A Novel Method for Preparation of Block Copolymers. Selective Multisite Functionalization of Block Copolymers *via* Metalation and Reaction with Electrophiles

Lubomír Lochmann,* Miroslav Janata, Petr Holler, Zdeněk Tuzar, and Pavel Kratochvíl

Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic, 162 06 Prague 6, Czech Republic

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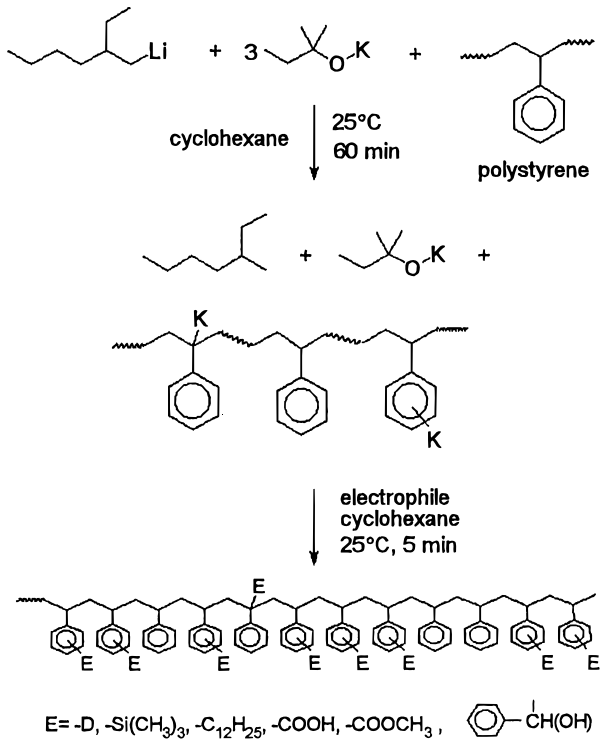
ABSTRACT: Nonpolar block copolymers may be selectively multisite substituted in only one block with various functional groups, like carboxyl, hydroxy, or alkyl groups. In this way, block copolymers with unusual structures are easily accessible. The degree of substitution in the functionalized blocks may be controlled in a wide range and copolymers with various concentrations of substituents arise. The procedure of functionalization involves selective multisite metalation of the block copolymer by Superbase, made from 3-(lithiomethyl)heptane and potassium *tert*-pentoxide, and subsequent reaction of the metalated copolymer with an electrophile. Hydrophilic−hydrophobic block copolymers prepared by this method were investigated with regard to formation of micellar solutions in aqueous media.

Introduction

Our interest in functionalized polymers led us to explore new approaches to chemical modification of polymers. Recently developed Superbases of the second generation (SB), prepared from 3-(lithiomethyl)heptane and an excess of potassium *tert*-pentoxide,[1,2] appeared to be useful for this purpose,[3−8] as shown for the functionalization of polystyrene (PS) in Scheme 1.[4,7] This procedure involves two steps: (i) metalation of PS by SB, resulting in a multisite metalated PS, and (ii) reaction of the metalated intermediate with an electrophile, giving rise to PS multisite substituted with functional groups. Due to the high reactivity of the metalated intermediate, the choice of electrophiles for step ii is broad (cf. Scheme 1), and thus, PS as well as other polymers substituted with various functional groups can be easily prepared. The degree of substitution, i.e. the ratio of the number of functionalized monomer units related to the number of all monomer units susceptible to metalation, may be varied in a wide range, typically between 0.1 and 1. Some polymers were metalated previously by other bases, e.g. PS or PS copolymers by butyllithium in the presence of tetramethylethylenediamine[9,10] or polybutadiene by butyllithium and alkali metal alkoxides.[11] The SB described above seems to be superior to these bases because of higher reactivity and efficiency. Another modification of block copolymers employing the Friedel−Crafts chemistry was published recently.[12]

Several methods for preparation of block copolymers have been described so far. Most of them are based on ionic polymerization or GTP mechanisms and this imposes inherently some limitations in the structure of the monomers used. Thus, not all types of block copolymers are easily accessible. This paper reports on functionalization of block copolymers using a novel method mentioned above and giving rise to new block copolymers, especially of the hydrophilic−hydrophobic type. The ability of these functionalized block copolymers to form micellar solutions in aqueous media was also investigated.

