Organometallic ABC-triblock copolymers

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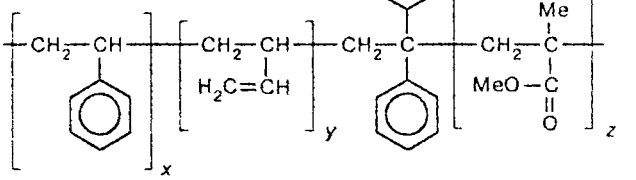
The interaction of Fe and Pd complexes with double bonds of the polybutadiene (PB) block in polystyrene—polybutadiene—poly(methyl methacrylate) block copolymers has been studied. The incorporation of $Fe(CO)_3$ fragments into the PB block was found to result in an increase in its rigidity. The presence of iron or palladium complexes in the PB block affects strongly the morphology of the triblock copolymers.

Key words: organometallic polymers, triblock copolymers, morphology; differential scanning calorimetry; transmission electron microscopy; IR spectra; ^1H NMR spectra.

Several recent publications[1—15] have reported on the synthesis of block copolymers containing compounds or colloids of metals in one of the blocks. The chemical modification of even one of these blocks can affect substantially the mechanical properties of the block copolymers, change the local permeability of the polymeric matrix, or direct the distribution of active centers in the polymeric catalyst. We have previously described[2—5] immobilization of different organometallic compounds in the polybutadiene block of triblock polystyrene—polybutadiene (SBC) block copolymers of the ABA type; however, changes in morphology of block copolymers were not studied.

It is noteworthy that the method for synthesis of Pt and Pd nanoclusters inside microsegregated diblock copolymers has recently been developed.[8] The diblock copolymers were obtained by metathesis with the cycle opening of organometallic complexes derived from norbornene and η^3-1-phenylallyl followed by film casting and reduction of the organometallic complexes with molecular hydrogen.[8] The same authors obtained Au and Ag nanoclusters by the chemical modification of the corresponding precursor (block copolymer) with gold and silver compounds.[6] In these cases, immobilization of metallocomplexes and formation of clusters did not change the morphology of microsegregated blocks. At the same time, in Refs. 12 and 13, a change in the morphology of polystyrene—poly-(2-vinylpyridines) during formation of gold colloids was observed. It was of interest to study immobilization of metallocomplexes in one of the blocks of triblock copolymers of the ABC type, whose morphology is substantially more sensitive to different changes. It can be assumed that, compared to modified diblock block copolymers, triblock metallocomplex ABC copolymers will allow one to monitor more thoroughly the morphology of microdomains.

In this work, we synthesized and studied new metallocomplex polymers obtained by the reactions of iron dodecarbonyl and bis(acetonitrile)palladium dichloride with triblock polystyrene—polybutadiene—poly(methyl methacrylate) (SBM) block copolymers with different lengths of the blocks, due to which these copolymers have various properties.



The x, y, and z values (mole fractions) were 0.42, 0.11, and 0.47, respectively, for copolymer SBM-6; 0.69, 0.07, and 0.24 for copolymer SBM-104; and 0.27, 0.43, and 0.30 for copolymer SBM-41.

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Experimental

IR spectra were obtained on a Bruker IFS 48 instrument in pellets with KBr. Differential scanning calorimetry (DSC) was performed on a Perkin—Elmer DSC 7 instrument. ^{1}H NMR spectra were recorded on a Bruker AC-200 instrument.

Triblock block copolymer of polystyrene (PS), polybutadiene (PB), and poly(methyl methacrylate) (PMMA) were synthesized by anionic polymerization in the presence of lithium alkoxides.[16,17] The copolymers obtained had the following characteristics:

Copolymer	M_n	M_w/M_n	[PS]	[PB]	[PMMA]
			(wt.%)		
SBM-6	225000	1.11	45	6	49
SBM-41	117000	1.09	35	28	37
SBM-104	140000	1.12	72	4	24

Molecular weights were determined by GPC. The polybutadiene block contained mainly 1,2-units, because polymerization was carried out in polar solvent (THF).

