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Novel diblock copolymers containing bidentate phosphine and phosphine oxide ligands

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Abstract

Novel block copolymers were synthesised by a two-step chemical modification of polystyrene–polybutadiene block copolymer (PS-b-PB). Such a modification includes hydrobromination or hydrosilylation of initial block copolymer and subsequent interaction of precursor with bidentate phosphine or phosphine oxide compounds. For interaction with the polymers, corresponding bidentate compounds were synthesised, which contained different amounts of carbon and silicon atoms between the phosphorus atoms. As both hydrobromination and hydrosilylation do not touch aromatic rings of polystyrene block, modification occurs solely in polybutadiene block. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Polymers with bidentate phosphine ligands; Hydrobromination; Hydrosilylation

1. Introduction

Organophosphorus compounds draw a stable and extensive interest because of their widespread use in coordination chemistry and catalysis. The soft-base character of the phosphorus centre combined with its ability to behave as an electron acceptor in relation to π-back donation results in the formation of a vast range of complexes with transition elements, and in the stabilisation of metal atoms in low formal oxidation states. In particular, an introduction of bifunctionality as in the α,ω-bis(phosphino)alkanes $PPh_2(CH_2)_nPPh_2$, can thus provide a way of bridging between two metal centres when $n = 1$ or chelating at a single metal atom for $n = 2$ or higher [1,2]. Compared to monodentate ligands with comparable donor groups, a bidentate ligand can simultaneously provide more thorough control on the coordination number [3] and increased basicity at the metal [4].

Organometallic polymers and polymeric materials with metal nanoparticles are supposed to be potential catalysts for many organic reactions because they might combine the advantages of both homogeneous and heterogeneous catalysts: high activity and selectivity which are found in homogeneous catalysis with processability which is inherent to heterogeneous processes [5–7]. Recently, we have described the synthesis of Pd-, Rh-, and Pt-containing polymers derived from polystyrene–polybutadiene block copolymers of various structures [8], where π-complexes are formed as a result of interaction with double bonds of polybutadiene block. In this way, metal complexes were located in one block of diblock copolymer. Similar modification within microphase-separated diblock copolymers has been carried out by Cohen and Schrock using ring-opening metathesis polymerisation of nonbornene-derived organometallic complexes and η^3-1-phenylallyl. Pd, Pt, Au, and Ag nanoclusters were prepared through chemical modification of such precursor diblock copolymers by corresponding compounds [9,10]. Saito et al. studied the complexation of poly-2-vinylpyridine block of polystyrene-poly-2-vinylpyridine (PS-b-P2VP) with Ag compounds by soaking of a partly crosslinked film (for preserving the initial morphology), and consequent reduction of silver from AgI [11]. Recently, a series of amphiphilic block copolymers with different active groups was synthesised by Antonietti and co-workers using polystyrene–polybutadiene (PS-b-PB) diblock copolymer by the chemical modification of polybutadiene (PB) block through epoxidation [12,13]. Later, such a block copolymer was converted into at least five different structures including diphenylphosphinite containing derivative.

As polymers with bidentate phosphine ligands provide wide opportunities for the subsequent metal complex formation, we searched for the way to attach the bidentate

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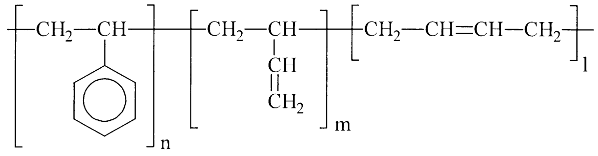


Scheme 1.

phosphine ligands of a different structure to the diblock copolymer, PS-b-PB, modifying only the PB block that would also result in a selective location of the phosphine ligands and metal complexes in one block. In this article, we have focused on the immobilisation of the bidentate phosphine groups in the PS-b-PB block copolymer.

2. Experimental

2.1. Characterisation

NMR analysis on the ^1H and ^{31}P nuclei was carried out on Bruker WP-200 SY at frequencies 200 and 81.01 MHz, respectively. Positive chemical shifts are downfield from 85% H_3PO_4.

GPC analysis was carried out in THF with detection at 260 nm with MAXIMA 820. Polystyrene standards were used for calibration.

2.2. Materials

Polystyrene ($N = 400$)–polybutadiene ($N = 430$) (PS-b-PB) diblock copolymer was synthesised via anionic polymerisation in the Max-Plank Institute for Colloid and Surface Science, Teltow, Germany, and has the structure given in Scheme 1.

