Synthesis of the Model Macroinitiators of Free Radical Polymerization and Their Application for the Preparation of Block Copolymers

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SYNOPSIS

A series of polystyrenes having low molecular weight (4600–23,100) and narrow molecular weight distribution and functionalized with a benzophenone group at one or both ends of the chain have been prepared through anionic polymerization. Then the terminal benzophenone groups have been transformed into 1,2-bis(trimethylsilyloxy)tetraphenylethane (or benzopinacolate) groups by the duplication reaction with free benzophenone in the presence of chlorotrimethylsilane and hexamethylphosphorous triamide (HMPT) or hexamethylphosphoramide (HMPA), producing model thermal macroinitiators of free radical polymerization with well-defined structure. Polymerization of MMA initiated by these macroinitiators was carried out yielding poly(styrene-b-methyl-methacrylate) (PS-b-PMMA). © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Living free radical polymerization has recently attracted a great interest of scientists. The most important advantage of this method is the possibility to obtain polymers with controlled structure in the conditions of radical polymerization, which simplifies significantly experimental techniques in comparison with living ionic methods and thus makes this method useful for practical application.[1]

A great contribution to the development of the concept of living radical polymerization was made by Otsu and co-workers,[2–4] who postulated the idea of using reversible termination of growing polymer chains in a free radical polymerization to give a polymer that is capable of stepwise chain growth. A number of functional groups providing living radical polymerization are known. Among them are 1,2-bis(trialkylsilyloxy)tetraphenylethane or benzopinacolate (BPC) groups,[5] which act as thermal C — C

splitting initiators. BPC groups can be introduced into the polymer chain, and thus prepared macroinitiators can be used for the synthesis of block or graft copolymers depending on the position of these groups (terminal or random throughout the chain, respectively). Synthesis of poly(ethylene oxide-b-styrene) (PEO-b-PS) using this approach was described earlier.[6] In our previous publication, we described preparation of graft copolymers PS-g-PMMA and PMMA-g-PS.[7]

In spite of the large number of publications devoted to living free radical polymerization, the mechanism of this process is not completely clear and is still being discussed.[8] For more detailed investigation of the mechanism, it is important to have macroinitiators with well-defined structures, which would allow one to monitor any change of the molecular weight (MW) and molecular weight distribution (MWD) in the course of polymerization. Here we describe the synthesis of the polystyrene-based macroinitiators with one or two terminal benzopinacolate groups having narrow MWD by the method of anionic polymerization. We also provide the results of the polymerization of MMA provided by these initiators.

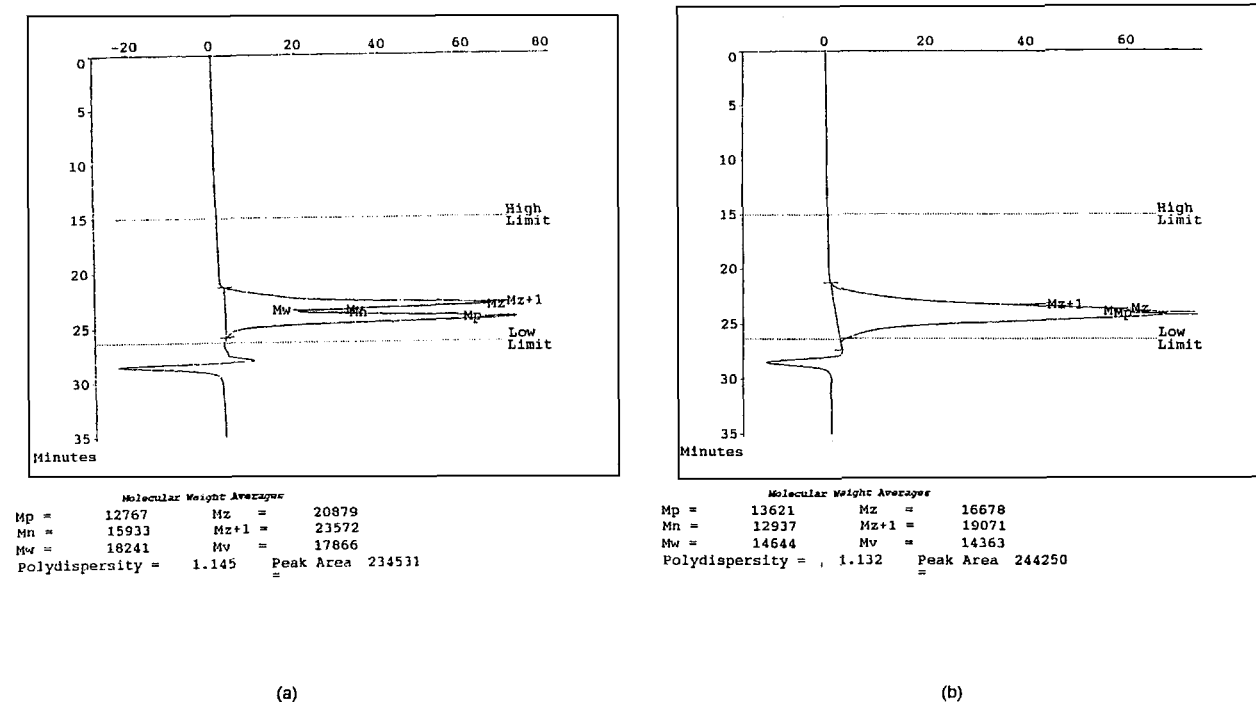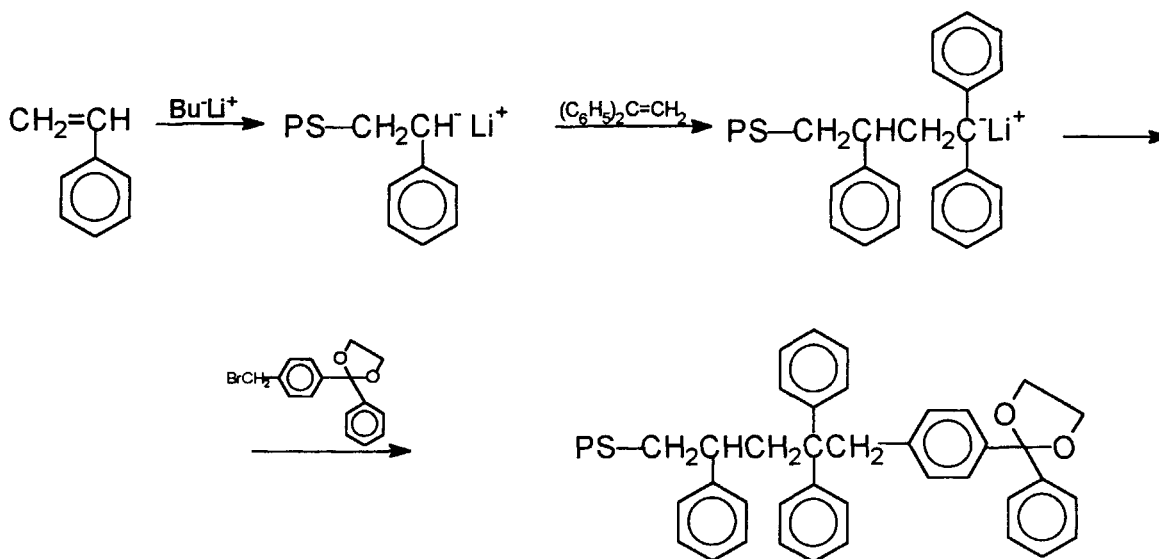* To whom correspondence should be addressed.

