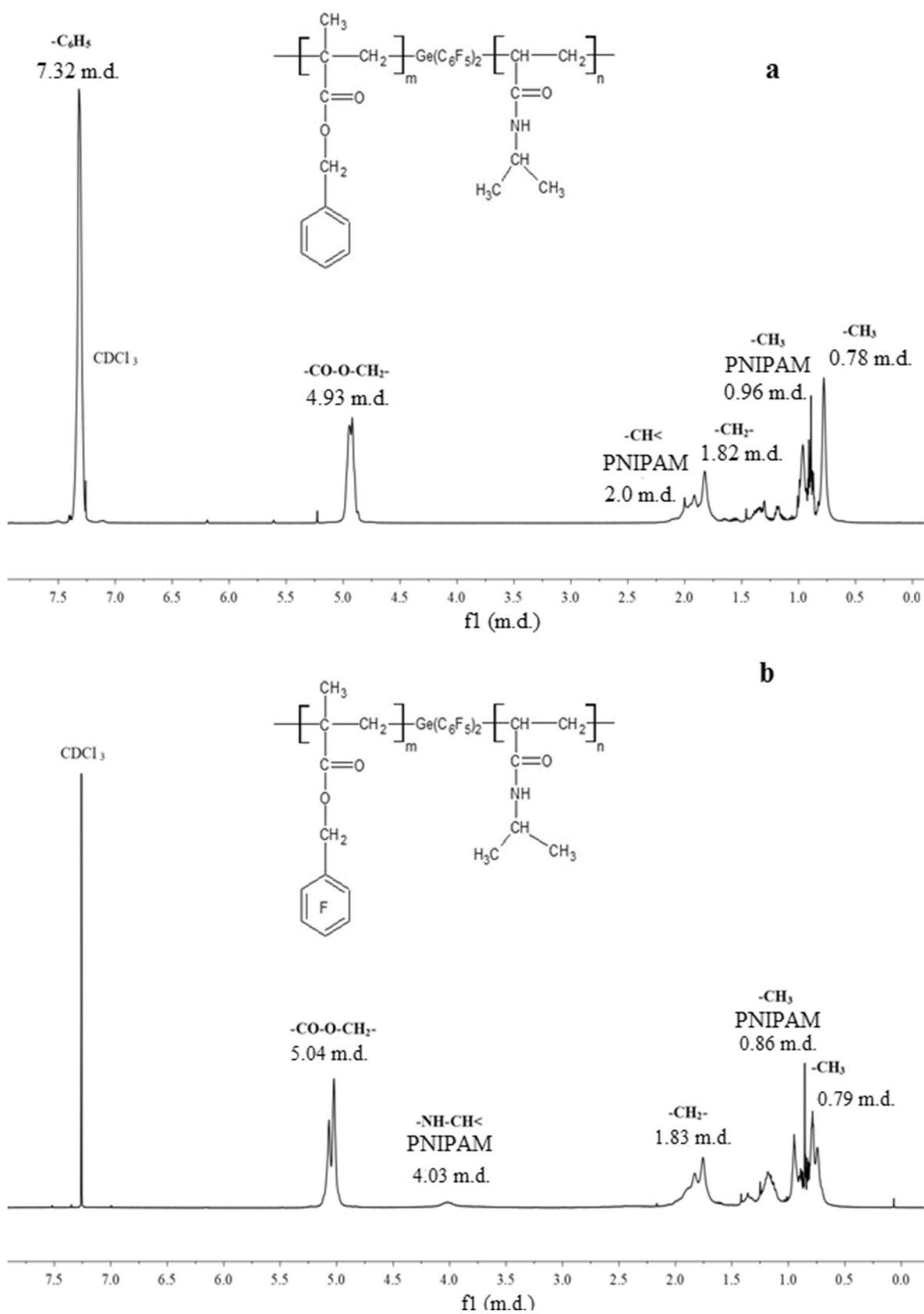


Fig. 2 ^1H NMR spectra of 3 (a) and 2 (b) BCPs

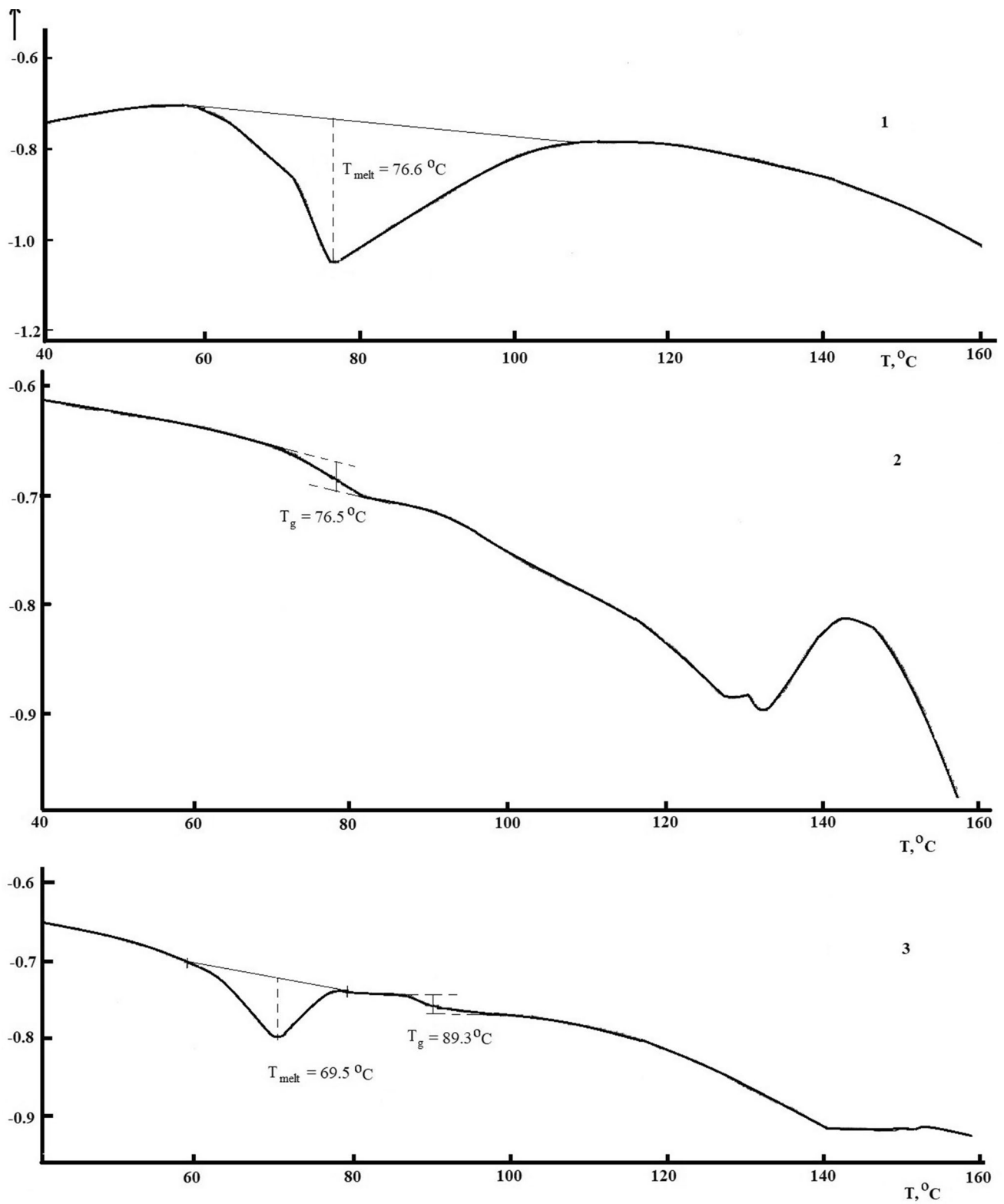


Fig. 3 The DSC curves of polymers 1, 2 and 3

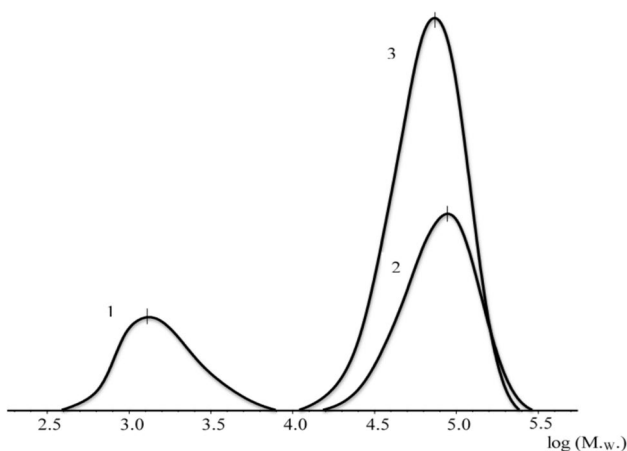


Fig. 4 Molar mass distribution for the functional polymer (1) and for its BCP(F) (2) and BCP (3)