According to ^1H NMR $n = 0.528$; $m = 0.433$; $l = 0.039$. The polymer was soluble in the common solvents (dichloromethane, benzene, THF) and was characterised by GPC data. By GPC, $M_n = 70\,000$, $M_w = 74\,000$ and $M_w/M_n = 1.06$. The content of vinyl(1,2-) fragments in polybutadiene block was 91.7%. The total content of the double bonds determined by ^1H NMR was 5.9 mmol/g of polymer.

The ^1H NMR spectrum of this polymer displays the following characteristic signals with the chemical shifts (ppm): 0.7–2.4 (m, CH_2, CH); 4.9 (m, CH_2=); 5.4 (m, CH=); 6.5–7.0 (m, C_6H_5).

Diphenylchlorophosphine, phenyldichlorophospine, triphenylphosphine, bis(diphenylphosphino)methane, methyldiphenylphosphine, dimethylchlorosilane, methyldichlorosilane, 1,2-dichloroethane, 1,3-dichloropropane, naphthalene, benzoyl chloride, bromine (Lancaster), *n*-BuLi (1.6 M, Fluka), paraformaldehyde (Merck) were used as received.

N,*N*,*N*′,*N*′-tetramethylethyelenediamine (TMEDA) (Lancaster) was stored under molecular sieves 4 Å.

Triethylamine was purified by boiling and distillation with benzoyl chloride with subsequent distillation under Na. Ethyl diphenylphosphinite (from diphenylchlorophosphine and ethanol in the presence of triethylamine), chloromethyldiphenylphosphine oxide (from diphenylchlorophosphine and paraformaldehyde), and tetraphenylmethylenediphosphine dioxide (DPMD) were prepared by following the method in Refs. [14,15]. For the preparation of the lithium salt of DPMD, the method described in Ref. [16] was used.

Phenylphosphine was synthesised by the reduction of diethylphenylphosphonite by lithium aluminium hydride. The boiling temperature of the product was 73–74°C at 50 Torr that matches the literature data (according to Ref. [17] $T_b = 72°C/50$ mm Hg).

2-chloroethyl- and 3-chloropropyldiphenylphosphines were prepared in liquid NH_3 by the method described in Ref. [18] from sodium diphenylphosphide (which in turn was prepared from PPh_3 and Na with subsequent treatment with 1 equivalent of NH_4Cl) and 1,2-dichloroethane or 1,3-dichloropropane, respectively. The ^{31}P and ^1H NMR spectra for the substances prepared related to the published data [18].

3-(Diphenylphosphino)propylphenylphosphine (PPP, $Ph_2P^2CH_2CH_2CH_2P^1(H)Ph$) was prepared from 3-chloropropyldiphenylphosphine and sodium phenylphosphide in liquid NH_3 (−78°C) by the method described in Ref. [19]. The ^{31}P NMR spectrum of the product contains two signals at $\delta_P^1 = -53.8$ ppm, $\delta_P^2 = -17.5$ ppm, and $J_{P-H}^1 = 212$ Hz that corresponds to published data: [19] −54.5 ppm, −18.0 ppm, and 203 Hz, respectively.

THF and diethylether were distilled under $LiAlH_4$. Benzene, toluene and *p*-xylene were distilled under metallic sodium. Methanol was degassed by boiling in Ar.

To avoid the oxidation of phosphorus(III) to phosphorus(V) that is accompanied with the crosslinking of phosphinated PS-b-PB, all operations including storage were carried out under Ar.

2.3. Preparation of 2-(diphenylphosphino)ethylphenylphosphine ($Ph_2P^2CH_2CH_2P^1(H)Ph$, PPE)

For the preparation of PPE, the method described for PPP was slightly modified [19]. A four-neck flask (0.25 l) provided with a mechanical stirrer, a dropping funnel, an argon inlet, and a septum, was filled with argon, cooled until −78°C and charged with 70 ml of liquid NH_3 distilled under sodium. Then, 0.28 g (11.8 mmol) of Na was added and 1.3 ml of $PhPH_2$ (11.8 mmol) was slowly injected by a syringe. Within 20 min of stirring, the colour of the reaction solution turned from blue to orange. After 1 h of stirring, the solution of 2.55 g (0.3 mmol) of $Ph_2PCH_2CH_2Cl$ in 42 ml of Et_2O was added dropwise for 1 h. NH_3 was then slowly evaporated at vigorous stirring (for 4 h). As this takes place, $Ph_2PCH_2CH_2Cl$ preliminary crystallised on the flask walls was completely dissolved at NH_3 boiling temperature. The solution was stirred overnight, then hydrolysed with

