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Synthesis of Poly(Styrene)-*block*-poly(methacrylate)-*block*-poly(styrene) via Site Transformation Reaction

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NOTES

SYNTHESIS OF POLY(STYRENE)-*block*-POLY(METHACRYLATE)-*block*-POLY(STYRENE) VIA SITE TRANSFORMATION REACTION

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ABSTRACT

Triblock copolymers with polystyrene outer blocks and an inner polymethacrylate block were synthesized by a site transformation reaction using anionic and cationic polymerization techniques. In order to obtain such ABA block copolymers, two synthetic routes have been applied. In the first case, different methacrylates (methyl methacrylate, 2-ethylhexyl methacrylate) were polymerized anionically with a bifunctional initiator to get poly(methacrylate) dianions later forming the inner block whereas in the second case poly(styrene)-block-poly(methacrylate) anions were synthesized by monofunctional initiation via sequential monomer addition. In a subsequent step, the living chain ends of the methacrylate dianions on one side, and the diblock copolymer anions on the other side, were functionalized with 1,4-bis(1-bromoethyl)benzene in order to obtain a potential bifunctional or monofunctional macroinitiator for the cationic polymerization of styrene. Then, styrene was polymerized cationically with the macroinitiator in the presence of $SnCl_4$ as coinitiator and $n\text{Bu}_4\text{NBr}$ as a common ion salt in CH_2Cl_2 at -15°C. Block formation was proven by SEC measurements, preparative SEC and NMR characterization.

INTRODUCTION

Since Szwarc's discovery, block copolymers, with well-defined structure and various compositions, have been synthesized using living polymerization techniques [1,2]. Living polymerization is a unique tool for the synthesis of polymers, which provide certain molecular weight, narrow molecular weight distribution and a well defined microstructure. Although the majority of block copolymers was polymerized anionically, great progress was reached in the field of cationic polymerization during the last decade [3,4]. Up to now, first successful attempts were made to synthesize block copolymers via "living" radical polymerization [5,6].

The aim of this work was the synthesis of triblock copolymers with outer polystyrene blocks and an inner poly(methacrylate) block. In case that the poly(methacrylate) block has a low glass transition temperature, such products could act as thermoplastic elastomers. In contrast to SBS, these triblock copolymers are resistant to ozone and UV-radiation because of the saturated inner block. While styrene and methacrylates can be polymerized anionically to well-defined diblock copolymers, such triblock copolymers are not accessible by a simple sequential monomer addition because the nucleophilicity of the living poly(methacrylate) chain end is not sufficient to initiate the polymerization of styrene [2]. One synthetic route to the desired triblock copolymers is a coupling reaction of diblock polyanions with a bifunctional electrophilic compound [7]. Examples for coupling agents for poly(methacrylate) anions are different dibromoxylenes [8]. However, coupling reactions are not quantitative in many cases, especially with higher molecular weight polyanions, because an exact molar amount of the coupling agent must be added and/or living chain ends will be deactivated by impurities.

In order to obtain block copolymers of such monomers which polymerize by different mechanisms, site transformation techniques for a wide range of monomer combinations were developed [9]. Styrene can be polymerized anionically [1] as well as cationically [10-12] in a living manner. This publication presents the results of an anionic to cationic site transformation as an alternative synthetic route for the preparation of triblock copolymers poly(styrene)-*block*-poly(methacrylate)-*block*-poly(styrene).

