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Comb-like triblock copolymers by Wurtz-Grignard coupling of syndiotactic PMMA anions to poly[(*p*-bromomethyl)styrene]-*b*-polyisobutylene-*b*-poly[(*p*-bromomethyl)styrene]

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Summary

Poly[(*p*-bromomethyl)styrene]-*b*-polyisobutylene-*b*-poly[(*p*-bromomethyl)styrene]s prepared by sequential monomer addition technique of living cationic polymerization were connected with living syndiotactic (*st*)-poly(methyl methacrylate) macroanions *via* Wurtz-Grignard-type coupling. In nonpolar medium (toluene), the coupling resulted in the formation of chemically crosslinked network. In polar solvent (tetrahydrofuran), however, a comb-like triblock copolymer with properties of thermoplastic elastomer was obtained.

Introduction

Triblock copolymers comprising rubbery polyisobutylene (PIB) middle segment and glassy poly(methyl methacrylate) (PMMA) end segments have been routinely synthesized by transforming the PIB chain ends into initiating sites for anionic polymerization of methyl methacrylate (MMA). Recently, PMMA-*b*-PIB-*b*-PMMA copolymers with syndiotactic (*st*-)[1] or isotactic (*it*-)[2] PMMA segments were prepared from α,ω–dilithiated PIB diisobutyrate. Kennedy and Price[3] have designed another cationic-to-anionic site transformation procedure for the synthesis of these triblock copolymers with predominantly syndiotactic PMMA outer blocks.

The common feature of these methods is that they include many steps, which has adverse effect on the overall yield even if the starting telechelic PIB with tertiary chlorines has perfect functionality (f=2). Multiple endgroup modification of high molecular weight PIB is rather tedious.

In this paper we propose a time-saving alternative to the earlier methods for connecting PIB and PMMA chains. First, by using the sequential monomer addition technique of living cationic polymerization, triblock copolymer with a middle PIB segment and short poly[*p*-bromomethyl)styrene] (poly(*p*-BMST)) blocks, poly(*p*-BMST)-*b*-PIB-*b*-

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poly(*p*-BMST) was prepared in a single process. In the second step living PMMA macroanions were connected to both ends of the PIB chain by Wurtz-Grignard coupling *via* the bromomethyl functional groups. In this triblock copolymer, the number of PMMA blocks should depend on the number of *p*-BMST unit on both ends of PIB prepolymer and the coupling efficiency. Although the polymer is not a simple triblock copolymer, it is called triblock copolymer for the simplicity.

In designing the method we made extensive use of the earlier results of Kennedy's group concerning triblock copolymer syntheses by sequential monomer addition.[4-8] Coupling of living PMMA to *p*-BMST was first reported by Anderson et al.[9] and was successfully performed in our laboratory in order to prepare highly isotactic and syndiotactic PMMA macromonomers with styrene end-group.[10]

In addition to its simplicity, this two-step process offers another advantage. Since the main constituents of the final structure, that is the PIB and PMMA chains, are prepared independently of each other, their chain length and stereoregularity (in the case of PMMA) can be precisely tailored before the coupling reaction takes place. Keeping in mind that the length of the individual segments (PIB, poly(*p*-BMST), PMMA) can be varied in a broad range, a fairly large array of triblock copolymers with possible thermoplastic elastomer properties can be prepared.

This publication reports the preparation of the first few examples of *st*-PMMA-*b*-PIB-*b*-*st*-PMMA triblock copolymers.

Experimental

Materials

5-*tert*-butyl-1,3-bis(1-chloro-1-methylethyl)benzene was prepared from 1-*tert*-butyl-3,5-dicarboxylbenzene (Amoco Chemicals Co.) as reported earlier.[11] Isobutylene (Tokyo Kasei) was dried by passing through Drierite-column and condensed prior to polymerization. (*p*-Bromomethyl)styrene was synthesized as described in Reference 10. Methylene chloride (Nacalai Tesque) and methylcyclohexane (Tokyo Kasei) were purified in the same way by refluxing over conc. H_2SO_4 for 24 h, washing with distilled water to neutrality, drying for 48 h on Molecular Sieves 4A, refluxing for 12 h, and distilling from calcium dihydride under nitrogen atmosphere. Titanium tetrachloride and 2,6-di-*tert*-butylpyridine (DTBP) (Aldrich) were used as received. Methyl methacrylate (MMA) was purified by fractional distillation, dried over calcium dihydride, and distilled *in vacuo* prior to polymerization. Treatments of toluene and tetrahydrofuran(THF) were the same as reported previously.[12] *tert*-Butyllithium (*t*-BuLi) and *n*-butyllithium (*n*-BuLi) (Aldrich) were used in heptane solution. 1,1-Diphenylethylene (Aldrich) was used after dried over calcium dihydride and distilled under vacuum.