10 ml of water and extracted with Et_2O (4 × 3.5 ml). The extracts were placed in a Schlenk flask. The solvents were removed in vacuo at room temperature and the rest was heated up to 40°C in vacuo (10^{-3} Torr) for 2.5 h to remove the volatile substances; 2.4 g (73% based on $Ph_2PCH_2CH_2Cl$) of colourless oil was obtained. This oil was crystallised in a refrigerator. The ^{31}P NMR spectrum of the product in Et_2O displayed $\delta^1_P = -46.8$ ppm, $\delta^2_P = -13.8$ ppm, $J^1_{P-H} = 200$ Hz, $J^{12}_{P-P} = 19$ Hz that corresponds to the published data ($\delta^1_P = -46.6$ ppm, $\delta^2_P = -14.1$ ppm, $J^1_{P-H} = 212 \pm 10$ Hz) [20].

2.4. Hydrobromination of PS-b-PB (1a)

To perform the reaction, the double-jacketed quartz reactor containing tubes for gas inlet and outlet (to provide the gas bubbling through the liquid) and a magnetic stir bar was employed. The reaction flask preliminary filled with argon was charged with 1.0 g of PS-b-PB in 20 ml of benzene. The lamp for UV-irradiation was placed at a distance of 12 cm from reactor. After the beginning of irradiation, gaseous HBr simultaneously generated by the method described in Ref. [21] was bubbled through the reaction mixture at a rate of 0.04 g/min under vigorous stirring for 80 min. Then, the delivery of the gas was stopped and irradiation was continued for 20 min more. After that the polymer solution was precipitated with 180 ml of methanol, washed on the filter by 7 ml of CH_3OH (three times) and dried at 60°C/10^{-3} Torr for 3–4 h. The yield of 1a was 1.39 g (94%). Found, %: Br, 32.00. Calculated for complete hydrobromination, %: Br, 32.31. By GPC data, $M_n = 69\,000$, $M_w = 170\,000$ and $M_w/M_n = 1.53$. The ^1H NMR spectrum of this polymer contains the signals with following chemical shifts (ppm): 0.7–2.0 (m, CH, CH_2); 3.4 (m, CH_2Br); 6.5–7.0 (m, C_6H_5).

2.5. Hydrosilylation of PS-b-PB by dimethylchloro- and methyldichlorosilanes (1b and 1c, respectively)

A double-jacketed glass reactor provided with an argon inlet and outlet, a magnetic stir bar, and a rubber septum was filled with argon and charged with 0.5 g of PS-b-PB (2.95 mmol of vinyl groups) and 8 ml of benzene. The reactor content was heated to 33°C (for $HSiMe_2Cl$) or to 40°C (for $HSiMeCl_2$), sealed, and 0.1 ml of the 0.03 M solution of $H_2PtCl_6 \cdot 6H_2O$ in THF were injected by a syringe after polymer dissolution. In 10 min, 0.39 g of $HSiMeCl_2$ or 0.321 g of $HSiMeCl_2$ (3.39 mmol, 15% excess) was also added by a syringe. The reaction solution was stirred over 7 h at the given temperature and after cooling, stirring was continued overnight at room temperature. The next day, the solution was analysed with GC. The degree of the vinyl group hydrosilylation determined by GC, by the decrease of silane content was 93 ± 2%. Then, in an argon counterflow, a reactor was joined with a distillation head and with a distillation receiver and 1.5–2.0 ml of benzene were distilled. The residue was cooled and sealed.

2.6. Modification of PS-b-PB by (diphenylphosphino)alkylphenylphosphine groups (2a and 2b)

PS-b-PB containing both 2-(diphenylphosphino)ethylphenylphosphine (2a) and 3-(diphenylphosphino)propylphenylphosphine (2b) groups were obtained in the same way.

For this, three-neck flask provided with a magnetic stir bar, a dropping funnel, an argon inlet, and a septum was filled with argon and charged with 8.6 ml (1.4 mmol) of preliminary prepared 0.16 M solution of PPE or PPP in THF. Then, 0.87 ml (1.4 mmol) of 1.6 M solution of *n*-BuLi was injected dropwise by a syringe and stirred at room temperature for 0.5 h. The solution of 0.284 g (1.21 mmol Br) of 1a in 10 ml of THF was then added dropwise for 1 h at room temperature. The reaction mixture was stirred for about 20 h at room temperature and heated for 2 h at 45–55°C. After this, the solvent was partially evaporated in vacuo at room temperature to a volume of 2.5–4 ml and the residue was precipitated with 40 ml of MeOH. The precipitate was filtered, washed with MeOH (3 × 4 ml) on the filter, and dried in vacuo at 10^{-3} Torr at room temperature for 3 h. The yield of 2a was 0.46 g (80%) and for 2b this value was 0.47 g (79%).