The $Fe_3(CO)_{12}$ complex was synthesized from $Fe(CO)_5$ by the known procedure.[18] Bis(acetonitrile)palladium dichloride was prepared according to the previously described procedure.[19] Polybutadiene-1,2 (PB-1,2) was obtained by anionic polymerization in the presence of lithium alkoxides; the PB-1,2 sample contained 86% 1,2-units, M_n = 130000. Polybutadiene-1,4 (PB-1,4) was synthesized in the Branch of the All-Russian Institute of Synthetic Rubber (Voronezh); the PB-1,4 sample contained 34.1% 1,4-*trans*-units, 56.8% 1,4-*cis*-units, and 9.1% 1,2-units, M_n = 150000.

Irontricarbonyl π-complexes immobilized in the PB block were synthesized as described in our previous works.[2,3] The content of iron in the SBM-41 samples (SBM-41-Fe) is presented in Table 1; SBM-6-Fe contained 1.57 wt.% Fe, which corresponds to a degree of complex formation of 51%; PB-1,2-Fe (3.3 wt.% Fe) and PB-1,4-Fe (3.9 wt.% Fe) samples were synthesized according to the previously described procedure.[2]

Palladium-containing SBM were obtained by the ligand exchange reaction between bis(acetonitrile)palladium dichloride and olefinic groups of the polymers.[4,5] Palladium complexes were also immobilized directly on the SBM-6 film. For this purpose, the SBM-6 film (0.07 g) was placed in a solution containing MeOH (14 mL), acetone (6 mL), and bis(acetonitrile)palladium dichloride (0.1 g). This mixture does not dissolve the polymer, but allows the palladium compound to penetrate the polymeric film. After 1-day exposure to the reaction mixture at ~20 °C, the film was washed in a MeOH—acetone (7 : 3) mixture for several hours and dried in a vacuum desiccator. Palladium-containing SBM-6 (SBM-6-Pd) is soluble in $CHCl_3$ and can be reprecipitated from Pr^iOH. The dried polymer contained 0.4 wt.% Pd, which corresponds to a degree of complex formation of 3.4 mol.%.

Samples for transmission electron microscopy (TEM) study were casted from solutions of polymers in $CHCl_3$ and dried slowly for several weeks in air and then at 160 °C. TEM analysis was performed with ultrathin sections obtained by a microtome with a diamond knife. To impart contrast to the PB block, OsO_4 was sputtered on sections of all samples. Microphotographs were obtained on a JEOL 100 CX transmission electron microscope (100 kV).

Table 1. Differential scanning calorimetry data for SBM samples

Block copolymer	[Metal] (wt.%)	T_g/°C PB	PS	PMMA	T_{endo} /°C
SBM-41	—	−12.1	105.1	133.0	—
SBM-41-Fe-1	1.32	−1.9	103.2	130.0	144.8
SBM-41-Fe-2	3.34	9.1	86.7	—	127.0
					145.1
SBM-41-Fe-3	4.20	42.1	78.0	—	108.3
SBM-41-Fe-4	6.10	64.6	84.6	—	118.3
SBM-41-Pd-1	2.62	—	—	—	124.2
SBM-41-Pd-2	11.50	—	81.8	—	135.3

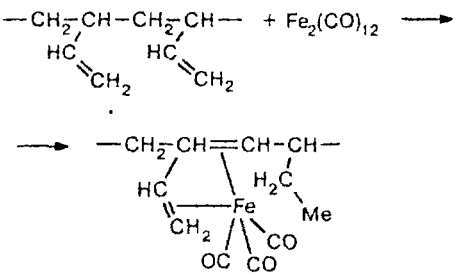
Results and Discussion

The reactions of SBM-104, SBM-6, and SBM-41 with $Fe_3(CO)_{12}$ and bis(acetonitrile)palladium dichloride $(MeCN)_2PdCl_2$ were studied. PS and PMMA were shown not to react with these metal compounds under experimental conditions; hence, the interaction with the Fe and Pd complexes occurs only in the PB block.