As is known, in the case of amphiphilic polymers, a linear chain surrounds the functional group, shielding it from the selective solvent [24, 28, 41]. Accordingly, such polymers are characterized by high intramolecular density in solutions. This may lead to underestimated MM values when determined by GPC.

As it can be seen from Table 3, the MM of BCP(F) is approximately 30% lower than the MM of PNIPAM-Ge(C₆F₅)₂-PBMA. Taking into account molar masses M_0 of the monomer units of the compared copolymers, one can expect that the difference in the chain lengths of PBMA(F) and PBMA will be larger. Actually, the polymerization degree m of PBMA(F) and PBMA components are related to the molar mass M_w of the block copolymers and M_{PNIPAM}

the functionalized polymer PNIPAM-Ge(C₆F₅)₂ by the following relationship

$$m = (M_w - M_{PNIPAM}) / M_0 \tag{9}$$

Calculations using formula (9) lead to $m = 153$ and 236 for PBMA(F) and PBMA, respectively. Thus, the length of the PBMA(F) and PBMA chains differs by a factor of 1.5.

Apparently, this is due to the different nature of the units in the resulting block copolymers. With similar degrees of conversion (12%) and almost the same rate of postpolymerization of the functional polymer in PBMA(F) and PBMA, the formation of a lower molar mass polymer in the case of PBMA(F) is associated with pronounced hydrophobic (in the case of a fluorinated unit) and hydrophilic interactions (for the unit N-isopropylacrylamide) in macromolecules, which leads to compression of the polymer coil during chain growth and restricts the access of growth radicals to the monomer, resulting in the formation of a polymer with a lower M_w than for PBMA.

It is interesting to compare the results obtained for block copolymers with the literature data for the poly(benzylmethacrylate) homopolymer. Figure 5 and Table 4 shows Kuhn-Mark-Houwink dependences ($[\eta] = K \cdot M^a$) for poly(benzylmethacrylate) in MEK and toluene according to the data of R. W. Richards [42].

The points for the block copolymers studied in this work are also presented there. It is seen that experimental point for 3 lie on the dependences polybenzylmethacrylate in MEK and toluene, while point for 2 is lower than ones dependencies. It indicates an increase in the intermolecular density at passage from of the BCP to BCP(F) and which is explained by the presence of fluorine in the polymer structure [43].

Table 2 The main characteristics of the obtained polymers

Polymers	GPC			DSC		TGA	CHN(S)
	M_n , g/mol	M_w , g/mol	M_w/M_n	T_{melt} , °C	T_g^* , °C	T_d^{**} , °C	N, %
1	$1.3 \cdot 10^3$	$1.9 \cdot 10^3$	1.40	76.6	-	76.2	9.80 ± 1
2	$5.7 \cdot 10^4$	$7.4 \cdot 10^4$	1.32	-	76.5	228.2	0.54 ± 0.05
3	$6.7 \cdot 10^4$	$8.8 \cdot 10^4$	1.31	69.5	89.3	150.0	0.33 ± 0.03

* T_g is glass transition temperature; ** T_d is decomposition start temperature

Table 3 The molar masses and hydrodynamic characteristics of polymers in dilute solutions

Polymers	$M_w \cdot 10^{-3}$, g/mol SLS	M_0 , g/mol	DP*	L , nm	R_{h-D} , nm	dn/dc , cm ³ /g	η , cm ³ /g	A_{0-hd} SLS/GPC erg/K mol ^{1/3}
1	5	377	13	3	1.3	0.07	6.2	3.2/ 2.3
2	120	786	153	38	6.7	0.04	15.5	2.9/2.5
3	163	691	236	59	8.3	0.11	30	3.2/2.2