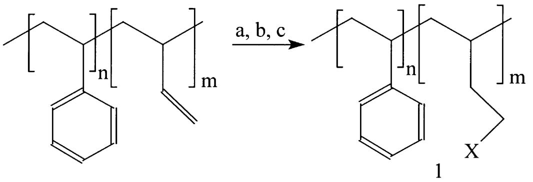
For 2a, it was found, %: C, 77.26; H, 7.44; P, 10.78; Br, 1.48. The calculated content of phosphorus after complete bromine substitution is 12.98%.

In the ^{31}P NMR spectrum of 2a (THF), two signals were observed: $\delta^1_P = -19.5$ ppm, $\delta^2_P = -12.6$ ppm.

For 2b, it was found, %: C, 76.38; H, 8.45; P, 11.13; Br, 1.55. The calculated content of P on complete bromine substitution was 12.62%. By ^{31}P NMR data (in THF), the product contained two non-equivalent phosphorus atoms with $\delta^1_P = -25.2$ ppm and $\delta^2_P = -17.5$ ppm.

2.7. Modification of PS-b-PB by bis(diphenylphosphinyl)methyl groups (2c)

The reaction was carried out in a three-neck flask (50 ml) provided with a distillation head, a distillation-receiver, an argon inlet, and a magnetic stir bar. The flask was charged with 1.63 g (3.91 mmol, 15% excess) of DPMD, filled with argon and then 16 ml of *m*-xylene was added. Dioxide was suspended at stirring and 2.44 ml (3.91 mmol) of *n*-BuLi were added. Reaction medium was heated to 50–60°C, kept at this temperature for 40 min, and then cooled to room temperature; 0.8 g of the polymer 1a (3.4 mmol of Br) was added in an argon counterflow to yellow solution obtained after described manipulations, then flask was heated to 148–151°C (oil bath) and hexane was removed for 30 min. After that the flask was sealed and kept at this temperature under constant stirring for 10 h. After cooling MeOH was added until homogeneous solution was formed (1.2–1.3 ml) and the reaction solution was precipitated by 150 ml of MeOH. Precipitate was isolated, washed on the



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a) HBr, hν, benzene, 25 °C

b) $HSiMe_2Cl$, H_2PtCl_6, benzene, 33 °C

c) $HSiMeCl_2$, H_2PtCl_6, benzene, 40 °C

1a) X = Br

1b) X = $SiMe_2Cl$

1c) X = $SiMeCl_2$

Scheme 2.

filter with 4 × 7 ml of MeOH, and dried in vacuo 10^{-3} Torr for 3 h at roomtemperature. The yield of 2c was 1.08 g (56%). Found, %: C, 77.58; H, 8.06; P, 6.35; Br, 3.54. The calculated content of P at complete substitution of bromine is 10.85%.

In the ^{31}P NMR spectrum (reaction solution) a new signal with $\delta_P = 33.3$ ppm appears.

2.8. Modification of PS-b-PB by bis(diphenylphosphino)methyldimethylsilyl groups (2d)

The suspension of bis(diphenylphosphino)methyllithium was prepared in Schlenk flask by method described in Ref. [22] from 0.907 g (2.36 mmol) of bis(diphenylphosphino)-methane, 0.274 g (2.36 mmol) of TMEDA, and 1.48 ml (2.36 mmol) of *n*-BuLi in 5.7 ml of benzene for 3 h at room temperature and for 30 min. at 45°C. Then, 12 ml of benzene solution of polymer 1b prepared by hydrosilylation of 0.4 g of PS-b-PB were added in one portion at room temperature. Reaction medium was stirred for 1.5 h and kept overnight without stirring. Then, solution was separated from LiCl by decantation and precipitated with 180 ml of MeOH. The collected product was washed with MeOH (3 × 7 ml) and dried in vacuo 10^{-3} Torr at room temperature for 3 h. The yield of 2e was 1.17 g (84%). The polymer is completely soluble in CH_2Cl_2 and toluene. Found, %: C, 76.75; H, 7.40; P, 9.04; Si, 4.91; Cl, < 0.5. The calculated content of P for complete hydrosilylation had to be 10.53%, while Si content had to be 4.77%.

In ^{31}P NMR spectrum (reaction solution), the signal with a chemical shift -13.3 ppm was observed. The ^1H NMR spectrum ($CDCl_3$) of collected product contains signals with the following chemical shifts (ppm): -0.3 (s, CH_3–Si); 0.0 (s, CH_2–Si); 0.5–2.4 (m, CH_2, CH); 2.9 (s, CH–P); 3.3 (s, CH_3O–Si); 6.5–7.3 (m, C_6H_5, C_6H_5–P).