Figure 1 SEC curves of the polystyrene functionalized with 2-(4-bromomethylphenyl)-2-phenyl-1,3-dioxolane without 1,1-diphenylethylene (a) and with addition of this reagent (b, sample V) using BuLi as initiator.

EXPERIMENTAL

In all the experiments, only freshly distilled solvents were used. Tetrahydrofuran (THF) was distilled over a sodium–benzophenone complex, and benzene was refluxed with 2–3 v/v % of 1.3 N solution of BuLi in hexane and several drops of 1,1-diphenylethylene. Styrene and MMA were distilled over sodium. All the reactives were from Aldrich Chemical Co. Nuclear magnetic resonance (NMR) spectra were recorded on a Varian 200-MHz spectrometer. Size exclusion chromatography (SEC) analysis was
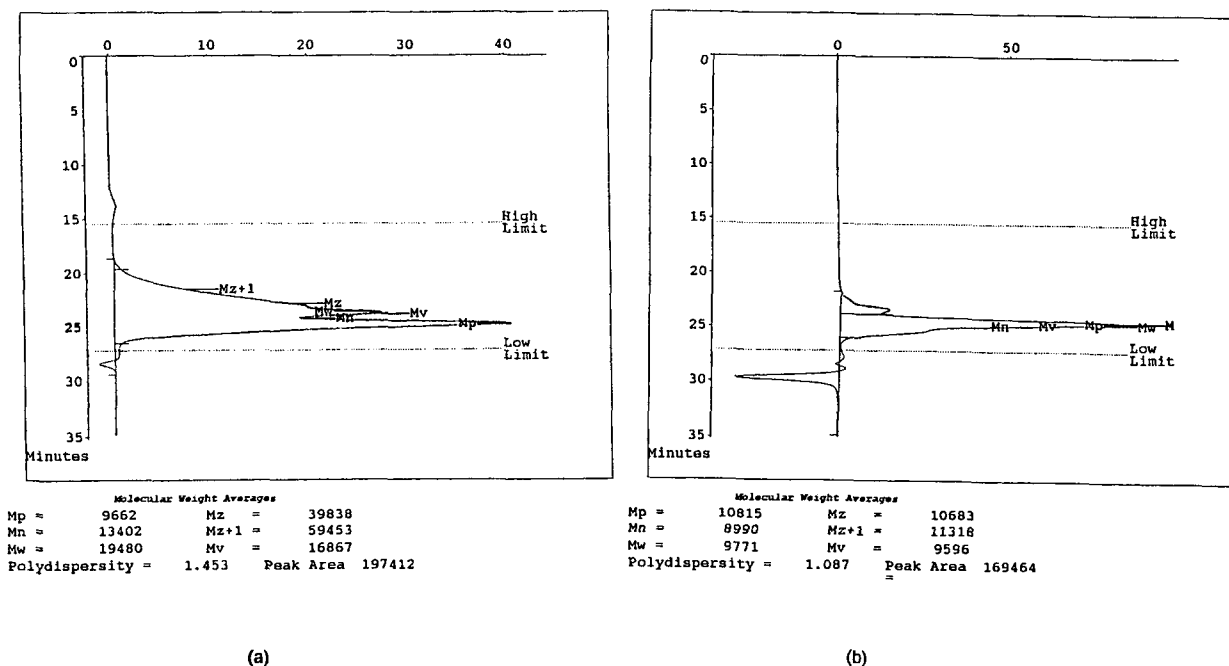

Scheme 1.

(a)

(b)

Figure 2   SEC curves of the polystyrene functionalized with 2-(4-bromomethylphenyl)-2-phenyl-1,3-dioxolane without 1,1-diphenylethylene (a) and with addition of this reagent (b, sample XI) using potassium salt of the tetramer of α-methylstyrene as initiator.

made on a Hewlett-Packard 1050 in THF with polystyrene standards and monitoring ultraviolet (UV) and refractometrically. Infrared (IR) spectra were recorded on an IR spectrometer Nicolet 550-Analitical plan. Elemental analysis was performed by Galbraith Laboratory Inc.

Synthesis of 4-Bromomethylbenzophenone

p-Methylbenzophenone (98 g, 0.5 mol) and 1,2-dibromoethane (200 mL) were placed in a quartz reactor fitted with condensor, dropping funnel, thermometer, and ultraviolet lamp. A solution of bromine (26.5 mL, 0.51 mol) in 1,2-dibromoethane (60 mL) was added dropwise under heating (60°C) and UV irradiation. The reaction mixture was stirred for 1 h 15 min under the same conditions, and then the solvent was removed in vacuum and the residue

was recrystallized twice from ethanol and once from benzene, yielding 103.26 g (75%) of 4-bromomethylbenzophenone, melting point (mp) 112°C (literature 112°C; ref. 9); ^{1}H-NMR (CDCl$_3$, δ, ppm): 7.44–7.82 (m, 9H), 4.53 (s, 2H).