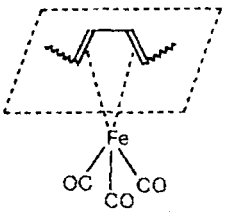
Irontricarbonyl π-complexes with SMB block copolymers and their properties

The compositions of the iron-containing copolymers based on SBM-41 are presented in Table 1. It can be seen that an increase in the content of $Fe_3(CO)_{12}$ in the reaction mixture results in an increase in the degree of complex formation up to 81 mol.% at the molar ratio PB : $Fe_3(CO)_{12}$ = 1 : 1. The IR spectra of ironcarbonyl SBM exhibit two intense bands at 1964 and 2032 cm^{-1} and a shoulder at 1956 cm^{-1} typical of $Fe(CO)_3$ fragments.[20] The formation of diene—$Fe(CO)_3$ π-complexes in the reactions of low-molecular-weight olefins with $Fe(CO)_{12}$ has been proved previously.[21] In the ^{1}H NMR spectra of the Fe-containing polymers, the signals of protons at the double bond (δ 4.94 and 5.32) have lower relative integral intensities. Although the appearance of new signals shifted upfield should be expected for coordination of Fe atoms, complexity of the spectrum of SBM does not allow their identification. To elucidate this problem, we carried out control experiments: similar complexes immobilized on PB-1,2 were synthesized and studied. The IR spectrum of PB-1,2-Fe exhibits the same changes as those in the IR spectrum of SBM-Fe. In the ^{1}H NMR spectrum of PB-1,2-Fe, the intensities of the characteristic signals of protons at the double bonds decrease, and a new signal with δ 1.46 appears, which can be assigned to protons of the double bonds involved in complex formation. This noticeable shift of the ^{1}H NMR signal indicates a strong π-interaction. Similarity of the IR and NMR spectra of the Fe-containing polymers based on PB-1,2 and PB-1,4 suggests the same type of binding of the ironcarbonyl fragments with these polymeric matrices. The complex formation is accompanied by migration of the double bonds and formation of irontricarbonyl complexes with the conjugated diene fragment (Scheme 1), as discussed previously.[2]

Scheme 1

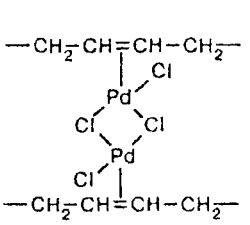


Metal-containing polymers based on SBM-41 were studied by DSC (see Table 1). As can be seen from the data in Table 1, an increase in the degree of complex formation in the SBM-41-Fe samples results in an increase in the glass transition temperature (T_g) of the polybutadiene block from −12.1 °C in the starting SBM to 64.6 °C for the polymer containing 6.10 wt.% Fe. At the same time, T_g of the PS phase decreases. The glass transition temperature of the PMMA block was not determined because of overlapping of the peak of this transition and a weak endothermic peak at 110—144 °C. The latter could be assigned to the decomposition of the metallocomplexes, but we have previously established[2,22] that the irontricarbonyl complexes in the PB-1,4 block lose CO only at $T \approx 170$ °C. In addition, the study of the decomposition of the SBM-41-Fe-3 sample by IR spectroscopy and DTA shows that the irontricarbonyl fragments in SBM decompose at 170—175 °C. Thus, the nature of the weak endothermic peaks on the DSC curves for the SBM-41-Fe samples remains unclear. Perhaps, they appear as a result of pseudo-melting of supramolecular structures formed due to the interaction of polar groups of $Fe(CO)_3$ at the interfaces. Some decrease in the T_g value of the PS block in the block copolymers can be explained by disintegration (loosening) of this block due to complex formation in the adjacent PB block. We believe that the considerable increase in the glass transition temperature of the PB block after complex formation with $Fe_3(CO)_{12}$ is related to an increase in the rigidity of the macromolecules due to the appearance of planar diene fragments in the polymer chain, as is shown below.[23]

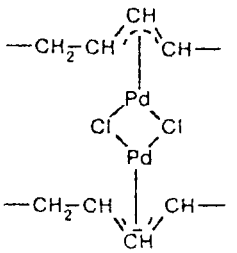


Palladium-containing SBM

According to the data of our earlier publications,[4,5] the interaction of the double bonds of the PB-1,4-block with $(MeCN)_2PdCl_2$ results in the formation of π-olefinic and π-allylic complexes (see below) that are formed by both intramolecular (between units of the same chain) and intermolecular (between different chains) interactions. The authors of Ref. 24 showed that dimeric complexes are mainly formed in the case of low-molecular-weight olefins. The precipitated and dried Pd-containing polymers based on SBM-41 (SBM-41-Pd) are insoluble, which additionally confirms the formation of intermolecular bonds. The data in Table 1 show that even at a low degree of complex formation (2.62 wt.% Pd), the PB phase has no glass transition temperature. A similar phenomenon for SBM-41-Pd can be explained by the appearance of intermolecular linkages due to complex formation.