2.9. Modification of PS-b-PB by bis(diphenylphosphinomethyl)methylsilyl groups (2e)

A three-neck flask of 50 ml volume provided with a dropping funnel, an argon inlet, and a magnetic stir bar was used. To the suspension of (diphenylphosphino)methyllithium prepared in accordance with Ref. [23] from 1.263 ml (6.31 mmol) of diphenylmethylphosphine, 3.94 ml (6.31 mmol) of *n*-BuLi, and 0.733 g (6.31 mmol) of TMEDA for 20 h at room temperature 10 ml of THF were added and stirred until a homogeneous solution was formed. After cooling to 0°C (ice/water bath), benzene solution of the polymer 1c prepared by hydrosilylation of 0.5 g of PS-b-PB was added dropwise for 10 min. The reaction solution was stirred for 4 h at room temperature and precipitated with 200 ml of MeOH. The residue was isolated, washed with 3 × 5 ml of MeOH, and dried in vacuo at room temperature for 3 h. The yield of 2e was 1.65 g (92%).

Found, %: C, 75.44; H, 7.65; P, 8.45; Si, 4.83; Cl, < 0.5. The calculated content of P for complete hydrosilylation is 10.14%, while Si content is 4.59%.

The ^{31}P NMR spectrum (reaction solution) displays one signal with $\delta_P = -22.7$ ppm.

3. Results and discussion

The modification of PS-b-PB was carried out in two-step polymer analogous reactions. In the first step, double bonds of polybutadiene block were converted into the new groups having a good reactivity for nucleophilic substitution. For this, simple reactions, such as hydrobromination and hydrosilylation, were used (see Scheme 2)[1].

The radical anti-Markownikoff addition of HBr allows us to prepare the primary bromide in which the bromine atom can be easily replaced by nucleophiles. The radical addition can be carried out either using peroxides as a radical source, or by UV irradiation [24]. The use of benzoyl peroxide in amounts of 5 mol% at 80°C was found to lead to low conversions (~20%). UV irradiation (mercury lamp, 25°C, 90–100 min) results in a nearly complete hydrobromination (99%) not only of terminal vinyl groups, but also of vinylene fragments of the polymer. At the same time, polymer branching took place, which was reflected in the increase of molecular weight and molecular weight distribution. Despite this, the polymer maintained a good solubility in common solvents. In the ^1H NMR spectrum of 1a, the

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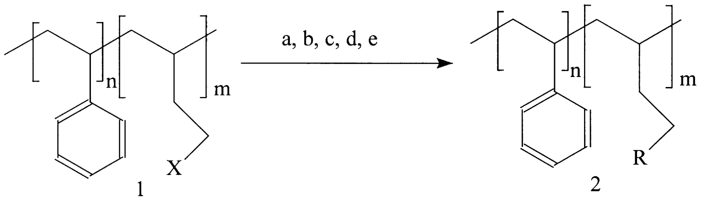
[1] Further polybutadiene-1,4 blocks are not presented for simplicity.



1a	
a) $Ph_2P(CH_2)_2P(Ph)Li$, THF, r.t., 20 h.	2a) R = $P(Ph)(CH_2)_2PPh_2$
b) $Ph_2P(CH_2)_3P(Ph)Li$, THF, r.t., 20 h.	2b) R = $P(Ph)(CH_2)_3PPh_2$
c) $[Ph_2P(O)]_2CHLi$, xylene, 140 °C, 10 h.	2c) R = $CH[P(O)PPh_2]_2$
1b	
d) $(Ph_2P)_2CHLi$ / TMEDA, benzene, r.t.	2d) R = $SiMe_2CH(PPh_2)_2$
1c	
e) Ph_2PCH_2Li / TMEDA, benzene / THF, 0 °C	2e) R = $SiMe(CH_2PPh_2)_2$

Scheme 3.

proton signals of initial CH= and CH_2= groups completely vanish and new signal appears with a chemical shift of 3.4 ppm, which is characteristic of primary alkyl bromides [25]. The signal of secondary bromide is absent in the spectrum because of, probably, a low content of polybutadiene-1,4 block and high selectivity of radical hydrobromination.

Hydrosilylation of PS-b-PB allowed us to prepare pendent chlorosilyl groups for subsequent replacement of chlorine. Hydrosilylation of PS-b-PB by dimethylchlorosilane and methyldichlorosilanes was carried out using the standard catalyst, H_2PtCl_6, in benzene. After 7 h of heating at 33 and 40°C, respectively, and keeping the reaction mixture overnight, the yield of the hydrosilylated products 1b and 1c was 93 ± 2%. As 1b and 1c contained numerous highly reactive groups, for the next step, reactions 1b and 1c were used without isolation from reaction solutions.