EXPERIMENTAL

Reagents and Solvents

Methyl methacrylate (MMA) and 2-ethylhexyl methacrylate (EHMA) were dried over CaH_2 for several days. Before polymerization, a 0,8 M solution of *i*Bu_3Al in hexane was added to the monomer until a persistent yellowish green color was observed [13] and then distilled under reduced pressure after some Koelsch radical was added. Styrene was treated with a 10 wt-% sodium hydroxide solution, washed with distilled water and dried over $CaCl_2$. Then it was distilled over copper metal under reduced pressure and stored over CaH_2 at 5°C. 1,1-Diphenylethylene (DPE, Fluka) was treated with sec-butyllithium (*s*BuLi) until a deep red color occurred, which indicates the formation of 1,1-diphenyl-3-methylpentyllithium, and distilled under reduced pressure. Tetrahydrofuran (THF) was purified by refluxing over a fresh sodium/benzophenone complex. CH_2Cl_2 was refluxed over CaH_2 and distilled prior to use. LiCl (99,99%, Aldrich) was dried at 120°C for at least 10 hours in vacuum and dissolved in dry THF. *n*Bu_4NBr (99%) was used without further purification after drying in vacuum. $SnCl_4$. was distilled under reduced pressure prior to use. 1,4-Bis(1-bromoethyl)benzene (BBrEB) was prepared according to [14] in a modified manner by reacting 1,4-bis(1 - hydroxyethyl)benzene and PBr_3 in $CHCl_3$. Recrystallization of the crude product from heptane was carried out three times. Furthermore, BBrEB was sublimed prior to use. BBrEB: yield 80%, ^1H NMR ($CDCl_3$) δ 2,02 (6H, d, CH_3), δ 5,17 (2H, q, CH), δ 7,39 (4H, s, ArH), ^{13}C NMR ($CDCl_3$) δ 26,65 (CH_3), δ 48,74 (CH), 127,13 (ArCH), δ 143,25 (ArC).

The monofunctional initiator sec-butyllithium (*s*BuLi) was prepared by reacting sec-butyl chloride with lithium wire in cyclohexane at 37°C. The bifunctional initiator 1,1,4,4-tetraphenylbutyldilithium (TPBLi) is the reaction product of DPE and lithium in THF at 0°C.

Polymerization Procedure

Polymerizations were carried out in carefully flamed glass reactors under inert argon atmosphere using syringe technique.

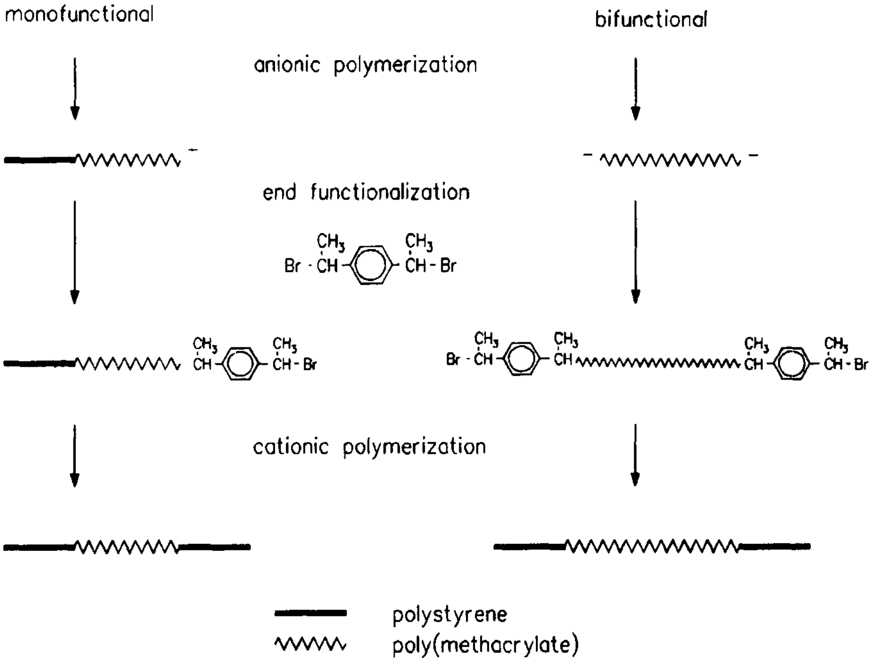
Anionic polymerization: a) monofunctional initiation; after several cycles of degassing styrene was introduced into the reactor by condensation under reduced pressure. THF was condensed from polystyrene anions into the reactor. Then LiCI ($n_{LiCl} = 5\ n_{BuLi}$) and the required amount of *s*BuLi (diluted with toluene) were added at -78°C. After 15 minutes, the living chain ends were capped with DPE and MMA was added dropwise. b) bifunctional initiation; in the case of TPBLi, the required amount EHMA was added to a solution of the initiator and LiCI (n_{LiCl} = 10 n_{TPBLi}) in THF. After completion of methacrylate polymerization, triple the molar amount of BBrEB (dissolved in dry THF) to initiator was added to the reaction mixture in order to functionalize the living chain ends. After 12 hours, the polymers were precipitated in cold methanol, dried under vacuum and extracted with *n*-heptane at T < -50°C in order to remove the excess BBrEB, then dissolved in 2-butanone and reprecipitated. Cationic polymerization: CH_2Cl_2, $n Bu_4NBr$, $SnCl_4$ and finally fresh condensed styrene were added to the ω-functionalized PS-*b*-PMMA or α,ω-functionalized PEHMA, respectively. The solution was stirred at -15°C for 20 hours. The polymers were precipitated in CH_3OH/diluted hydrochloric acid.