Scheme 1



Experimental Section

Materials. Crystalline potassium *tert*-pentoxide was prepared by reaction of potassium with *tert*-pentyl alcohol in a heptane−tetrahydrofuran (THF) mixture (2:1 v/v). 3-(Lithiomethyl)heptane was prepared by reaction of 3-(chloromethyl)-heptane with Li powder (containing 2% Na) in cyclohexane at 40 °C. The purity of both of these compounds, especially of the alkoxide, is of substantial importance for the process of (co)polymer metalation. *tert*-Pentyl alcohol, 3-(chloromethyl)-heptane, ethyl acetate, and chlorotrimethylsilane were distilled with calcium hydride. Cyclohexane and THF were distilled prior to use with dibutylmagnesium and sodium anthracenide, respectively. A diethyl ether solution of diazomethane was prepared from Diazald (Aldrich). Polyformaldehyde (FMC Corp.) was dried over phosphorus pentoxide *in vacuo* and stored under argon atmosphere in the dark. All operations with the organometallics were carried out under an atmosphere of purified argon.

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Copolymers Used for Functionalization. (i) Polystyrene-*block*-polyisoprene, in which the polyisoprene block was fully hydrogenated after polymerization [PS-*b*-PIH; i.e. SHELLVIS SV-50, Shell Co., M_w(SLS) = 95 000, M_w(SEC) = 130 000, M_n(SEC) = 124 000, M_w/M_n = 1.05, w_{PS} = 0.42], (ii) Polystyrene-*block*-polybutadiene-*block*-polystyrene, in which the polybutadiene block was similarly hydrogenated [PS-*b*-PBH-*b*-PS; i.e. KRATON G-1650, Shell Co., M_w(SLS) = 74 000, M_w(SEC) = 114 000, M_n(SEC) = 107 000, M_w/M_n = 1.07, w_{PS} = 0.34], and (iii) poly(4-methylstyrene)-*block*-polystyrene (PMS-*b*-PS), prepared by anionic polymerization [M_n(SEC) = 155 000, M_w/M_n = 1.02, w_{PMS} = 0.53] were used. All copolymers were dried *in vacuo* and stored under argon before use. Static light scattering (SLS) and size exclusion chromatography (SEC) were used for determination of molecular weights.

Multisite Substitution of Copolymers. (a) Metalation. A cyclohexane solution of 3-(lithiomethyl)heptane (0.015 mol) was added to a stirred solution of potassium *tert*-pentoxide in heptane (0.045 mol) at room temperature. After 2 min the mixture was cooled to 0 °C and a solution of a copolymer in cyclohexane was added [containing 0.01 mol of monomer units susceptible to metalation; the final concentration of these units in the reaction mixture was adjusted to 0.050 mol/L with cyclohexane (or benzene in the case of the copolymer PMS-*b*-PS)]. The reaction mixture was then stirred for 3 h at 0 °C. An intensive red or red-brown color developed mostly within a few minutes. The amounts of 3-(lithiomethyl)heptane and the alkoxide are appropriately adjusted for copolymers substituted to lower degrees.

(b) Reaction of the Metalated Copolymer with Various Electrophiles. (i) a sample of the reaction mixture was added to a 2-fold molar amount of chlorotrimethylsilane in THF (based on the content of all alkali metal compounds). After 15 min the trimethylsilylated polymer was isolated by precipitation in methanol. (ii) The metalation mixture was slowly added with stirring to a mixture of solid carbon dioxide in THF. The alkali salts were converted into free carboxylic acids by reaction with a large excess of chlorotrimethylsilane (2 h of reflux) and subsequent hydrolysis of the trimethylsilyl ester with water (2 h of boiling). In this way, complete liberation of all carboxylic groups was ensured. The multisite carboxylated copolymer was purified by precipitation from THF solution in water followed by a reprecipitation in ethyl acetate. (iii) Solid polyformaldehyde was added to the metalation mixture and stirred at room temperature until discoloration occurred (ca. 30 min). A slight excess of acetic acid was then added and the hydroxylated copolymer was isolated by precipitation in water and reprecipitated in ethyl acetate.

