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MACROMOLECULAR CHEMISTRY AND POLYMERIC MATERIALS

Synthesis and Surface Properties of Amphiphilic Block Copolymers Polyvinylpyrrolidone-block-Polystyrene

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Abstract—Amphiphilic block copolymers of N-pyrrolidone and styrene were prepared by chain transfer to organogermanium compounds bis(pentafluorophenyl)germane and tris(pentafluorophenyl)germane. The relative chain-transfer constants were determined. The surface properties of the isolated block copolymers with various numbers of units in the hydrophilic block were studied. The polar and dispersive components of the surface tension of films of the amphiphilic block copolymers were calculated by the Zisman method.

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An important trend in the progress of chemistry and technology of polymeric materials is search for the possibility of preparing materials with new characteristics on the basis of the preset combination of properties of known polymers [1]. Of much interest in this respect is the development of block copolymers whose macromolecules combine blocks differing in the chemical structure and nature. Depending on the chemical nature of blocks, their length, number, and sequence of alternation, and also on the tendency to crystallize, it is possible to prepare materials whose structure and properties differ essentially from those of the homopolymers [2].

Block copolymerization as a route to amphiphilic copolymers allows the properties of hydrophobic and hydrophilic fragments to be combined. Thanks to advantages over common polymeric materials, block copolymers found wide use in molecular biology, chemical diagnostics, radioimmunotherapy, and also in fine chemistry; new fields of their application are also being outlined.

The most convenient and widely used procedure for preparing block copolymers is based on chain-transfer reactions. Chain-transfer reactions are of practical interest for controlling the properties of polymeric materials.

It was shown previously that some perfluorinated germanium compounds are good chain-transfer agents in polymerization of vinyl monomers [4].

The goal of this study was preparation of amphiphilic block copolymers polyvinylpyrrolidone–$Ge(C_6F_5)_2$–polystyrene. Our study involved the following steps: synthesis of functional polyvinylpyrrolidone (PVPD) containing active hydrogen at the chain terminus by chain transfer to bis(pentafluorophenyl)germane; subsequent postpolymerization of the isolated PVPD in styrene; characterization of the isolated amphiphilic block copolymers and study of their surface properties.

EXPERIMENTAL

All the monomers and solvents used in the study were purified. *N*-Vinylpyrrolidone (VPD) was dried over sodium sulfate. Styrene (St) was dried over CaH_2 and distilled at reduced pressure. To prevent polymerization in the course of distillation, we added to the monomers an inhibitor, 2,2',6,6'-tetramethylpiperidine-1-oxyl. The solvents used were purified by standard procedures [5]. As radical polymerization initiator we used AIBN which was purified by double recrystallization from diethyl ether. As chain-transfer agents we used bis(pentafluor ophenyl)germane $(C_6F_5)_2GeH_2$ and tris(pentafluoroph enyl)germane $(C_6F_5)_3GeH$, which were synthesized as described in [6].

Radical polymerization of VPD was performed in the presence of 0.005 M AIBN. The concentration of the

Table 1. Synthesis conditions and main characteristics of functional polymers prepared at 60°C in the presence of $(C_6F_5)_2GeH_2$

Polymer no.	$[(C_6F_5)_2GeH_2]$, M	$M_w \times 10^{-5}$	$M_n \times 10^{-5}$	p_n
1	8×10^{-5}	3.54	1.7	2.065
2	1×10^{-5}	1.11	0.51	2.177
3	2×10^{-5}	0.36	0.18	1.865

chain-transfer agents $(C_6F_5)_2GeH_2$ and $(C_6F_5)_3GeH$ was varied in the range 0–0.02 M. The relative constants of chain transfer to $(C_6F_5)_3GeH$ in St polymerization were determined in the bulk, and in VPD polymerization, in tetrahydrofuran (4.71 M VPD). The relative constants of chain transfer to $(C_6F_5)_2GeH_2$ in polymerization of St and VPD were determined in the bulk by the Mayo method [7]. Polymerization was performed in dilatometric ampules. The monomeric mixtures were preliminarily purified by threefold freezing–pumping–thawing.

Upon reaching 10% conversion, the ampules were withdrawn from the thermostat and cooled with liquid nitrogen to stop the reaction. The polymers were purified by threefold reprecipitation from chloroform with diethyl ether and vacuum-dried at 40°C to constant weight.

Postpolymerization of PVPD prepared in the presence of various additions of $(C_6F_5)_2GeH_2$ was performed in St in the presence of chloroform. The amount of PVPD was 4 wt % relative to the monomer. The solvent : monomer ratio was 2. As initiator we used AIBN (0.005 M). The polymers obtained were isolated by threefold reprecipitation from chloroform with diethyl ether and were vacuum-dried at 40°C to constant weight.