Synthesis of 2-(4-Bromophenyl)-2-phenyl-1,3-Dioxolane (I)

4-Bromomethylbenzophenone (15 g, 0.054 mol), ethylene glycol (4.79 g, 0.077 mol), a crystal of p-toluenesulfonic acid, and benzene (130 mL) were placed into a round-bottom flask fitted with a Dean and Stark water separator and a reflux condensor. The reaction mixture was heated until no more water collected. The product was purified by column chromatography using silicagel as stationary phase and mixture benzene : hexane 7 : 3 as eluent. The yield
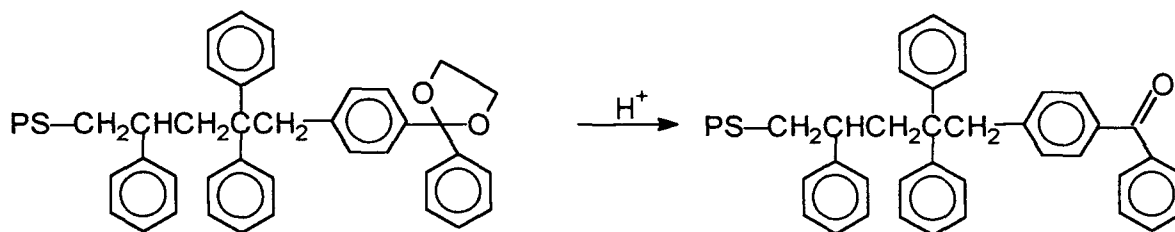
Scheme 2.

Table I Characteristics of the Prepared Polystyrenes Having One (samples II–IX) or Two (samples IX–XIV) Terminal Benzophenyl Groups

Sample	$M_n \times 10^{-3}$	$M_w \times 10^{-3}$	M_w/M_n
II	4.6	6.0	1.28
III	8.0	8.9	1.11
IV	10.1	11.3	1.12
V	12.9	14.6	1.13
VI	13.4	17.3	1.29
VII	15.0	17.4	1.15
VIII	23.1	26.5	1.15
IX	38.9	50.8	1.30
X	4.5	6.3	1.42
XI	9.0	9.8	1.09
XII	10.4	11.2	1.08
XIII	19.4	22.4	1.16
XIV	14.4	18.3	1.27

was 9.33 g (53.9%) of 2-(4-bromophenyl)-2-phenyl-1,3-dioxolane (**I**); ^{1}H-NMR (CDCl$_3$, δ, ppm): 7.30–7.53 (m, 9H), 4.47 (s, 2H), 4.06 (s, 4H).

Synthesis of 4-Vinylbenzophenone (4VBP)

4VBP was prepared by the reaction of 4-ethenyl-phenyl magnesium chloride with benzonitrile in dry THF according to the procedure described in ref. 7.

Initiators of the Anionic Polymerization

Solutions of the BuLi in hexane and potassium salt of the tetramer of α-methylstyrene in THF were used as initiators. Concentration of the BuLi was determined by the titration using 1,2-diphenyl-2-propanone tosylhydrazone.[10] Concentration of the potassium salt of the tetramer of α-methylstyrene was determined by the titration of the solution of the quoted quantity of acetanilide in THF.

Synthesis of Polystyrenes with Terminal Benzophenone Groups

Full description of the preparation of one of the samples of polystyrene with one terminal benzophenone group is given (all the operations were carried out under argon): In a 500-mL three-necked flask, 250 mL of benzene were collected from distillation apparatus, and then 1–2 drops of styrene were added and 1.36N solution of BuLi in hexane was added dropwise until the point zero was achieved. Then 1.36N BuLi in hexane (3.83 mL, 5.21 mmol) was introduced in the reaction flask and freshly distilled styrene (32.2 mL, 0.28 mol) was added during 15 min. The reaction mixture was stirred for 30 min; after that 1,1-diphenylethylene (1.06 mL, 5.99 mmol) in 5 mL of benzene was introduced. After 15 min of stirring, compound **I** (1.83
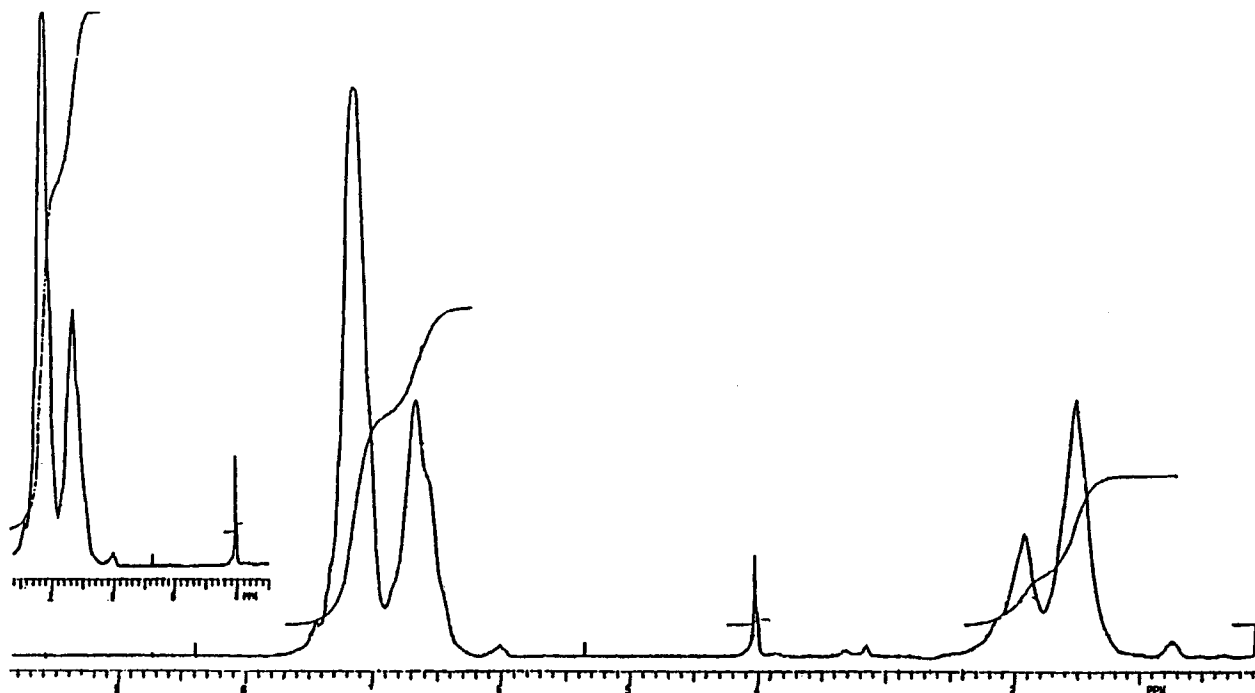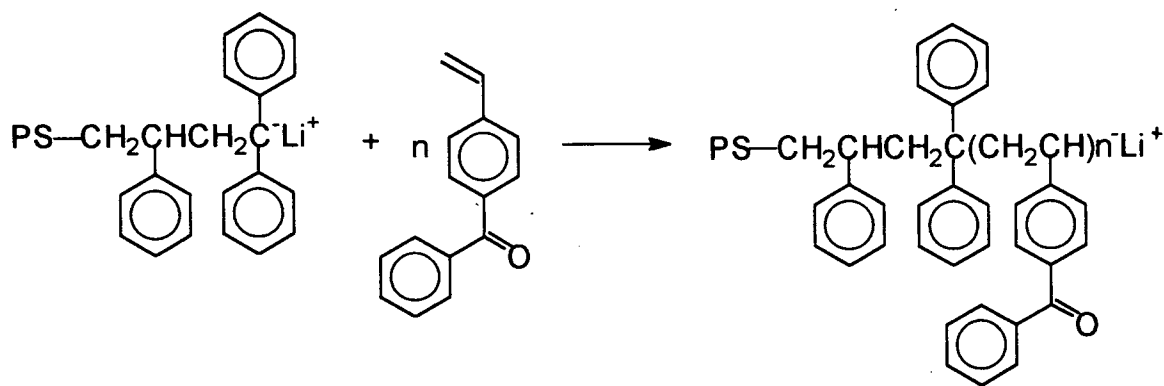