π-Olefinic complexes



π-Allylic complexes

In the case of SBM with a low content of the PB block (4 and 6 wt.%), the SBM-104-Pd and SBM-6-Pd copolymers remain soluble even after precipitation and drying. When the length of the PB block decreases, the decrease in probability of formation of intermolecular complexes should be expected; however, in sufficiently concentrated solutions used under experimental conditions, the formation of intermolecular linkages is still possible. In this case, the solubility of SBM-104-Pd and SBM-6-Pd is most likely explained by the formation of micelle-like aggregates due to complex formation in the PB block similar to that observed previously[25] for the diblock polystyrene—polybutadiene block copolymer with 15.5 wt.% PB.

The IR spectrum of the SBM-41 sample contains absorption bands at 910 and 994 cm^{-1}, which can be assigned to vibrations of C—H of the vinyl group $CH=CH_2$, and a weak band at 970 cm^{-1} related to vibrations of C—H in *trans*-1,4-olefins. A band at 1638 cm^{-1} is observed in the region of vibrations of C=C. The IR spectrum of the SBM-41-Pd sample exhibits a significant weakening of the intensities of the bands at 994, 910, and 1638 cm^{-1}, which suggests complex formation with vinyl groups. The band at 1638 cm^{-1} (C=C) should be shifted to the low-frequency region due to complex formation; however, none these changes were observed, probably due to overlapping with other bands in the region of 1500—1400 cm^{-1}.

The data of elemental analysis presented in Table 2 show that the molar ratio Pd : Cl in the polymers depends on the molar ratio of the starting reagents. When the molar ratio (PB unit) : $(MeCN)_2PdCl_2$ increases, the Pd : Cl value also increases. The molar ratio Pd : Cl characterizes the type of Pd complex: it is

Table 2. Elemental analysis data for Pd-containing SBM

Block copolymer	PB unit * $(MeCN)_2PdCl_2$	[Pd] (wt.%)	[Cl] (wt.%)	Pd : Cl*
SBM-41-Pd-1	1.00 : 0.06	2.62	1.03	1.00 : 1.16
SBM-41-Pd-3	1.00 : 0.08	2.95	1.14	1.00 : 1.15
SBM-41-Pd-4	1.00 : 0.30	7.04	3.43	1.00 : 1.42
SBM-104-Pd-1	1.00 : 0.30	0.92	0.50	1.00 : 1.60

* Molar ratio.

1 : 1 for the π-allylic complex, while in the case of the π-olefinic complex, Pd : Cl = 1 : 2. According to the results of our previous studies of the PS—PB block copolymer,[4] the polymer structure depends substantially on the solvent used: for example, in CH_2Cl_2 the Pd : Cl molar ratio reaches 1.0 : 1.6, which indicates predominance of π-olefinic structures. In the case of SBM, π-allylic structures predominate for a low degree of complex formation. It has previously been shown that polar compounds (for example, EtOH) favor the formation of π-allylic complexes from π-olefinic complexes. In the case of SBM, it can be assumed that the polar groups in the PMMA block exert a similar effect, which is more evident when the fraction of Pd complexes is low.

Palladium complexes were immobilized directly in films (see Experimental) to retain to a maximum extent the structure of the starting block copolymer. This was possible because the ligand exchange reaction occurs at room temperature. Complex formation was found to occur readily in a film placed in a solution of bis(acetonitrile)palladium dichloride in the MeOH—acetone mixture; the SBM-6-Pd thus obtained is soluble in toluene and CH_2Cl_2.