Preparation of poly(*p*-BMST)-*b*-PIB-*b*-poly(*p*-BMST)

Polymerization of IB was carried out in 100 ml total volume at -78°C in a baked and nitrogen-filled 500 ml glass ampoule equipped with 3-way stopcock. The solvent was a mixture of methylcyclohexane and methylene chloride in 60/40 volume ratio. Starting concentrations: [IB] = 1.1 M and 1.6 M (for the preparations of PIB with molecular weight of 60000 and 90000, respectively); [5-*tert*-butyl-1,3-bis(1-chloro-1-methylethyl)benzene] = 1×10^{-3} M; [$TiCl_4$] = 3.6×10^{-2} M; [DTBP] = 2×10^{-3} M. Polymerization began upon injecting $TiCl_4$ as the last component. During the polymerization vigorous stirring was maintained by magnetic stirrer. After 30 min of the polymerization 0.2 ml of *p*-BMST (1.0 mmol) was added to the living polymerization system in one shot. The color of the system changed immediately from pale yellow to intensive red, which indicated the change of the propagating chain end structure from PIB^+ to $p\text{-}BMST^+$. After 10 min the polymerization was terminated by injecting 1 ml of prechilled methanol into the reaction mixture. The polymer formed was precipitated by pouring the reaction mixture into a large amount of methanol. The crude product was purified by redissolving in toluene and repeated precipitation in methanol. Traces of *p*-BMST homopolymer were removed by extraction with methyl ethyl ketone. ^1H NMR spectrum of the resulting triblock copolymer showed that each chain contained 12 p-BMST units, i.e., in average 6 units at both ends (Figure 1), that is a little larger than but close to the expected value of 5 units.

Preparation of *st*-PMMA-*b*-PIB-*b*-*st*-PMMA triblock copolymers

A 50 ml glass ampoule was baked under vacuum and then filled with dry nitrogen. Ten ml of toluene was vacuum distilled into it, and then 0.6 ml of $(n\text{-}Bu)_3Al$/heptane solution ([$(n\text{-}Bu)_3Al$]=0.935 M) was injected *via* a three-way stopcock attached to the ampoule. The mixture was cooled to -78°C, and 0.2 ml *t*-BuLi/heptane solution ([*t*-BuLi]=0.932 M) was introduced. The polymerization started by adding the monomer (MMA, 1.07 ml (=10 mmole)) slowly to the polymerization mixture. After 24 h the toluene solution of 2 grams of poly(*p*-BMST)-*b*-PIB-*b*-poly(*p*-BMST) was mixed with the living PMMA system. After 12 h at -78°C the reaction mixture was inspected. As a result, crosslinked gel formed, from which the PMMA was not extractable by acetone.

The coupling experiments were repeated in THF medium to avoid crosslinking. *n*-BuLi was added to equimolar 1,1-diphenylethylene in THF at room temperature under dry nitrogen atmosphere (amounts are listed in Table 1). Immediate deep red coloration indicated the formation of the initiating species; 1,1-diphenylhexyllithium. After 1 h the initiator solution was cooled to -78°C, then MMA was added dropwise ito the solution during vigorous shaking. Upon the addition of monomer the deep red coloration immediately disappeared and fast polymerization of MMA started. After 2 h of polymerization, poly(*p*-BMST)-*b*-PIB-*b*-poly(*p*-BMST) dissolved in dry THF was added dropwise to the living PMMA system during vigorous shaking. Since the prepolymer freezed out of the solution at -78°C, the temperature of the system was allowed to rise near 0 °C in order to redissolve the precipitate. After complete dissolution the ampoule was kept at -78°C (Sample 1) or -60°C (Samples 2 and 3) for 12 h.