Figure 3 ^{1}H-NMR spectrum of the polystyrene having a terminal benzophenone group before deprotection (sample X).

$$PS-CH_2\overset{|}{C}HCH_2\overset{|}{C}^-Li^+ \quad + \quad n \quad \longrightarrow \quad PS-CH_2\overset{|}{C}HCH_2\overset{|}{C}(CH_2\overset{|}{C}H)_n^-Li^+$$

Scheme 3.

g, 5.73 mmol) in 10 mL of benzene was added. Stirring was continued for 30 min, and then the reaction mixture was poured into 2.5 L of methanol. The precipitate was separated and dried under vacuum at 60°C for 24 h, and then the precipitation from methanol was repeated once more. The yield was 27.8 g of polystyrene having M_n 8000, $M_w/M_n = 1.11$ (determined by SEC).

Monofunctional polystyrenes of other molecular weights were prepared similarly. α,ω-Dibenzophenone polystyrenes were prepared in a similar way using potassium salt of the tetramer of α-methylstyrene as initiator. The ^{1}H-NMR spectra of the prepared polymers contains, besides ordinary signals of polystyrene, a signal at 4.03 ppm belonging to the methylenes of the 1,3-dioxolane ring.

To remove the protection from the carbonyl group in the terminal functional groups, the polymer was dissolved in THF and stirred with diluted hydrochloric acid for several hours. The resulting end-terminated benzophenone polymer was precipitated twice from methanol.

Synthesis of PS-*b*-4VBP

First, anionic polymerization of styrene was carried out as described earlier, using 3 mL (2.73 g, 26.1 mmol) of styrene, 0.25 mL of 1.2N solution of n-BuLi in hexane (0.3 mmol), and 40 mL of benzene. After addition of 1,1-diphenylethylene (0.09 mL, 0.346 mmol) to the reaction mixture, stirring was continued for 10 min, and then a solution of 4-vinylbenzophenone (0.6 g, 2.88 mmol) in 7 mL of benzene was added. Stirring was continued for 30 min, the reaction mixture was poured into methanol, and the resulting polymer was separated, dried under vacuum, and precipitated from methanol once more. Then 2.5 g of PS-*b*-4VBP was obtained. The M_n of this sample determined by SEC was 7150, M_w/M_n

1.38, oxygen content determined by elemental analysis 0.74%.

Preparation of the Model Macroinitiators by the Reductive Duplication of the Terminal Benzophenone Group

Freshly distilled THF (200 mL), benzophenone (18.2 g, 0.1 mol), Mg powder (1.22 g, 0.05 mol), and anionically prepared polystyrene (10 g) with deprotected benzophenone groups were placed in a reaction flask, and then slowly 13 mL (0.1 mol) of trimethylchlorosilane was added. After stirring for 10–20 min, 10 mL of hexamethylphosphoramide was added and the reaction mixture was left stirring overnight. Then the solution was filtrated and the solvent was removed in vacuum. The residue was dissolved in CH_2Cl_2 and precipitated in ethanol. Precipitations were repeated until the resulting polymer did not contain free benzopinacolate (it was controlled by thin-layer chromatography).

Synthesis of the Poly(Styrene-*b*-Methylmethacrylate)s

In a typical experiment, 0.50 g of the macroinitiator containing terminal BPC groups, 1.5 g of methylmethacrylate, and 3.0 g of benzene were placed in a glass tube. The tube was evacuated, sealed, and kept at 90° for 3 h. When the polymerization was finished, the tube was cooled, opened, and the content was precipitated in the excess of methanol. Block copolymers were isolated from homopolymers by selective extraction with cyclohexane and acetonitrile of PS and PMMA, respectively.
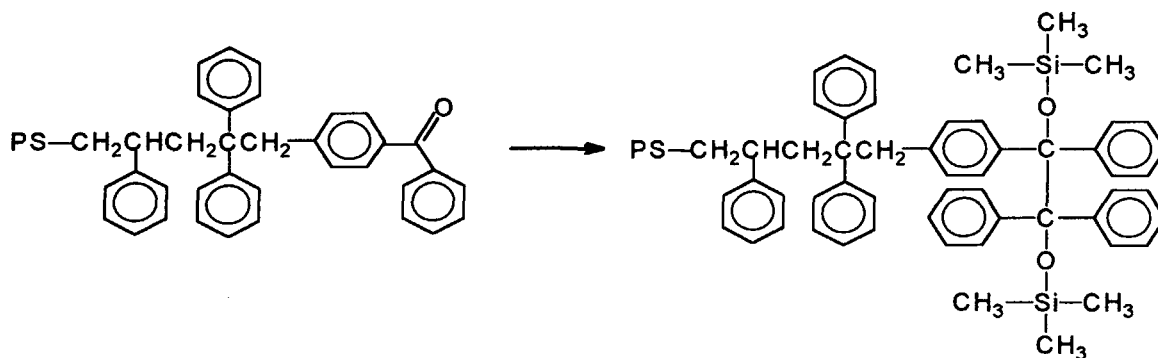
Scheme 4.

RESULTS AND DISCUSSION

Preparation of the model macroinitiators of living radical polymerization consists of two steps: The first one is synthesis of polystyrene having benzophenone function at one or two ends of the chain by anionic polymerization, and the second one is transformation of benzophenone groups into benzopinacolates.