Characterization

Molecular weights and molecular weight distributions were determined by size exclusion chromatography (SEC) in THF using a Knauer SEC with a refractive index/viscosity detector and a PSS 10^3 Å column or a PSS linear column. ^1H NMR spectra were recorded on a Bruker 200 spectrometer, ^{13}C NMR spectra under inverse gated decoupling conditions at 125,7 MHz on a Varian 500 spectrometer.

RESULTS AND DISCUSSION

Block copolymers were synthesized according to Scheme 1. Both synthetic routes, the method of monofunctional initiation and the bifunctional one, were used in order to synthesize triblock copolymers ABA with outer polystyrene blocks (A) and an inner poly(methacrylate) block (B). The monofunctional initiation was chosen considering the fact, that in the polymerization of styrene with an bifunctional macroinitiator it can not be proven by SEC measurements whether a triblock copolymer was obtained. In the case of the bifunctional macroinitiator, the formation of only diblock polymer is possible too because of an incomplete introduction of the functional end groups or termination reactions. Diblock copolymers AB were synthesized anionically with *s*BuLi as initiator in presence of LiCl [15]; the poly(methacrylate) was prepared with the bifunctional initiator TPBLi. The polymerization was terminated with 1,4-bis(l-bromoethyl)benzene (BBrEB) in order to introduce a 1-bromoethylbenzene end group. 1-Bromoethylbenzene, in combination with a Lewis acid as coinitiator, is able to initiate the living cationic polymerization of styrene [16,17]. The end functionalization was carried out with a molar excess of BBrEB to the living chain ends. The end group functionality of α,ω–functionalized polymers was determined by the use of ^1H-NMR spectroscopy comparing the intensity of aromatic protons of the initiator molecule (δ= 6,7 - 7,2 ppm) with the intensity of one of the end group protons (CH) (δ = 5,17 ppm). For



scheme 1

sample B57 (Table 2), an almost quantitative functionalization of more than 90% was found. For polymers with higher molecular weight only a qualitative proof of the end functionalization was possible. In the case of functionalized diblock copolymers AB, the introduction of the end group was shown by ^{13}C-NMR characterization. Figure 1 presents the ^{13}C-NMR spectrum of sample AB25 (Table 1).

It was proven that the living anionic chain end could be functionalized with BBrEB, although only a qualitative proof was possible.

The purified mono- and bifunctional polymers were used as macroinitiators in the cationic polymerization of styrene. The problem of controlling the concentration of initiating groups $[C^+]_O$ resulted from the difficulties in determining the end group functionality. A quantitative functionalization was assumed for the calculation of the concentration of initiating groups $[C^+]_O$. That concentration should exceed $[C^+]_O \geq 0{,}005$ M.

According to experiments to the cationic homopolymerization of styrene with 1-bromoethylbenzene or BBrEB/$SnCl_4$/nBuNBr$_4$ a styrene concentration $[S]_O$