DP*—the degree of polymerization

Fig. 5 MKH dependences for polybenzylmethacrylate in MEK (green line) and toluene (red line). The red and green symbols correspond to the $[\eta]$ values for polymers **3** and **2** in chloroform, respectively

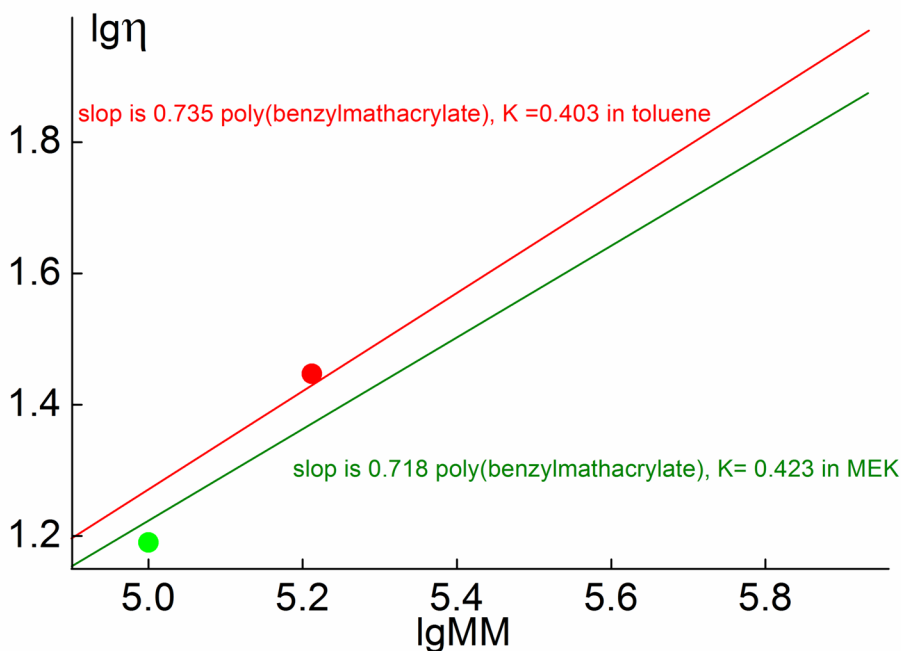


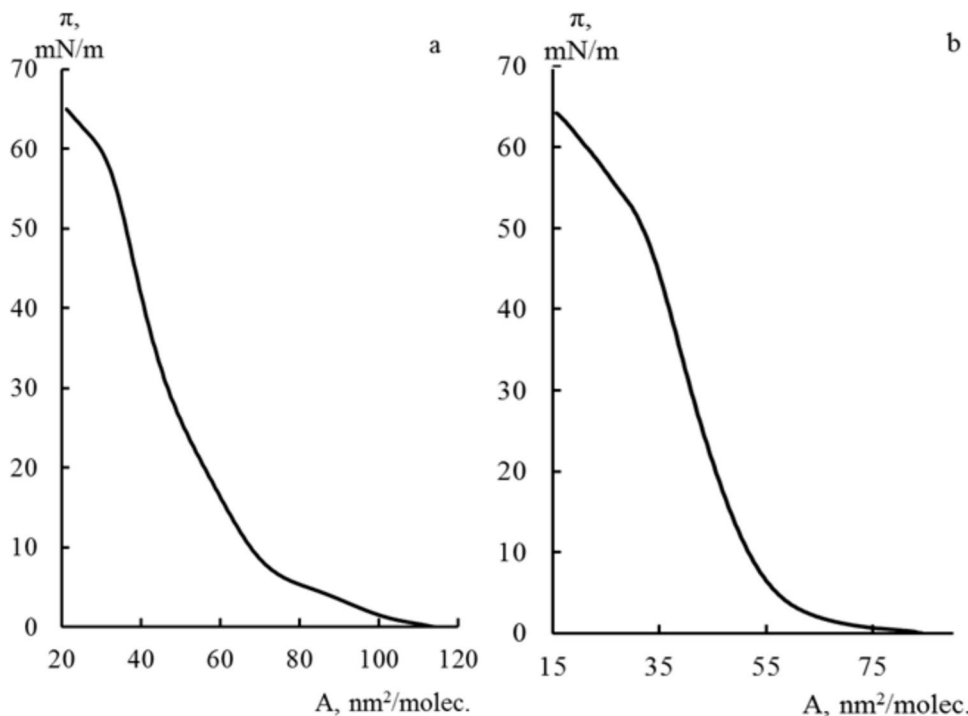
Table 4 Kuhn-Mark-Houwink parameters for solutions of polybenzylmethacrylate in MEK and toluene at various temperatures [42]