During the coupling reaction no gel formation was observed. The reaction mixture was poured into MeOH containing 1 mol % HCl. The product was dried, and extracted subsequently with *n*-hexane and with acetone.

^{1}H NMR spectrum showed the presence of both PMMA and PIB sequences in the product. Block copolymer composition was obtained from the intensity ratio of the methoxy peak of PMMA (3.6 ppm) to the methylene peak of PIB (1.42 ppm) (Figure 2).

Measurement

^{1}H NMR measurements of the block copolymers were performed on a JNM GSX-270 NMR spectrometer at 270 MHz. Gel permeation chromatograms were recorded on a JASCO 880-PU instrument equipped with Shodex GPC columns of KF-80M (30 cm x 0.80 cm) and KF-802.5 (30 cm x 0.80 cm) with maximum porosities of 2 x 10^7 and 2 x 10^4, respectively using tetrahydrofuran as an eluent. Column temperature was maintained at 40.0°C. The eluent was THF. The chromatograms were calibrated against standard polystyrene samples.

Results and Discussion

In a nonpolar solvent (toluene) the coupling reaction resulted in the formation of crosslinked product. Most probably interchain coupling takes place between the lithiated ($-CH_2Li$) and non-lithiated bromomethyl groups. In this medium the lifetime of the intermediate radical species $-CH_2\cdot$ presumed in the coupling reaction may be long enough to allow these moieties to diffuse into the proximity of each other. Since the acetone extraction did not give PMMA, the main reaction pathway was the coupling between $-CH_2Br$ and $PMMA^-Li^+$.

The products obtained from the coupling reaction carried out in THF were soluble, comb-like triblock structures. Coupling efficiency depended on the molecular weights of the triblock prepolymer and of the PMMA, as well as on the temperature. It can be explained by the low solubility of PIB in THF at -78°C. Indeed, after mixing the solution of the triblock prepolymer poly(*p*-BMST)-*b*-PIB-*b*-poly(*p*-BMST) with

Table 1 Preparation and characterization of PMMA-*b*-PIB-*b*-PMMA triblock copolymer

Sample	MMA Polymerization[a]					PIB prepolymer			Triblock copolymer					
	Initiator[b] (mmol)	MMA (mmol)	THF (ml)	$\overline{Mn}$ (GPC)	$\overline{Mw}^c/\overline{Mn}$	Weight (g)	$\overline{Mn}$ (GPC)	$\overline{Mw}^c/\overline{Mn}$	PMMA in copolymer[d] (wt%)	$\overline{Mn}$ (GPC)	$\overline{Mn}$ (NMR)	$\overline{Mw}^c/\overline{Mn}$	N[e]	eff.[f] (%)
1	3.2	40	160	1250	1.42	2.000	90000	1.18	5.6	94000	95000	1.22	3.2	40
2	0.4	10	20	2500	1.28	0.245	90000	1.18	23	106000	110000	2.21	6.4	80
3	0.2	20	20	10000	1.19	0.193	60000	1.21	43	82000	86000	2.54	2.2	40

[a] Polymerization temperature -78℃, time 2hr. [b] Initiator prepared form equimolecular amounts of n-BuLi and 1,1-diphenylethylene in THF at room temperature. [c] Determined by GPC. [d] Determined form the intensity ratio of the ^{1}H NMR signals due to methoxy protons (3.6ppm) of the PMMA segment and the methylene protons (1.42ppm) of the PIB segment.

[e] Number of branches calculated from the $\overline{Mn}$ increment from the starting PIB prepolymer. [f] Coupling efficiency calculated from composition of the coupling product and $\overline{Mn}$ of the starting PIB prepolymer.