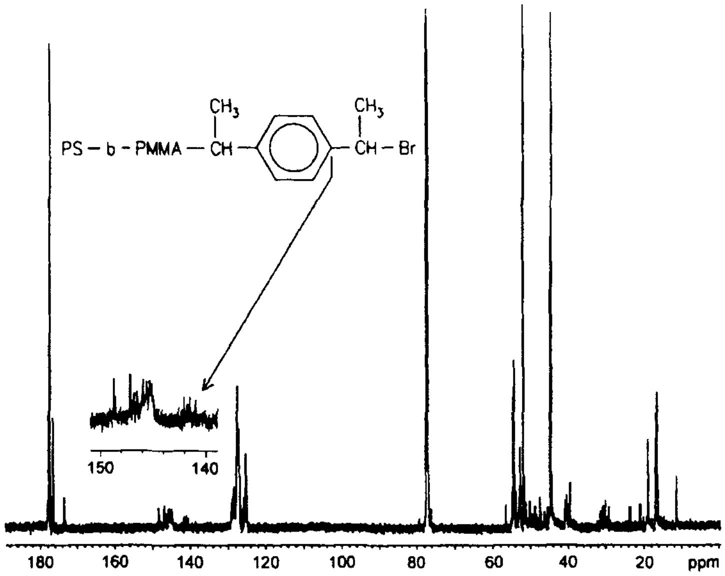


Figure 1. ^{13}C-NMR spectrum of a functionalized diblock copolymer (sample AB25).

TABLE 1: Cationic Polymerization of Styrene with Functionalized Diblock Copolymers

sample	time (h)	AB[a] (g)	S_O (mole) $*10^3$	$SnCl_4$ (mole) $*10^3$	Bu_4NBr (mole) $*10^3$	solv[b] (ml)	$M_{n(SEC)}$ (g/mole)	D	PS[c] (%)	conv.[d] (%)
AB25 [e]							3000	1,15	20	
ABA25/1	15	1	7	5,38	2,17	8	6300	1,36	52	92
ABA25/2	15	1	2	1,15	0,456	11	3500	1,16	33	91
AB50[f]							20500	1,08	15	
ABA50	20	0,8	2	4,1	1,65	6	24500	2,1	25	51
AB51[f]							19800	1,08	10	
ABA51	20	1	3,9	4,61	1,25	6,5	30300	2,4	35	92

CH_2Cl_2, polymerization temperature: -15°C; AB = macroinitiator, ABA = triblock copolymer; [a] amount of diblock copolymer AB as macroinitiator; [b] solvent CH_2Cl_2; [c]polystyrene content of the final product in wt.% (^{1}H-NMR); [d]converstion of styrene,determined by ^{1}H-NMR; [e]PS-*b*-PMMA; [f]PS-*b*-PEHMA; D = M_w/M_n

TABLE 2: Molecular Weight and Polydispersities of the Macroinitiator and the ABA Block Copolymer

sample	V_e[a] (ml)	$M_{n(SEC)}$ (g/mole)	$M_{w(SEC)}$ (g/mole)	D	PS[b]
B 57	10,54	6400	7870	1,23	-
ABA 57	9,826	13600	29600	2,18	70

[a] elusion volume (SEC), peak maximum, [b] wt.% PS, ^{1}H-NMR

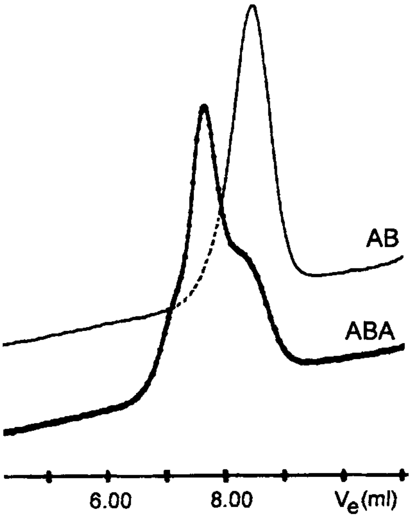


Figure 2. SEC elusion curves of samples AB25 and ABA25/1.

= 0,5 - 1,0 M was found to be suited to reach a sufficient fast polymerization rate. The results of the cationic polymerization of styrene with different monofunctional macroinitiators PS-*b*-PMMA, PS-*b*-PEHMA and an α,ω-functionalized PEHMA as initiator which were obtained by anionic polymerization and end group functionalization are listed in Tables 1 and 2.

Block formation was proven by SEC measurements. Figure 2 shows the SEC chromatograms of the final product ABA25/1 and the macroinitiator AB25 (Table 1), which were polymerized according the monofunctional synthetic route in Scheme 1.