$K \cdot 10^5, \text{dL/g}$	a	$T, \text{°C}$	Solvent
4.23	0.718	25	MEK
4.03	0.7335	25	Toluene

Isotherms of surface pressure of the copolymers

Surface pressure isotherms were received for the **2** and **3** BCPs (Fig. 6) while compression. Functional polymer molecules (**1**) do not form Langmuir monolayers, which is evidenced by the low surface pressure (10 mN/m) and the isotherm type, which indicates micelle formation at the water–air interface.

Fig. 6 Surface pressure isotherms of amphiphilic BCPs **2** (a) and **3** (b) ($V_{s,\text{sol.}} = 30 \mu\text{L}$)



The surface pressure isotherm for the **2** (Fig. 6a) demonstrates that the compressible monolayers undergo several phase transitions. The segment of the obtained isotherm at a pressure close to zero, describes the area of a so-called two-dimensional gas, in which the molecules interact little with each other and are quite far from each other. With further compression of the film, the molecules begin to contact in the area of a two-dimensional liquid; the first increase in surface pressure is observed with a sufficiently large fall in the film area. At the interphase, there is a short linear segment on the isotherm i.d. a plateau. In this region the macromolecules begin to rearrange: the hydrophilic groups associate in water, while the hydrophobic ones remain on the surface. With further compression of the barrier, a sharp jump in surface pressure occurs with a small increase in the area of the film. Further compression of the film leads to its destruction ($\pi_{\text{coll}} \sim 58 \text{ mN/m}$), since in this area of the isotherm the film is in the most compressed state.

Figure 6b shows an isotherm, which has no “liquid area”, but demonstrates intensive transfer from the area of the two-dimensional gas to the area of a “two-dimensional solid”, which shows that the molecules form a dense ordered monolayer on the water surface, in which each molecule adjoins the adjacent and contacts with the aqueous subphase Table 5.

To determine the stability of monolayers, isotherms were obtained for regime of compression and expansion (Fig. 7). The hysteresis of the isotherm curves takes place.

The value rigidity of the monolayer (β) was calculated of the tangent of the linear section of the isotherm with the maximum steepness. β describes the phase state with the stiffest packing of the condensed films [44]:

Table 5 The characteristics obtained from the isotherms of surface pressure (the volume of the spreading solution $V_{\text{s.sol}}$ 30 μL)

Polymers	A_0 , nm^2/molec	π_{coll} , mN/m	$\beta \cdot 10^{-17}$, N/m^3
2	60.00	58	1.9
3	54.00	50	2.1

$$\beta = -\frac{d\pi}{dA} \quad (10)$$

For the non-fluorinated polymers, the pressure on the isotherms also drops, but not as much as for fluorinated ones. The hysteresis loop is smaller in magnitude in the case of **3**, which indicates minor inter- and intramolecular interactions in the polymer chains at the water–air interface (Fig. 7).

Surface properties of LB films researched by AFM and wetting

The surface topography of the LB films was investigated by the AFM. Figure 8 shows that the surface of the films is close to a flat with a large number of irregularities. One can see many protrusions oriented vertically with respect to the substrate surface.

Contact wetting angles of the LB films for block copolymers **2** and **3**, installed into silicon plates, were determined. The value of the equilibrial contact angle of water on a pure silicon substrate was 56° . For BCP **2** and **3** these angles were 73° and 68° , respectively, which meant the surfaces of those films were hydrophilic (Scheme 4).