The molecular-weight characteristics of the polymers soluble in THF were determined by gel permeation chromatography (GPC) at 40°C on a Prominence LC-20VP liquid chromatograph (Shimadzu). The columns were packed with styrene–divinylbenzene copolymer, pore size 1×10^6 and 1×10^5 Å. As detectors we used a differential refractometer and a spectrophotometer. As references we used polystyrene samples with molecular weights from 10^4 to 2.5×10^6. The eluent was tetrahydrofuran (flow rate 5 ml min^{-1}). PVPD, which is insoluble in tetrahydrofuran, and PVPD block copolymers were anlayzed in chloroform (flow rate 1 ml min^{-1}) with

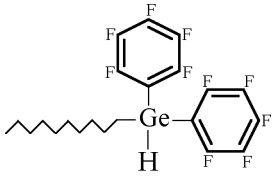
Table 2. Relative constants C_s of chain transfer to $(C_6F_5)_3GeH$ and $(C_6F_5)_2GeH_2$ in polymerization of St and VPD

Monomer	C_s	
	$(C_6F_5)_2GeH_2$	$(C_6F_5)_3GeH$
St	3.0	3.4
VPD	1.8	0.02

a Knauer liquid chromatograph equipped with RI and UV detectors and a Phenomenex Linear column, 10 μm (7.8 × 300 mm), using Phenomenex polystyrene references with the molecular weight from 12.6×10^3 to 1.09×10^6.

The IR spectra were recorded on an IRPrestige-21 device (Shimadzu). The surface properties of polymer films were studied by the wetting procedure. Solutions of the polymers (0.035 g of polymer was dissolved in 10 ml of chloroform) were cast onto quartz supports to obtain films. Water was used as wetting liquid. The contact angles of the films with water were determined in the advancing mode. The surface tension and its polar and dispersive components were determined by the Zisman method [8] using a series of hydrocarbons (hexane, heptane, octane, hexadecane) with known polar and dispersive components of the surface tension.

By the chain transfer to $(C_6F_5)_2GeH_2$ in the course of VPD polymerization, we prepared polymers containing bispentafluorophenyl groups and active hydrogen at the chain terminus. The relative constant of chain transfer to $(C_6F_5)_2GeH_2$ in VPD polymerization was 1.8, i.e., a macromolecule of functional PVPD can be presented as follows:



The synthesis conditions and characteristics of functional PVPD samples are given in Table 1. The presence of active hydrogen at the macromolecular chain terminus upon preparation of the functional polymer was proved by IR spectroscopy. It allows further postpolymerization in the presence of a monomer with different properties, e.g., of styrene. The IR spectra of PVPD (prepared in the absence of chain-transfer agents) and functional PVPD are shown in Fig. 1. The presence of an absorption band at about 2100 cm^{-1}, characteristic

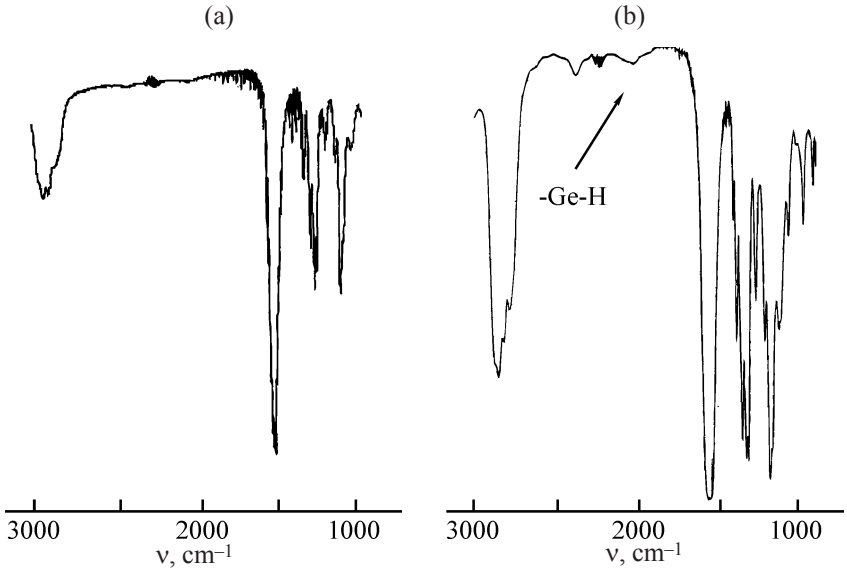


Fig. 1. IR spectra of (a) PVPD and (b) functional PVPD. (ν) Wavenumber.

of the –Ge–H group, suggests that the chain transfer in polymerization of VPD in the presence of $(C_6F_5)_2GeH_2$ involves one hydrogen atom.