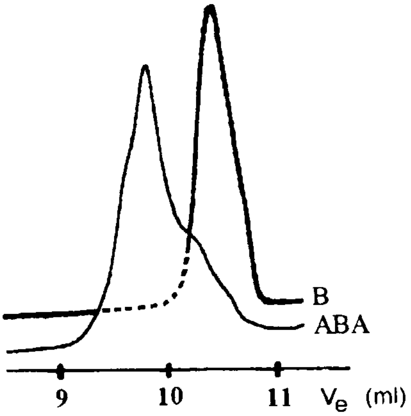


Figure 3a. SEC elusion curves of the macroinitiator B 57 and the final product ABA 57.

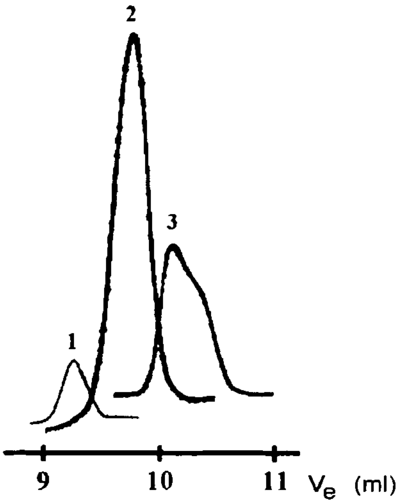


Figure 3b. SEC curves of the three fractions (1-3) of ABA 57 prepared by preparative HPLC.

Although a small amount of diblock copolymer is still present in the final product, the formation of triblock copolymer PS-*b*-PMMA-*b*-PS with a low polydispersity is obvious. The increase in molecular weight is the result of the formation of desired triblock copolymer. In separate experiments styrene was polymerized cationically with 1-bromoethylbenzene/$SnCl_4$/*n*$BuNBr_4$ in the presence of non functionalized homopolymers PMMA and PEHMA. Polystyrene with a narrow molecular weight distribution (M_n = 9100 g/mole, D = 1,15) was obtained and no grafting-from reaction of styrene on the poly(methacrylate) chain occurred.

The polymer samples ABA50 and ABA5 1 (Table 1) made with a macroinitiator AB of $M_n \approx 20000$ g/mole have broader molecular weight distributions. That result is probably caused by the higher polymer concentration in solution which possibly causes a more difficult and different accessibility of active carbocationic centres for styrene molecules. The conversion of styrene is not quantitative and a prolongation of polymerization time did not result in higher conversions. This observation may be due to transfer or termination reactions.

In the case of an α,ω–functionalized PEHMA as macroinitiator, a product with broader molecular weight distribution was obtained in cationic styrene polymerization (Table 2). Obviously, this is the result of the formation of triblock copolymer and a small amount of diblock copolymer (Figure 3a).

The crude final product ABA 57 (Table 2) was divided into three fractions (1-3) by preparative HPLC (Figure 3b) and the fractions were investigated by ^{1}H-NMR. All fractions contain between 19 and 32 wt.% PEHMA. This fact proves the formation of block copolymers.

In conclusion, triblock copolymers with outer polystyrene blocks and an inner PMMA or PEHMA block can be synthesized by a site transformation reaction using anionic and cationic polymerization techniques. Triblock copolymers were obtained via monofunctional as well as bifunctional initiation.

However, this synthetic route requires a great deal of care over the removal of surplus 1,4-bis(1-bromoethyl)benzene (BBrEB) after functionalization of the living methacrylate chain ends because otherwise polystyrene homopolymer is formed. An uncomplete functionalization of the macroinitiator inevitably leads to a triblock copolymer which contains traces of diblock copolymer.

Nevertheless, the above represented synthetic routes are limited since the starting concentration for styrene [S] and the initiator groups [C^+] only could have been varied within a small range. A decrease in the concentration of styrene and initiator groups at the beginning of the cationic polymerization resulted in a strongly reduced polymerization rate.

Even after long polymerization times (t > 40h), the use of macroinitiators with higher molecular weight (M_n > 20000 g/mole) only leads to a small styrene conversion. The reason for this may be due to the more difficult accessibility of active carbocationic centers for the styrene molecules as well as transfer or termination reactions.

It might be concluded that the synthetic routes described above (site transformation anionic → cationic) apparently are only suited for the synthesis of triblock copolymers with relatively small molecular weight.

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