Fig. 7 Compression-expansion curves of **2** (a) and **3** (b) ($V_{\text{s.sol}} = 30 \mu\text{L}$)

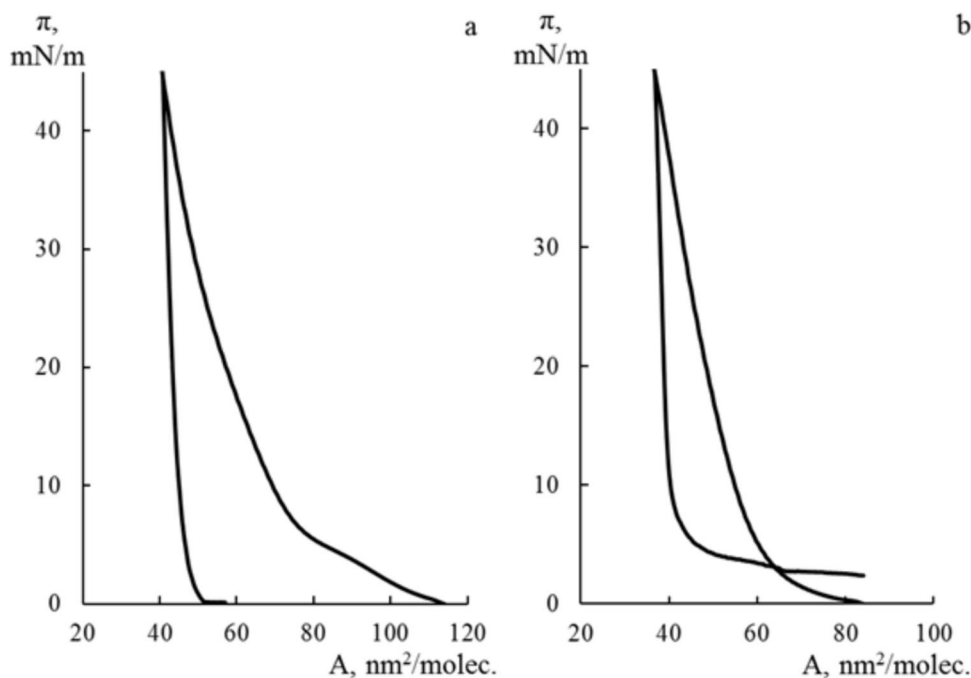
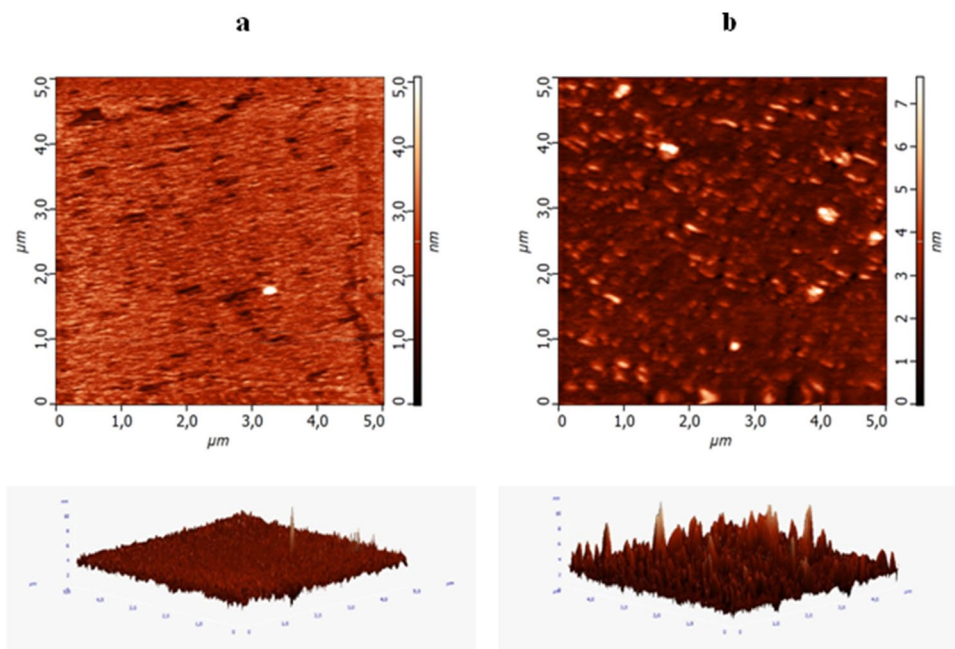
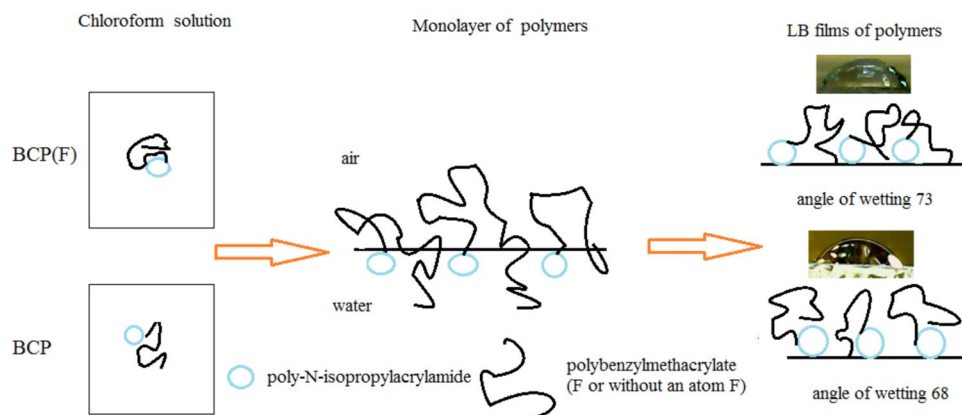