Analytical Methods. Degree of substitution of copolymers, defined as the ratio of the number of substituted monomer units to the number of all monomer units susceptible to metalation, was determined (i) by ^{1}H NMR spectroscopy, trioxane (for trimethylsilylated copolymers) and hexamethyldisiloxane (for methyl esters and hydroxy derivatives) being used as internal standards in quantitative analyses; (ii) by alkalimetric titration (for polyacids) in methanol−water−THF mixture, with phenolphthalein as indicator; and (iii) by elemental analysis (for all oxygen-containing substituents), according to the oxygen contents.

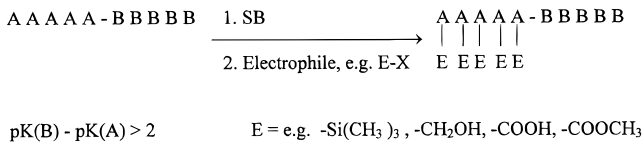
Physical Methods. (i) ^{1}H NMR spectra of the substituted copolymers were measured with a Brucker AFC 300 spectrometer (300.1 MHz) in deuteriochloroform solutions (the hydroxylated copolymer in perdeuterated THF). (ii) Molecular parameters of substituted copolymers were determined using SEC with RI and UV detection. A 600 × 7.5 mm PSS 10^{4}A column (PSS GmbH Mainz, Germany) packed with 5 μm sorbent and THF as a mobile phase were used. Calibration was carried out with polystyrene standards (Polymer Laboratories), and chromatographic data were processed using the DataMonitor integration system (Watrex, Prague). (iii) Molecular weights of block copolymers and their micelles were also measured by SLS with a Sofica goniometer, equipped with a He−Ne laser. Refractive index increments (dn/dc) were measured with a Brice-Phoenix differential refractometer. When an aqueous solution of LiCl was used as a solvent, dn/dc was measured after establishment of osmotic equilibrium between the copolymer solution and solvent.[13] Hydrodynamic radii of micelles, R_H, were measured by dynamic light scattering (DLS) with an LV-5 000 correlator and evaluated as described previously.[14]

Results

A. Selective substitution of block copolymers. Block copolymers of nonpolar monomers may be functionalized similarly to corresponding homopolymers, i.e. by a procedure involving their metalation and reaction with electrophiles (cf. Scheme 1 and refs 3−7).

An especially useful situation occurs with copolymers composed of blocks with monomer units A and B, differing in C−H acidity by two or more pK units. In such a case it is possible to introduce the functional groups selectively into the more acidic units only. Consequently, new block copolymers may be prepared according to Scheme 2.

Scheme 2



The procedure outlined above was tested with the following block copolymers: (i) poly(4-methylstyrene)-*block*-polystyrene (PMS-*b*-PS); (ii) polystyrene-*block*-polyisoprene, where the original polyisoprene block was fully hydrogenated (PS-*b*-PIH); and (iii) polystyrene-*block*-polybutadiene-*block*-polystyrene, with similarly hydrogenated polybutadiene blocks (PS-*b*-PBH-*b*-PS), the last two being products of the Shell Co. Properties of these starting copolymers are shown in the Experimental Section.

It was found that, under specific conditions developed individually for each copolymer, only one type of block was selectively substituted, while the other type of block remained virtually untouched. In the first copolymer, the poly(4-methylstyrene) block is metalated preferably, as the methyl group is the most reactive site in the copolymer. The difference in acidity of hydrogens of the methyl groups bonded on aromatic rings and aromatic hydrogens is relatively small, and therefore, this copolymer is a sensitive proof of the selectivity of the metalation. In the other copolymers, both the benzylic and aromatic hydrogens are more acidic than the aliphatic ones, and thus, only the polystyrene blocks are substituted. It was shown earlier for polystyrene[7] that metalation of aromatic sites is preferred to benzylic ones, although the latter hydrogens should be more acidic. Their kinetic reactivity is obviously decreased due to steric reasons.