Preparation of Polystyrenes Functionalized with One or Two Terminal Benzophenone Groups

To prepare polystyrenes with one terminal benzophenone group, the hexane solution of BuLi was used as initiator. The reaction of styrene with BuLi was carried out in benzene at room temperature, varying the molar ratio styrene: BuLi from 48 : 1 (M_n 5000) to 190 : 1 (M_n 20,000). To introduce the benzophenone function in the polymeric chain, 4-bromomethylbenzophenone with protected carbonyl group (compound I) was used in order to avoid side reactions leading to the reduction of the carbonyl group. It was found that the direct addition of I to the reaction mixture produces the coupling of polymer chains. The SEC trace of the polymer thus obtained consisted of two narrow peaks; one of them had the molecular weight corresponding to the ratio of the reagents and the second one had M_w two times higher [see Fig. 1(a)]. We suppose that the reac-

Molecular Weight Averages			
Mp =	6099	Mz =	7804
Mn =	4701	Mz+1 =	9739
Mw =	6084	Mv =	5849
Polydispersity =	1.294	Peak Area	215924

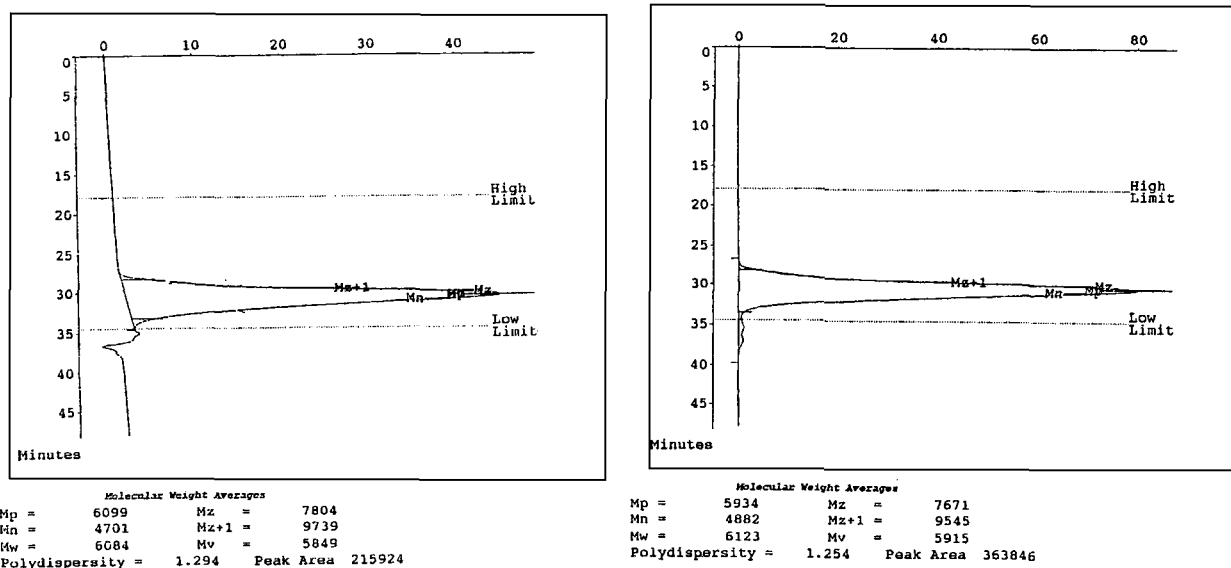| Molecular Weight Averages			
Mp =	5934	Mz =	7671
Mn =	4882	Mz+1 =	9545
Mw =	6123	Mv =	5915
Polydispersity =	1.254	Peak Area	363846

Figure 4   SEC curves of the polystyrene before (a, sample II) and after (b, sample IIa) transformation of terminal benzophenone groups into BPC.

Table II Characteristics of the Prepared Macroinitiators

Sample	$M_n \times 10^{-3}$	$M_w \times 10^{-3}$	M_w/M_n	Yield of Benzopinacolization (%)
IIa	4.9	6.1	1.25	28%[a]
IIIa	6.3	8.1	1.30	87%[b] (0.77)
VIIIa	21.4	24.1	1.13	41%[a]
Xa	4.2	6.1	1.44	11%[a]
XIa	9.1	9.8	1.08	62%[b] (0.76)
XIIa	10.4	11.2	1.08	84%[b] (0.90)
XIIIa	19.2	21.3	1.14	74%[a]
XVa	8.1	11.2	1.38	66%[b] (1.47)

[a] Calculated from ^{1}H-NMR and SEC data.
[b] Determined from the elemental analysis of Si content (Si content is given in parentheses).

tivity of the terminal carbanion of the polystyrene chain is too high, so that partial destruction of the protecting group takes place along with substitution of bromine in **I**. To reduce the reactivity of the polystyrene carbanion, after the polymerization was completed, we added to the reaction mixture 1,1-diphenylethylene and then compound **I**. Addition of 1,1-diphenylethylene (1) decreases nucleophilicity of the terminal carbanion because of greater resonance stabilization by two phenyl groups, and (2) increases significantly sterical hindrance and thus makes much less probable the reaction involving the protecting group. The experimental results confirmed our point of view, and we succeeded in decreasing significantly the coupling of the chains and in obtaining polymers having narrow MWD [see Fig. 1(b)] by the sequence of reactions shown in Scheme 1.

Polystyrenes with two terminal benzophenone groups were prepared in a similar way using a difunctional initiator. We checked several initiators, such as naphtalene-sodium, sodium salt of the dimer of 1,1-diphenylethylene, and potassium salt of the tetramer of α-methylstyrene. We found the potassium salt of the tetramer of α-methylstyrene to be the most appropriate since it produced polymers having the narrower polydispersities. In this case also it was necessary to add 1,1-diphenylethylene to prevent undesirable side reactions leading to coupling of polymer chains (see Fig. 2).

Mild acidic hydrolysis of the prepared polymers removes the protection from the carbonyl group and produces polystyrenes having one or two terminal benzophenone groups (Scheme 2).

Using the method described earlier, we prepared a series of the polymers having relatively narrow

MWD (1.07–1.42) terminated with one or two benzophenone groups (see Table I). The yield of functionalization was calculated from the ^{1}H-NMR spectra of the prepared polymers before deprotection using the ratio of the integrals of the aromatic protons to the protons of the dioxolane ring (see Fig. 3) and the average molecular weight of the polymer determined by SEC analysis. The yield of functionalization thus determined was 83–92%.