Using precursors 1, a number of modified polymers containing bidentate phosphine ligands were prepared by the second step as shown in Scheme 3.

Polymers modified by 2-(diphenylphosphino)ethyl- and 3-(diphenylphosphino)propylphenylphosphine groups (2a and 2b, respectively) were prepared by the interaction of lithium salts of corresponding phosphines (PPE and PPP) with 1a.

The structure of polymers was confirmed by the ^{31}P NMR data of reaction solutions of the polymers in THF (before their precipitation by methanol) and by elemental analysis. The polymer 2b had a NMR spectrum Fig. 1 consisting of two signals of nearly equal intensity. One of them is a signal of Ph_2P- group with $\delta_P^2 = -17.5$ ppm, this chemical shift practically did not change because of the far distance of this group from the reaction centre (-P(Ph)-) in the initial phosphine PPP (-17.5 ppm). Another one has an upfield shift ($\delta_P^1 = -25.2$ ppm) and relates to -P(Ph)- groups of dialkylphenylphosphines. The latter agrees with the upfield shifts (4–10 ppm) of signals of dialkylphenylphosphines [26] as compared to chemical shifts of corresponding alkyldiphenylphosphines. By elemental analysis, the conversion of double bonds into phosphine ligands was 88%, while the degree of bromine substitution calculated from Br content was 95%. Supposedly, this discrepancy can be connected with the fact that the secondary alkylbromide groups of 1a (about 8% as a result of HBr addition to 1,4-fragments of polybutadiene block) took part in elimination instead of substitution.

The ^{31}P NMR spectrum of polymer 2a (Fig. 2) had signals of Ph_2P-group with $\delta_P^2 = -12.6$ ppm (-13.8 ppm in initial PPE, small change) and of -(Ph)P- group with $\delta_P^1 = -19.5$ ppm. The conversion of double bonds to phosphine ligands was 83%, while the degree of bromine substitution was 95%.

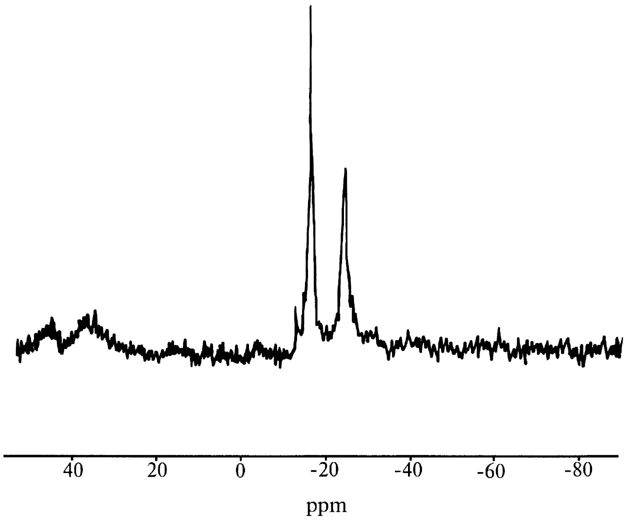


Fig. 1. The ^{31}P NMR spectrum of 2b.

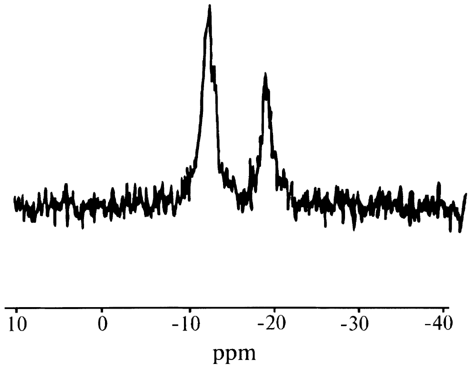


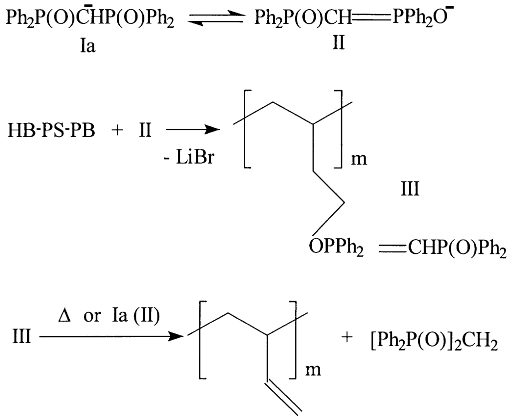
Fig. 2. The ^{31}P NMR spectrum of 2a.