The relative constants of chain transfer to $(C_6F_5)_3GeH$ and $(C_6F_5)_2GeH_2$ in polymerization of St and VPD are given in Table 2. High relative constants of chain transfer show that these organogermanium compounds are active chain-transfer agents [9]. This fact was used for further postpolymerization of functional PVDP in St.

Table 3. Molecular-weight characteristics of extracted PS

PS	$M_w \times 10^{-4}$	$M_n \times 10^{-4}$	Content, wt %	
			PS	nitrogen in PS
PS-1	4.5	2.5	82	5.5
PS-2	4.4	2.4	56	5
PS-3	4.8	2.7	37	7

Postpolymerization of functional polymers in styrene can be accompanied by formation of PS homopolymer. The latter was removed by extraction in a Soxhlet apparatus in a specially chosen solvent (cyclohexane) in which the homopolymer dissolved and the block copolymer was insoluble. By hot extraction of three polymerization products obtained from functional PVPD samples with the molecular weight of (3.5–0.36) × 10^5, we isolated various amounts of extracted PS. The results are given in Table 3.

The molecular-weight characteristics of the isolated amphiphilic block copolymers and their nitrogen content determined by the Kjeldahl method [10] are given in Table 4. It can be seen that, the larger the length of the PVPD block, the smaller the fraction of the amphiphilic block copolymer, i.e., to obtain a diblock copolymer in a higher yield (>44%), it is necessary to take for post-polymerization the functional prepolymer with a lower block length ($M > 1.1 \times 10^5$), as also indicated by an increase in the molecular weight in the course of the subsequent polymerization.

Table 4. Characteristics of isolated polymers

Functional PVPD		Amphiphilic block copolymer		
sample no.	$M_w \times 10^{-5}$	content, wt %	$M_w \times 10^{-5}$	nitrogen content, wt %
1	3.54	18	2.45	66
2	1.11	44	2.35	65
3	0.36	63	1.06	71

It can be seen from the MWD curves (Fig. 2a) that, for the high-molecular-weight PVPD with MW = 3.5×10^5, the mode shifts toward lower MW values. As the amount of the extracted homopolymer (PS-1) in this case is 82%, it can be assumed that, in the course of postpolymerization, PS homopolymer is formed preferentially, but the terminal functional groups $(C_6F_5)_2GeH$ can also be active centers for the formation of block copolymer molecules (their fraction is about 17%). Formation of the large amount of the homopolymer is due to the fact that the functional groups $(C_6F_5)_2GeH$ occur insight dense coils and approach of the propagating styrene radical to them is hindered.

For the functional PVPD with MW = 1.1×10^5 (Fig. 2b), the MW of the PVPD–PS block copolymer increases by a factor of 2.1 relative to functional PVPD, with the polydispersity parameter remaining unchanged. This fact suggests formation of an amphiphilic block copolymer (content of PS homopolymer in separation by hot extraction was 56%). It should be noted that the MWD curve for the block copolymer is bimodal, which may be due to the occurrence of two mechanisms of macromolecule termination.

For low-molecular-weight functional PVPD with MW = 3.6×10^4 (Fig. 2c), the MWD curve of the block copolymer is shifted toward higher MW (increase by a factor of 3), and the polydispersity parameter p_n increases by a factor of 1.3. The content of extracted PS-3 is 37%. This fact confirms formation of the amphiphilic diblock copolymer.

It should be noted that, despite different lengths of the PVPD block in P(VPD–PS) block copolymers, the content of VPD units in the isolated amphiphilic diblock copolymers is essentially similar, 65–71%.

Thus, we prepared and isolated amphiphilic block copolymers P(VPD-block-PS) with different content of the hydrophilic fragment (65–71 and 5–7 wt %). Since PS is a hydrophobic polymer, it was interesting to study how the presence of PVPD units in the block copolymer affects the surface properties of the films.

The contact angles and the calculated polar and dispersive components of the surface tension and, for comparison, also the data for a mechanical blend consisting of 7% PVPD and 93% PS are given in Tables 5 and 6. Table 6 shows that the surface of the film of the mechanical blend has low surface tension and can be considered as hydrophobic. For PS with low nitrogen content, the surface tension is high, which suggests formation of a PVPD–PS block copolymer rather than