Preparation of the Poly(Styrene-*b*-4-Vinylbenzophenone) Copolymer, (PS-*b*-4VBP), with Short Blocks of 4-VBP

We also tried an alternative way to introduce benzophenone function into the polymeric chain with controlled molecular weight and polydispersity index, by successive anionic polymerization of styrene and 4-vinylbenzophenone in order to obtain PS-*b*-4VBP. This method has some limitations, connected with the properties of 4-vinylbenzophenone and its behavior in the reaction of anionic polymerization. The first one is the impossibility to protect the carbonyl group of 4-vinylbenzophenone by formation of a 1,3-dioxolane derivative because prolonged heating and acidic catalysis lead to polymerization of this compound. We minimized the side reaction involving the carbonyl group by adding 1,1-diphenylethylene and thus decreasing the reactivity of the polystyrene carbanion, similar to the reaction of the functionalization using 4-bromomethylbenzophenone with a protected carbonyl group. The second limitation seems to be unavoidable and is connected with the nature of the polymeric carbanion formed by 4-vinylbenzophenone. The benzophenone group
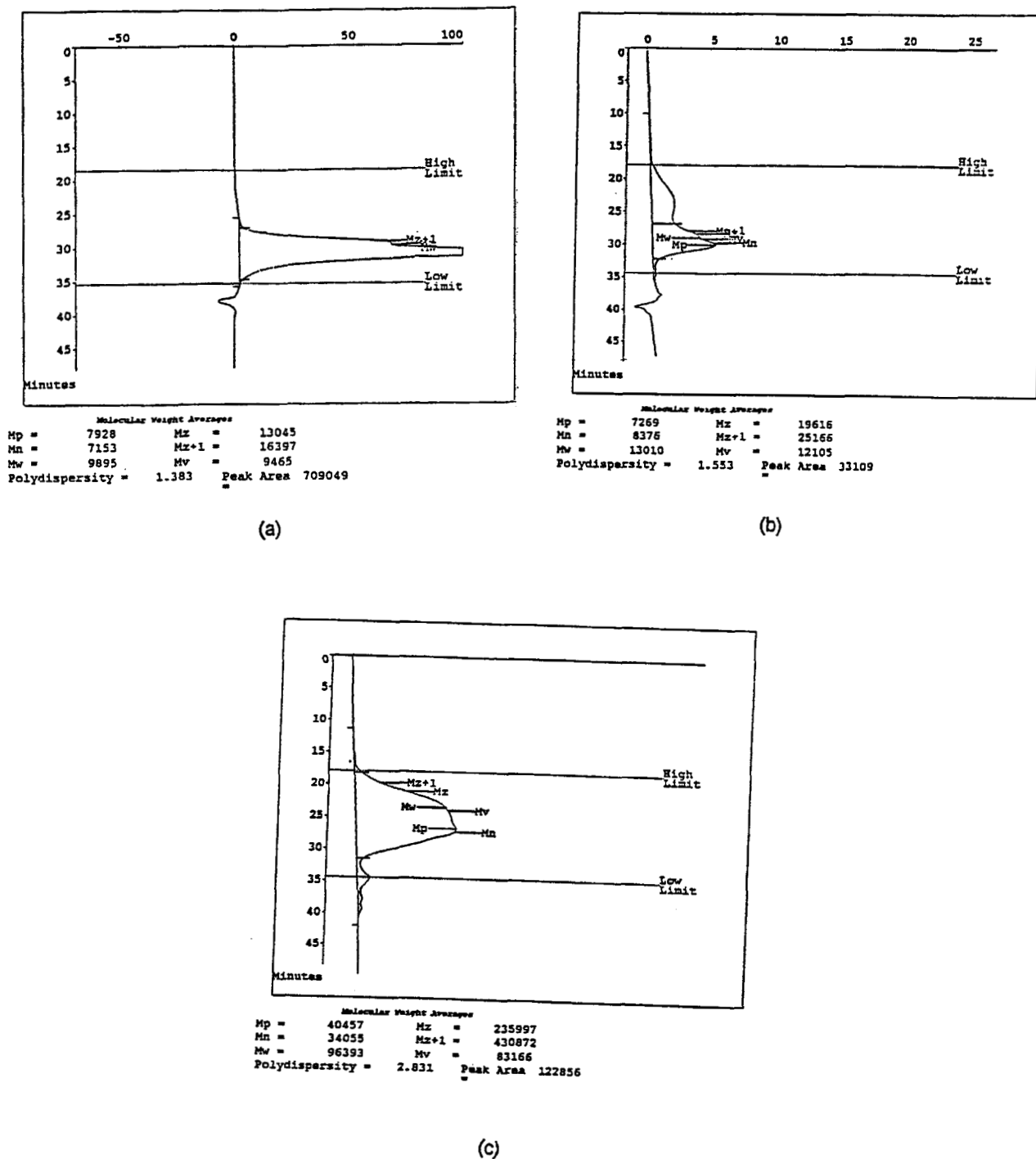
(a)

Molecular Weight Averages

Mp =	7928	Mz =	13045	
Mn =	7153	Mz+1 =	16397	
Mw =	9895	Mv =	9465	
Polydispersity =	1.383	Peak Area	709049	

(b)

Molecular Weight Averages

Mp =	7269	Mz =	19616	
Mn =	8376	Mz+1 =	25166	
Mw =	13010	Mv =	12105	
Polydispersity =	1.553	Peak Area	33109	

(c)

Molecular Weight Averages

Mp =	40457	Mz =	235997	
Mn =	34055	Mz+1 =	430872	
Mw =	96393	Mv =	83166	
Polydispersity =	2.831	Peak Area	122856	

Figure 5 SEC curves of the taken macroinitiator (a), resulting mixture of polymers after the polymerization (b), and purified block copolymer (c) (for sample **XVa** as an example).

strongly stabilizes the formed carbanion both by electron and resonance effects, thus decreasing significantly its reactivity and consequently slowing down the rate of propagation. The copolymer PS-

b-4VBP thus obtained (XV) had the M_n 7150, M_n/M_w 1.38. In according with the elemental analysis of oxygen and based on its M_n, it contained an average of 3.2 benzophenone groups per chain.

The reaction given in Scheme 3 represents preparation of the PS-*b*-4VBP.