The yields of functionalized block copolymers are mostly high and the selectivity in substitution of the blocks is very good, the degree of substitution of the less reactive block being below 1% (Table 1). The degree of substitution of the more reactive blocks (A) may be varied similarly to the substitution of homopolymers: block copolymers with nearly all A units substituted as well as copolymers with A blocks substituted to a low degree may be prepared by varying the [SB]/[A] ratio. Some excess of SB is usually necessary to achieve the required degree of substitution. Under such conditions, nearly all A monomer units could be metalated and substituted.

Functional groups $Si(CH_3)_3$, CH_2OH, and COOH have been introduced into block copolymers so far, as repre-

Table 1. Selective Substitution of A−B or A−B−A Type Block Copolymers ($pK_A < pK_B$) via Metalation by Superbase and Subsequent Reaction with Electrophiles

substituted block copolymer[a]	Superbase/A units molar ratio	electrophile	degree of substitution			molecular weight[d] × 10^{-3}	
			block A[b]	block B[b]	total[c]	M_n	M_w/M_n
[PS-*b*-PIH]-[$Si(CH_3)_3$]$_n$	0.55	$(CH_3)_3SiCl$	0.34	<0.05		131	1.05
[PS-*b*-PIH]-[$Si(CH_3)_3$]$_n$	1.7	$(CH_3)_3SiCl$	0.95			133	1.10
[PS-*b*-PIH]-[COOH]$_n$	0.55	CO_2			0.38, 0.35[e]		
[PS-*b*-PIH]-[COOH]$_n$	1.7	CO_2			0.95, 0.9[e]		
[PS-*b*-PIH]-[$COOCH_3$]$_n$	0.55	(1) CO_2, (2) CH_2N_2	0.31	<0.05		131	1.06
[PS-*b*-PIH]-[$COOCH_3$]$_n$	1.7	(1) CO_2, (2) CH_2N_2	0.93		0.91	128	1.07
[PS-*b*-PIH]-[CH_2OH]$_n$	1.7	$[CH_2\text{-}O]_x$	0.70		0.80	346	*f*
[PMS-*b*-PS]-[$Si(CH_3)_3$]$_n$	2	$(CH_3)_3SiCl$	0.94	<0.01		167	1.07
[PMS-*b*-PS]-[COOH]$_n$	2	CO_2			1.07, 0.9[e]		
[PMS-*b*-PS]-[$COOCH_3$]$_n$	2	(1) CO_2, (2) CH_2N_2	>0.95	<0.01	1.01	156	1.21
[PS-*b*-PBH-*b*-PS]-[$Si(CH_3)_3$]$_n$	1.5	$(CH_3)_3SiCl$	0.83			106	1.07
[PS-*b*-PBH-*b*-PS]-[COOH]$_n$	1.5	CO_2			1.1, 0.94[e]		
[PS-*b*-PBH-*b*-PS]-[$COOCH_3$]$_n$	1.5	(1) CO_2, (2) CH_2N_2	0.90		0.98	101	1.07

[a] For symbols, see the Experimental Section. [b] By ^{1}H NMR. [c] From elemental analysis data. [d] By SEC (polystyrene calibration). [e] By alkalimetric titration [f] Polymodal MWD.

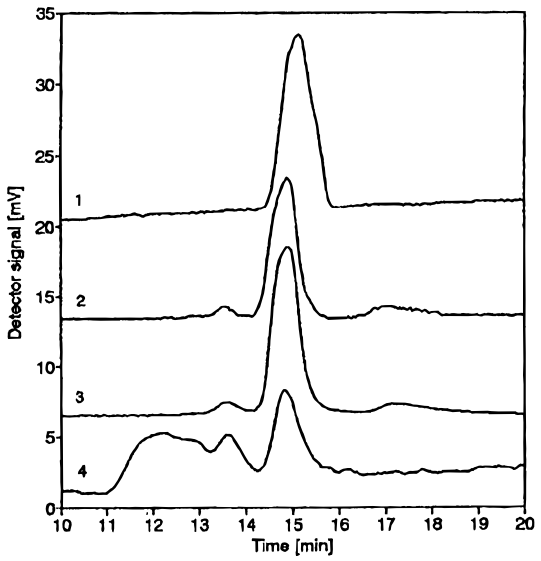


Figure 1. SEC eluograms of PS-*b*-PIH and of its highly functionalized derivatives (cf. Table 1). PS-*b*-PIH: (1) unsubstituted and (2) substituted with (2) trimethylsilyl groups, (3) methoxycarbonyl groups, and (4) hydroxymethyl groups.