The polymer 2a was soluble in common solvents, while 2b was insoluble. We suppose that the partial formation of crosslinks because of quaternisation of some phosphorus atoms (especially in a solid state) causes the loss of solubility of 2b after isolation. This polymer produces solutions containing small, very well swellable microgels.

For the preparation of a completely soluble polymer we attempted using the radical addition of PPP to PS-b-PB [27]. UV irradiation of an equimolar mixture of PS-b-PB and phosphine in a benzene solution at 70°C for 10 h leads to polymer, which contains only 17% of diphosphine groups. At the same time, after an isolation procedure the polymer was also insoluble. We think that low reaction ability of PPP in this reaction is first of all caused by steric hindrances making the stage of chain propagation difficult.

Modification of PS-b-PB with bis(diphenylphosphinyl)-methyl group (2c) was carried out using a lithium derivative of DPMD [17] because of its better solubility and simplicity of the preparation.

Boiling of 1a in benzene with 15% excess of DPMD over 10 h results (by elemental analysis data) in about 24% bromine substitution for diphosphine dioxide groups, while the polymer loses more than 50% of bromine. Use of more rigorous conditions (xylene, 140°C) allows us to synthesise 2c containing about 59% of diphosphine dioxide groups. In this case, the polymer loses about 89% of bromine. The last fact is an evidence of a side reaction, which leads to bromine elimination, and a decrease of the yield of the desirable product. Presumably, this is an alkylation of dioxide on phosphoryl oxygen [28,29] with subsequent mono- or bimolecular elimination as in Scheme 4.



Scheme 4.

In the ^{31}P NMR spectrum of the reaction mixture (xylene + methanol + LiBr) the signal with $\delta_P = 33.3$ ppm can be assigned to modified polymer, while the signal with $\delta_P = 32.1$ ppm is responsible for the DPMD. After the polymer isolation (precipitation), 2c was not soluble anymore and only swellable in THF and $CHCl_3$.

The reaction of 1b with the nearly equimolar amount of the complex of bis(diphenylphosphino)methyllithium and

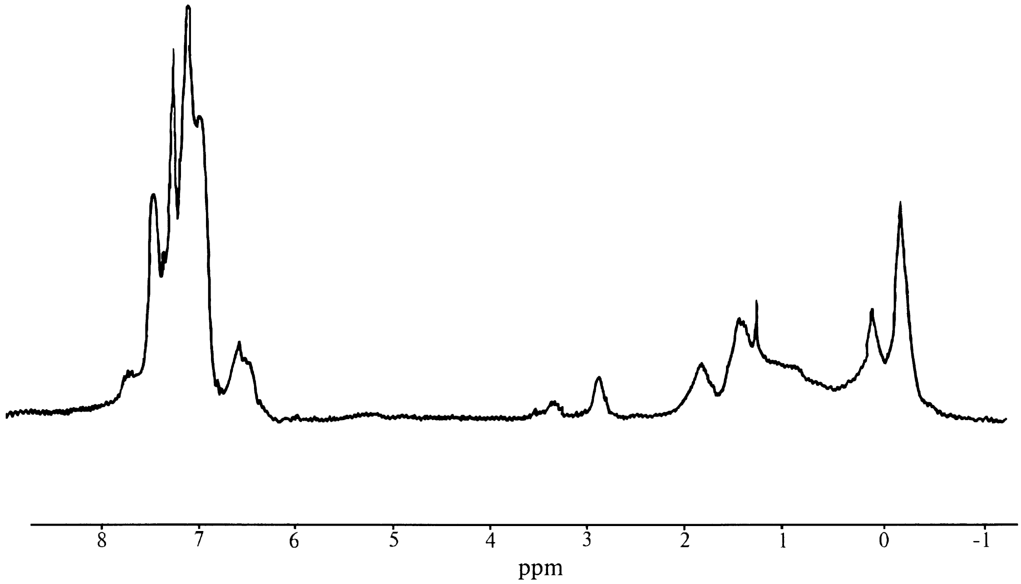


Fig. 3. The ^{1}H NMR spectrum of 2d.

Table 1
Characterisation of modified PS-b-PB containing bidentate phosphine ligands

Polymer notation (%)	Conversion of double bonds	Content of *X* or *R*[a] (mmol/g)	^{31}P NMR parameters (ppm)	Solubility
1a	99	4.25		Sol
1b	93	3.61		Sol
1c	93	3.36		Sol
2a	83	3.56	-19.5, -12.6	Sol
2b	88	3.60	-25.2, -17.5	Swell
2c	59	2.05	33.3	Swell
2d	86	2.92	-13.3	Sol
2e	83	2.72	-22.7	Swell

[a] The structures of *X* and *R* are presented in Schemes 2 and 3.