Fig. 8 AFM images of the LB films of **2** (a) and **3** (b)**Scheme 4** Schematic image of behavior of BCPs **2** and **3** in chloroform solution, monolayers of polymers and LB films of polymers

Conclusion

New amphiphilic block copolymers based on N-isopropylacrylamide and 2,3,4,5,6-pentafluorobenzyl methacrylate and benzyl methacrylate were synthesized in high yields (89–94 wt. %) due to the double sequential chain transfer reaction with *bis*-(pentafluorophenyl)groups germanium. The relative constants of chain transfer to *tris*-(pentafluorophenyl)germanium during the radical polymerization of 2,3,4,5,6-pentafluorobenzyl methacrylate and benzylmethacrylate were 1.26 and 0.45, respectively.

The samples of block copolymers were dissolved molecularly in chloroform. It makes it possible to determined molar mass and hydrodynamic characteristics of block copolymers. Molar masses of block copolymers and functionalized polymers differed thirty times. Analysis of the values of molar

mass of intrinsic viscosities and hydrodynamic radii showed that the synthesized copolymers are the typical flexible-chain polymers. The molecules of the non-fluorinated sample had a swollen coil conformation. In the case of PNIPAM-Ge(C₆F₅)₂-PBMA(F), the presence of a fluorinated block leads to compaction of molecules and, accordingly, an increase in intramolecular density. It was shown that the amphiphilic block copolymers PNIPAM-Ge(C₆F₅)₂-PBMA and PNIPAM-Ge(C₆F₅)₂-PBMA(F) formed stable Langmuir monolayers ($\pi = 50\text{--}58$ mN/m). The AFM and wetting methods demonstrated the Langmuir–Blodgett films received of the block copolymers are hydrophilic. The study of surface pressure isotherms in Langmuir monolayers is necessary to determine the potential area of application of these objects, since if polymers are able to orient themselves in

monomolecular films, this opens up wide opportunities in various fields from medicine to nanotechnology, since it is possible to control the self-organization of macromolecules at various interfaces.

Thus, the obtained we have proposed a non-labor-intensive two-step synthesis of new amphiphilic block copolymers with different structures containing a hydrophobic fragment of polybenzylmethacrylate and poly(2,3,4,5,6-pentafluorobenzyl methacrylate) with low surface energy and a hydrophilic poly(N-isopropylacrylamide) block may be one of the promising materials suitable for biomedical applications. This comprehensive approach to studying the physicochemical properties of polymers makes it possible to determine their potential area of use, for example, in the formation of polymerosomes during the delivery of drugs.

Author contributions Investigation, visualization, writing-original draft preparation, methodology O.Z. and M.S.; conceptualization, project administration O.Z. and A.P.; synthesis, analysis of polymers and obtaining surface pressure isotherms O.Z. and E.O.; research by the method of AFM M.B.; wettability E.O.; DSC and TGA analysis A.M; molar masses and hydrodynamic characteristics M.S. and M.Z. All authors have read and agreed to the published version of the manuscript.

Data availability The datasets generated during the study are available from the corresponding author upon reasonable request.

Declarations

Conflict of interest The authors declare no conflict of interest.

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