sentatives of substituents of different polarity. In these substitutions, trimethylchlorosilane, polyformaldehyde, and solid carbon dioxide were used as electrophiles. Methyl esters of carboxylated polymers were prepared for analytical purposes by esterification using diazomethane. The choice of electrophiles for the reaction is wide, and blocks substituted with various functionalities are often easily accessible in this way.

Molecular weights (MW) and molecular weight distribution (MWD) of the substituted block copolymers were determined by SEC, and the results are shown in Table 1. It appeared that MW's of substituted copolymers are in many cases close to the expected value. The slight broadening of MWD, observed after substitution in most cases, is caused by side reactions, like polymer chain splitting or coupling. The extent of MWD broadening depends on the degree of substitution of the copolymer as well as on the type of the substituent introduced. Usually a small amount of copolymers with higher and lower MW than that of the expected product are found in eluograms, as shown in Figure 1 for typical copolymers PS-*b*-PIH substituted with various group. Copolymers substituted to a higher degree exhibit a broader MWD than those substituted to a lower degree, which do not differ very much from the MWD of the parent block copolymer. Regarding the electrophile, the smallest MWD broadening was observed in the reaction of the metalated copolymers with trimethylchlorosilane, and therefore, this MWD was regarded as characteristic of its broadening taking place during metalation (Figure 1). In reactions of the metalated copolymers with carbon dioxide or polyformaldehyde, additional MWD broadening was observed, due to some side reactions like copolymer chain coupling through carboxylic groups.[15]

Reactions of multisite metalated copolymers with aldehydes, although giving rise to the expected hydroxylated copolymers in the following cases need some comments: (i) In the reaction of the metalated PS-*b*-PIH with benzaldehyde, only a low degree of substitution with hydroxy groups was reached. This could be due to other side reactions of the metalated copolymer. In this way, the number of organometallic bonds available for the reaction with the electrophile might have been reduced.

(ii) On the other hand, the product of reaction of metalated PS-*b*-PIH with polyformaldehyde exhibited a high content of $PhCH_2OH$ groups according to the ^{1}H NMR spectra and elemental analysis (Table 1). However, its MW and MWD were much higher than expected (Figure 1d). This product became insoluble in THF after a few weeks at room temperature. Obviously, a transformation of the product took place during this time, probably due to network formation through multiple aggregation bonds. Another explanation for the high molecular weight values of this product could be linking of two or more hydroxylated macromolecules through acetal formation (cf. ref 16).

B. Salts of Highly Carboxylated PS-*b*-PIH. Even highly carboxylated PS-*b*-PIH is insoluble in water. In order to enhance the hydrophilic character of the carboxylated blocks, the following salts of this polyacid were prepared and isolated: lithium, potassium, ammonium, (2-hydroxyethyl)ammonium, and tris(2-hydroxyethyl)ammonium salts. Of these salts, the tris(2-hydroxyethyl)ammonium salt exhibited the highest dispersability, giving a 1% solution in 1:1 (v/v) aqueous THF. The behavior of some of these salts was confusing: freshly isolated tris(2-hydroxyethyl)ammonium salt was soluble in aqueous THF to the extent mentioned above; however, after the solid salt stood for a few days at room temperature, an almost insoluble compound was obtained. On the other hand, solution of this salt in 1:1 aqueous THF prepared from the components without isolation of the salt was stable for several

months without precipitation.