Synthesis of Model Macroinitiators of Radical Polymerization

The next step in the preparation of the macroinitiators was the transformation of the benzophenone groups into benzopinacolate ones which are thermolabile and give rise to radical polymerization under heating. This transformation takes place under the action of free benzophenone and trimethylchlorosilane in the presence of hexamethylphosphoramide[11] (Scheme 4). We introduced into this reaction the functionalized polystyrenes **II, III, VIII, X–XIII**, and PS-*b*-4VBP copolymer **XV**. Several precipitations of the resulting polymers after transformation were made to ensure the absence of free benzophenone, which was taken in excess, or free BPC, which was formed as one of the products of this reaction. Thin-layer chromatography confirmed elimination of both of the mentioned compounds. The prepared macroinitiators were analyzed by SEC and NMR methods. The SEC analysis showed that after the transformation, the main characteristics of the polymers (M_n, M_w/M_n) did not change (see Fig. 4, Table II; the numbers of the samples corre-

Table III   Conversion of MMA in Polymerizations Initiated by Polystyrenes Having One (IIa, IIIa, VIIIa) or Two (Xa–XIIIa) Terminal Benzopinacolate Groups

Macroinitiator	MMA Conversion (w/w %)
IIa	57.4
IIIa	42.3
VIIIa	60.0
Xa	35.8
XIa	40.2
XIIa	45.3
XIIIa	38.7

spond to the numbers of polymers before transformation). In the NMR spectra we observed disappearance of the signals of the protons adjacent to carbonyl group (7.3–7.8 ppm) and appearance of a signal at 0 ppm (protons of trimethylsilyl groups in benzopinacolate substituents). IR spectra show the appearance of two peaks at 840 and 1250 cm^{-1} characteristic for the Si(CH$_3$)$_3$ group. Quantitative determination of the yield of transformation of benzophenone groups was made based on the data of elemental analysis (silicone content) in the polymers or from the integral ratios of the signals of
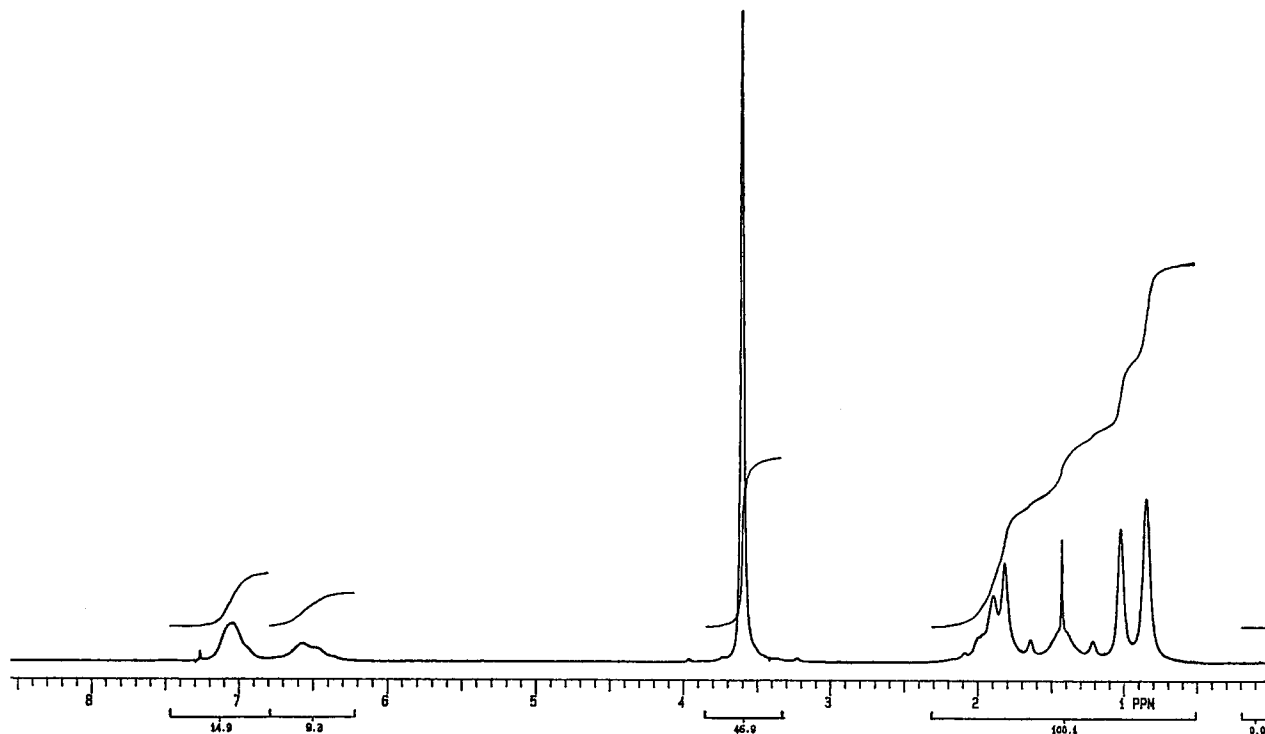

Figure 6 ^{1}H-NMR spectrum of the purified block copolymer PS-*b*-PMMA obtained in polymerization initiated by sample **XVa**.

Table IV   Block Success (U_b), Block Efficiency (ϵ), and Degree of Blocking (π) in MMA Polymerizations Initiated by XVa

Polymerization Time (min)	U_b (%)[a]	ϵ (%)[b]	π (%)[c]	Conversion (%)
7	31.9	100	—	—
14	41.1	100	78.4	15.2
21	41.5	100	82.6	19.8
28	15.5	100	88.9	20.6

[a] U_b = [polystyrene in poly(St-b-MMA)]/(polystyrene initiator) × 100.
[b] ϵ = [PMMA in poly(St-b-MMA)]/(PMMA total) × 100.
[c] π = [PMMA in poly(St-b-MMA)]/(poly(St-b-PMMA) × 100.

trimethylsilyl groups to the signals of aromatic protons.

Synthesis of Block Copolymers Using Prepared Macroinitiators

The ability of benzopinacolate groups to yield free radicals, splitting the C — C bond, has been proved by electron spin resonance (ESR)[12] at temperatures above 70°C. Due to the resonance effect,[13] these radicals are unable to initiate polymerization if the temperature is close to this ceiling temperature. However, at temperatures on the order of 90–100°C, the ability to initiate is increased and polymerization proceeds following a pseudoliving mechanism of chain formation.[14]

To check prepared macroinitiators terminated with BPC groups, we made a series of polymerizations with obtained macroinitiators using methyl-

methacrylate as a monomer. Polymerizations were carried out in the sealed glass tubes in vacuum at 100°C in benzene for 3 h. The resulting polymers were precipitated in methanol and analyzed by SEC, and then precipitated successively from acetonitrile and cyclohexane to remove homopolymers. The residue insoluble both in acetonitrile and cyclohexene represented desirable block copolymer PS-b-PMMA. These copolymers display prominent iridescence in cyclohexane or acetonitrile due to diffraction phenomena resulting from the presence of two discrete phases. This iridescence can be also visible in films obtained by casting.