TMEDA results in a formation of completely soluble 2d with an yield of 86% (based on double bond content).

The ^{31}P NMR of the reaction solution contained one new signal with $\delta_P = -13.3$ ppm that is close to chemical shift of known low-molecular analogue bis(diphenylphosphino)-methyltrimethylsilane prepared by a similar way [30] and displaying $\delta_P = -15.3$ ppm. The ^{1}H NMR spectrum (Fig. 3) matches to supposed structure. The signal of methine proton of bis-(diphenylphosphino)methyl group had a chemical shift 2.9 ppm that is close to chemical shift of this proton (2.3 ppm [30]) in analogue mentioned earlier. The signal 3.3 ppm presumably relates to the protons of the CH_3O–Si groups, which were produced as a result of the substitution of chlorine for methoxyl during precipitation in methanol. However this signal is weak as compared to the methine proton.

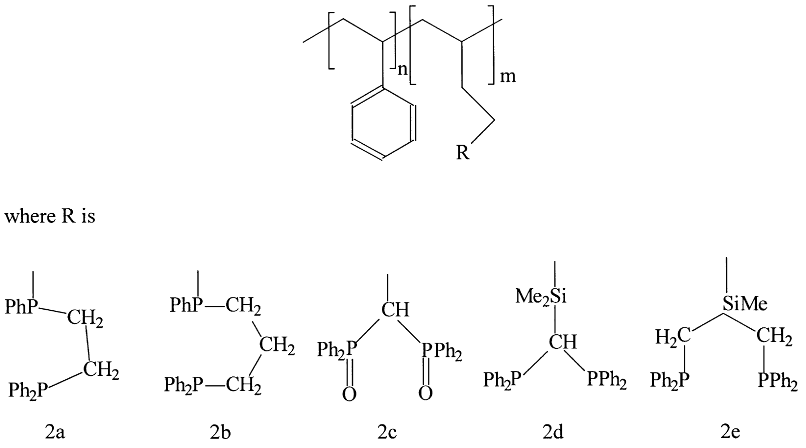
PS-b-PB with bis(diphenylphosphinomethyl)methylsilyl groups (2e) was of particular interest to us because to some extent it can be considered as a silicone analogue of polymer 2b. The reaction of 1c with 15% excess of a complex of (diphenylphosphino)methyllithium and TMEDA synthesised by the method described in Ref. [23] led to a formation of 2e with an yield of 92%. Conversion of all the double bonds to phosphine ligands was 83%.

The ^{31}P NMR spectrum of the reaction solution contained only one signal with $\delta_P = -22.7$ ppm that fits well with chemical shift ($\delta_P = -23.5$ ppm) of (diphenylphosphino)-methyl-trimethylsilane described in Ref. [31].

Unlike 2d, the polymer 2e was not soluble in CH_2Cl_2, though the method of synthesis of both polymers are similar. It is likely that the hydrolysis of $HSiMeCl_2$ provokes the crosslinking more actively than the possible hydrolysis of $HSiMe_2Cl$ containing one chlorine atom. The results of modification are summarised in Table 1 and Scheme 5.

4. Conclusions

The novel block copolymers were synthesised in two-step polymer analogous reactions. The procedure of complete UV hydrobromination of diblock polystyrene–polybutadiene block copolymer was elaborated. For the preparation of PS-b-PB with (diphenylphsophino)alkylphenylphosphine groups the subsequent interaction of hydrobrominated PS-b-PB with the lithium salts of $Ph_2P(CH_2)_nP(H)Ph$ with $n = 2, 3$ was used permitting to prepare the corresponding polymers with an yield of about 70–90% based on the total double bond amount of PS-b-PB. These polymers stay soluble in the reaction solution that allows their purification and characterisation, but become partly insoluble during isolation.



Scheme 5.

The novel polymer derived from hydrobrominated PS-b-PB and containing the bis(diphenylphosphinyl)methyl group was prepared.

Hydrosilylation of PS-b-PB by silanes $HSiMe_nCl_{3-n}$ with $n = 1, 2$ permits us to prepare PS-b-PB with pendent chlorosilyl groups for the subsequent replacement of chlorine. Using such polymers as precursors, polymers containing bis(diphenylphosphino)methyldimethylsilyl and bis(diphenylphosphinomethyl)methylsilyl groups were synthesised with high yields and degrees of modification. The two polymers (2a and 2d) prepared were soluble in toluene and CH_2Cl_2 after isolation that provides further opportunity to synthesise soluble organometallic polymers.

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