C. Micellar Solution of Multisite-Carboxylated Copolymer PS-*b*-PIH. A solution of the tris(2-hydroxyethyl)ammonium salt of the multisite carboxylated block copolymer PS-*b*-PIH (Table 1) ($c = 0.0100$ g/mL) in tetrahydrofuran−water mixture (1:1 v/v) was diluted with an 0.1 M aqueous solution of LiCl to make the resulting solution 10 vol % in THF. The solution was then dialyzed six times against a 10-fold excess of a 0.1 M solution of LiCl in water. In this way, a micellar solution of the Li salt of this copolymer in water was obtained. SLS data for these solutions at five concentrations ($c_{max} = 1.66 \times 10^{-3}$ g/mL) provided the molecular weight of micelles as $M_w = 6.8 \times 10^6$. The procedure was described in ref 17. DLS from the same solutions gave $R_H = 31$ nm and a very low polydispersity. It can be concluded that the solutions contained uniform micelles with ca. 70 macromolecules per micelle.

Conclusions

Using the method described, nonpolar block copolymers can be selectively substituted in one type of blocks with various functional groups, like alkyl, carboxyl, or hydroxy groups. Thus, novel block copolymers can be easily prepared. The choice of functional groups for substitution is broad, and block copolymers with unusual structures are accessible. The degree of substitution in functionalized blocks can be controlled in a wide range, and copolymers with blocks substituted to a low degree or almost completely arise. Functionalized block copolymers may find wide use, e.g. as compatibilizers in polymer blends, reactive polymers for synthesis of cross-linked polymers, polymeric reagents in organic synthesis, or for special purposes like surface active materials for preparation of micellar solutions or selective membranes.

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References and Notes

(1) Lochmann, L.; Trekoval, J. *J. Organometal. Chem.* **1987**, *1*, 326.
(2) Lochmann, L.; Petránek, J. *Tetrahedron Lett.* **1991**, *32*, 1483.
(3) Lochmann, L.; Wooley, K. L.; Ivanova, P. T.; Fréchet, J. M. J. *J. Am. Chem. Soc.* **1993**, *115*, 7043.
(4) Lochmann, L.; Fréchet, J. M. J. *Polym. Prepr.* **1993**, *34 (2)*, 588.
(5) Lochmann, L.; Fréchet, J. M. J.; Wooley, K. L.; Šmigol, V. *Polym. Mat. Sci. Eng.* **1993**, *69*, 426.
(6) Fréchet, J. M. J.; Lochmann, L.; Šmigol, V.; Švec, F. *J. Chromatogr. A*, **1994**, *667*, 284.
(7) Lochmann, L.; Fréchet, J. M. J. *Macromolecules* **1996**, *29*, 1767.
(8) Lochmann, L.; Šmigol, V.; Švec, F.; Fréchet, J. M. J. *Macromolecules*, submitted.
(9) Catala, J. M.; Clouet, G.; Brossas, J. *Eur. Polym. J.* **1983**, *19*, 213.
(10) Beinert, G. J.; Zilliox, J. G.; Herz, J. E. *Makromol. Chem.* **1993**, *194*, 3183.
(11) Halasa, A. F.; Mitchell, G. B.; Stayer, M.; Tate, D. P.; Oberster, A. E.; Koch, R. W. *J. Polym. Sci., Polym. Chem. Ed.* **1976**, *14*, 497.
(12) Lu Liu; Ming Jiang *Macromolecules* **1995**, *28*, 8702.
(13) Tuzar, Z.; Kratochvíl, P. *Collect. Czech. Chem. Commun.* **1967**, *32*, 3358.
(14) Tuzar, Z.; Kratochvíl, P.; Procházka, K.; Munk, P. *Collect. Czech. Chem. Commun.* **1993**, *58*, 2362.
(15) Quirk, R. P.; Chen, W.-C. *Makromol. Chem.* **1982**, *183*, 2071.
(16) Gilman H.; Catlin W. E. In *Organic Synthesis*, 2nd ed.; J. Wiley, New York, 1956; Collect. Vol. I, p 188, Note 8.
(17) Tuzar, Z.; Webber, S. E.; Ramireddi, C.; Munk, P. *Polym. Prepr.* **1991**, *32 (1)*, 525.

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