Morphology of metal-containing SBM

The SBM-6 film is known[26] to contain lamellar structures of the PS and PMMA blocks, and spheres of the PB block are localized at their boundaries. The electron microphotograph of the SBM-6-Fe sample stained by OsO_4 is presented in Fig. 1. Evidently, the PS blocks do not form lamellas, but form cylindrical structures covered by small spherical objects, which can be presented as a modified PB block. This morphology is similar to that observed[24] for the hydrogenated SBM-6, where rings of the central block surround cylinders formed by the PS block. Since the introduction of $Fe(CO)_3$ complexes favors an increase in the rigidity of the PB chain, this change is also similar to an increase in the chain rigidity after hydrogenation of double bonds.

In the case of the SBM-6-Pd copolymer, a quite different, highly ordered morphology was observed (Fig. 2). This morphology seems to be continuous with respect to both the PS and PMMA blocks, *i.e.*, the structure is gyroidal with PB microdomains arranged at the interface.

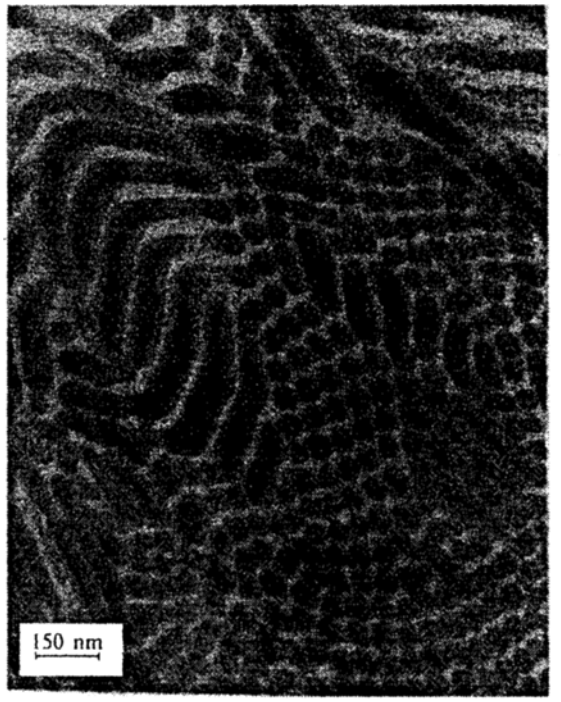


Fig. 1. Microphotograph of irontricarbonyl complex SBM-6-Fe (hereinafter in Fig. 2, contrast OsO_4).

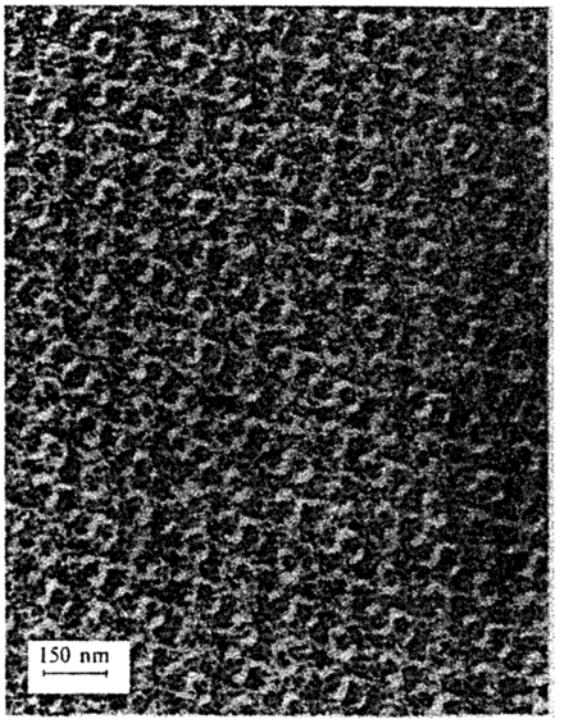


Fig. 2. Microphotograph of Pd-containing copolymer SBM-6-Pd.

Thus, immobilization of the Fe and Pd complexes in the PB block of the polystyrene—polybutadiene—poly(methyl methacrylate) block copolymer changes the properties of the PB phase itself, increasing the rigidity of the chain or resulting in cross-linking of PB, and affects the morphology of the whole system as well.

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