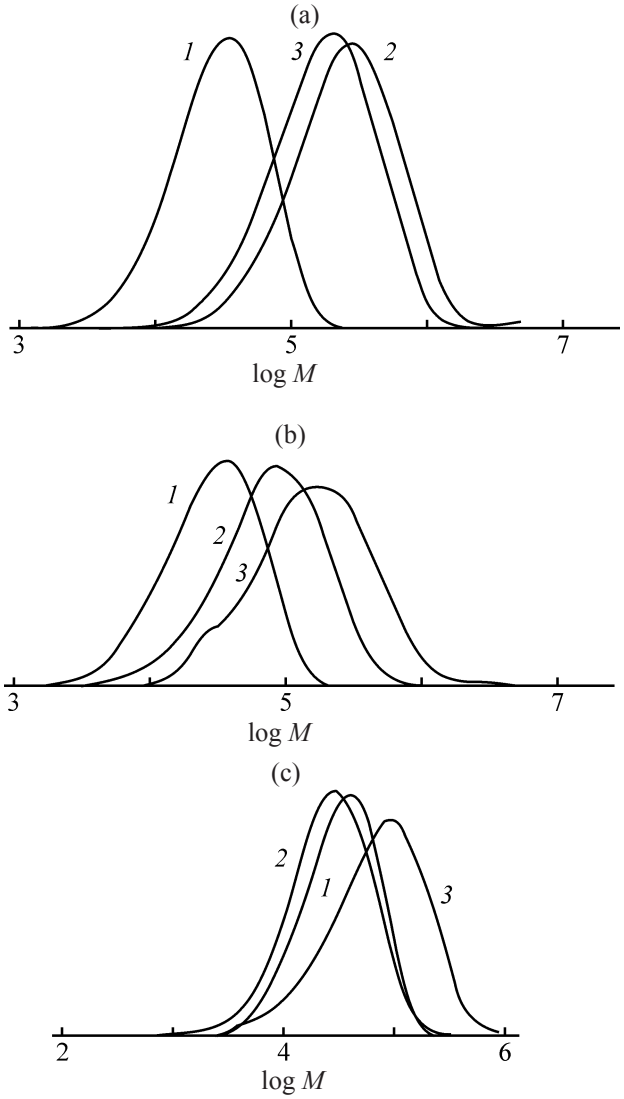


Fig. 2. Gel chromatograms of samples of the (a) first, (b) second, and (c) third series. (M) Molecular weight. (*1*) Extracted PS, (*2*) functional PVPD, and (*3*) P(VPD–PS) block copolymer.

of a blend of the individual polymers. Apparently, hot extraction leads to isolation of not homo-PS but a block copolymer with a small length of the hydrophilic PVPD block. In this case, the decisive role in the polymer films is played by the dispersive component responsible for the intermolecular interaction. In the case of block copolymers with high nitrogen content, the major contribution to the surface tension is made by the polar component.

Analysis of the σ^p and σ^d values obtained suggests that, owing to surface segregation in the film, hydrophilic groups in the molecules of the block copolymer are oriented toward the support (which is also hydrophilic), with hydrophobic PS blocks remaining on the surface. Similar pattern is observed with the mechanical blend,

Table 5. Contact angles of P(VPD–PS)

Sample no.	Content of VPS units, wt %	θ				
		water/water	water/ hexane	water/ heptane	water/ octane	water/ hexadecane
1	5.5	93	116	124	119	125
2	5	104	123	121	125	125
3	7	107	126	121	123	125
PVPD–PS mechanical blend	7	97	127	124	125	124

Table 6. Polar and dispersive components of the surface tension of films of the copolymers and mechanical blend

Sample	Content of VPD units, wt %	σ^d	σ^p	σ
		mJ m^{-2}		
PS-1	5.5	69.08	3.11	72.19
PS-2	5	37.44	2.59	40.03
PS-3	7	26.63	2.48	29.11
PVPD–PS mechanical blend	7	15.22	2.26	17.48
Block copolymer:				
P(PVD–PS)-1	66	21.75	50.28	72.03
P(PVD–PS)-2	65	22.23	50.42	72.66
P(PVD–PS)-3	71	26.21	50.70	76.91

with the principal difference that the surface tension of the blend is low (17.48 mJ m^{-2}), whereas for the block copolymers containing the same amount of PVPD it varies from 29.11 to 72.19 mJ m^{-2}. This difference is due to the fact that in block copolymer molecules the PS and PVPD blocks are linked via $–Ge(C_6F_5)_2$ groups which significantly affects the surface properties of the films. The wetting angle of the films with water also deserves attention. For the extracted polymers $\theta_{adv} > 90°$, whereas for pure PS it is 76°. In the case of block copolymers containing 67–71 wt % PVPD units, water spreads over the surface, which is due to high content of hydrophilic units, as also indicated by high σ (72–77 mJ m^{-2}).

CONCLUSIONS

(1) Organogermanium compounds bis(pentafluorophenyl)germane and tris(pentafluorophenyl)germane are good chain-transfer agents, which opens wide prospects for their use for preparing not only superbranched perfluorinated polyphenylenegermane, but also various diblock copolymers.

(2) A new procedure was suggested for preparing amphiphilic block copolymers with various lengths of the hydrophilic block by postpolymerization of functional polyvinylpyrrolidone in styrene.

(3) Depending on the content of vinylpyrrolidone units in the block copolymer, the isolated polymers have different surface properties. The surface properties of the block copolymer differ from those of the mechanical blend of the same composition.

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