The first SEC analysis [see Figs. 5(a) and 5(b)] showed a significant decrease of the sharp peak of the initiator and the appearance of a broad peak corresponding to a higher molecular weight. Incomplete disappearance of the peak of the initiator is caused by the fact that the yield of the reaction of
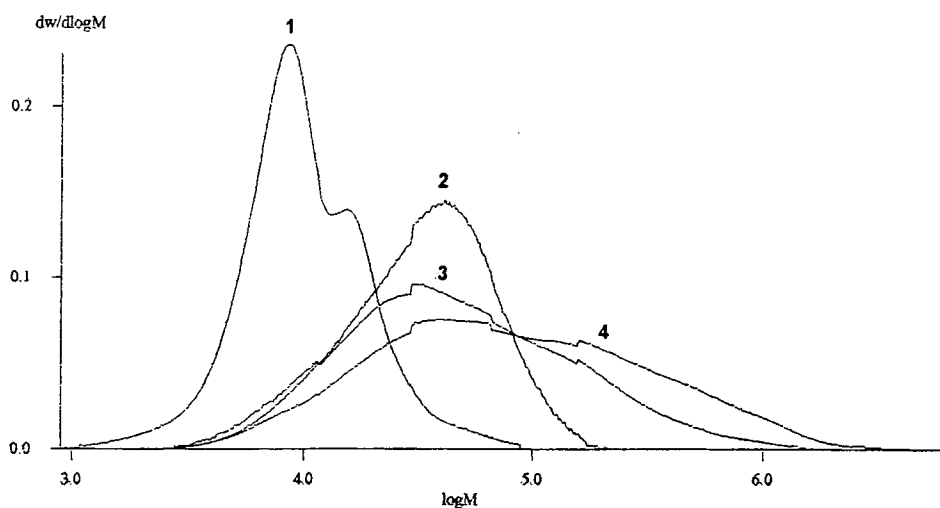

Figure 7   SEC traces of macroinitiator **XVa** (curve 1) and block copolymers obtained using this initiator (curve 2 reaction time 7 min, curve 3 reaction time 14 min, curve 4 reaction time 28 min).

benzopinacolization is on the average about 50–60%,[7] which means that the prepared initiator contains a significant amount of the polystyrene with an untransformed benzophenyl group (which is inert as an initiator), and because of similar solubility it seems to be impossible to separate it from the macroinitiator.

Analysis of the residue after the removal of homopolymers clearly confirms the formation of the block copolymer. ^{1}H-NMR spectra contain both signals of the aromatic protons and a characteristic peak of the methoxy group of MMA (see Fig. 6). The SEC analysis shows a complete disappearance of the peak corresponding to the macroinitiator and contains only a broad peak of the copolymer [see Fig. 5(c)]. The yields of the purified block copolymers are rather low (5–9%). This can be explained as follows: The method of successive removal of the homopolymers by washing with appropriate solvents inevitably also removes part of the formed block copolymers, in which the size of blocks differs considerably. For example, copolymers in which the PMMA block is much longer than the PS one can be also washed out by acetonitrile together with homo-PMMA, and the copolymers in which the PS block is much longer than PMMA can be washed out with cyclohexane. This was confirmed by NMR analysis. The ^{1}H-NMR spectrum of the fraction soluble in acetonitrile contains signals belonging to aromatic protons of the PS chain (two broad signals at 6.3–7.3 ppm). The fraction soluble in cyclohexane also contains signals of PMMA—a sharp singlet at 3.5 ppm. There is no other way to separate the block copolymer from the other products formed in this reaction.

Conversion of the MMA was 43–60% for the monofunctional macroinitiators and 35–45% for the bifunctional ones (see Table III). Conversion of MMA in polymerization initiated by the macroinitiator **XVa** was 50%, which is comparable with conversions in polymerizations initiated with polystyrenes terminated with one or two BPC groups. The fact that the efficiency of macroinitiator prepared from PS-*b*-4VBP copolymers was lower than could have been expected on the basis of larger content of benzophenone groups per polymeric chain can be explained by sterical hindrance (1) for the formation of the adjacent bulky benzopinacolate groups, and (2) for the approach of MMA molecules to adjacent centers of polymerization.

Macroinitiator **XVa** was chosen to undertake kinetic studies in order to verify the living character of the polymerization mechanism. A series of bulk block polymerizations initiated by **XVa** (10% w/w,

110°C, different polymerization times) was carried out. Obtained block copolymers were isolated by successive precipitations from cyclohexane and acetonitrile. Block success (U_b), block efficiency (ε), and degree of blocking (π) were calculated and are quoted in Table IV. In a blank experiment, pure thermal polymerization under similar conditions was found to be lower than 1%.

In the ideal case, U_b (corresponds to the percent of effective polystyrene initiator) should be equal to 100%. The lower values are obtained because of incomplete transformation of the benzophenone group into BPC (in this case 66%) and partial removal of PS during precipitation from acetonitrile, as was explained before. The parameter π indicates the content of PMMA in the block copolymers and is controlled by the ratio macroinitiator/monomer, the average number of BPC per each initiator chain, and polymerization time and temperature. However, the most important parameter is ε, the value of which (100%) indicates the absence of free homopolymethylmethacrylate. The SEC traces of the macroinitiator and obtained block copolymers are shown in Figure 7. It can be seen that purified block copolymers do not contain any inactive polystyrene, but species of higher molecular weight appear in the course of polymerization and their content increases with time. These facts confirm the living character of polymerization initiated by BPC functional groups at least at low conversions.

CONCLUSIONS

A method for synthesis of polystyrenes terminated with one or two benzophenone groups with good yields has been suggested. The method includes anionic polymerization of styrene with mono- or bifunctional initiator, addition of 1,1-diphenylethylene to prevent side reactions, interaction with 2-(4-bromomethylphenyl)-2-phenyl-1,3-dioxolane, and subsequent removal of the protecting group by treatment of the resulting polymer with diluted hydrochloric acid. Synthesized mono- and bifunctional polystyrenes have been transformed into macroinitiators of free radical polymerization by the reaction of coupling of free benzophenone with a terminal one. Prepared macroinitiators have rather narrow MWD (in the range of 1.08–1.44) and have been shown to initiate polymerization of MMA, producing PS-*b*-PMMA. Conversion of MMA is 35.8–60%.

Successive anionic polymerization of styrene and 4-vinylbenzophenone leads to formation of the block copolymer PS-*b*-4VBP. Benzophenone groups in

this copolymer have also been transformed into benzopinacolate ones, and thus prepared macroinitiators have been shown to polymerize MMA, but with efficiency not exceeding that of one of the macroinitiators with one or two terminal BPC groups.

The macroinitiators described in this article can find application in the future investigations dealing with the mechanism of living radical polymerization due to their well-defined structure, which allows us to observe clearly the changes of the molecular weight in the course of the polymerization.

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