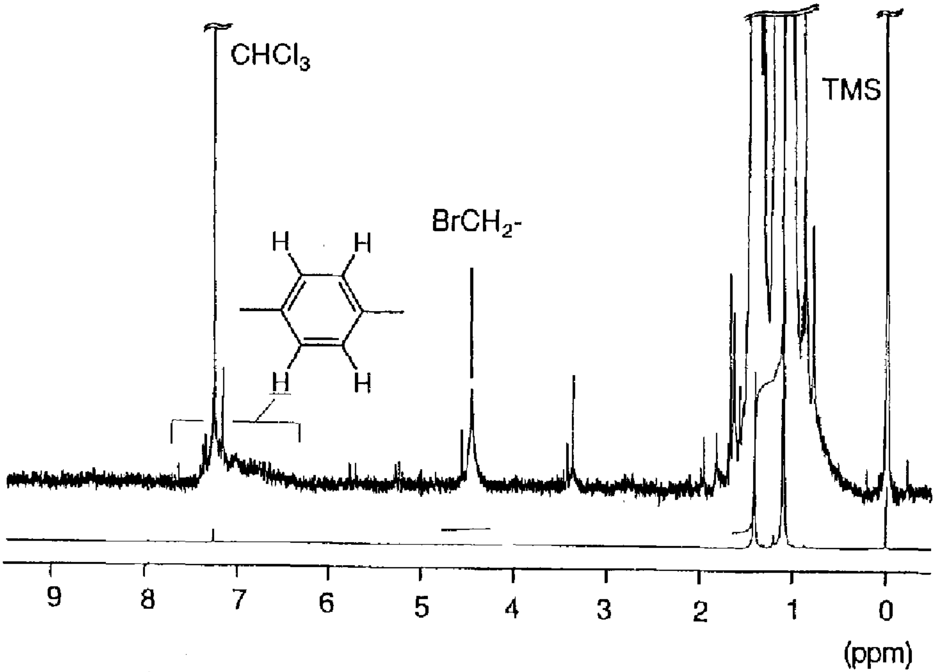

Figure 1 ^{1}H NMR spectrum of the poly[(*p*-bromomethyl)styrene]-*b*-PIB-*b*-poly[(*p*-bromomethyl)styrene] ($\overline{M}$n=90000) measured in $CDCl_3$ at 35°C

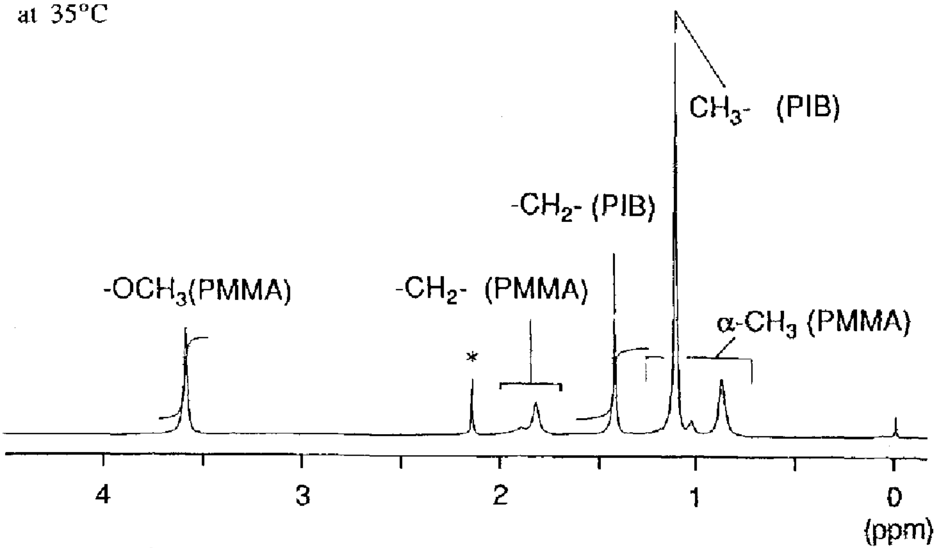

Figure 2 ^{1}H NMR spectrum of *st*-PMMA-*b*-PIB-*b*-*st*-PMMA triblock copolymer (Sample 3) measured in $CDCl_3$ at 55°C
* Impurity

the living PMMA solution, a white suspension formed and persisted at -78°C. By warming up the system to -60°C the haziness disappeared completely.

The solubility of the products depends on the PMMA content, too. Similarly to PIB, Sample 1 was soluble in hexane and insoluble in acetone. The PMMA content was not extractable even during a 24 h extraction in boiling acetone. *st*-PMMA-*b*-PIB-*b*-*st*-PMMA triblock copolymers with higher PMMA content (Samples 2 and 3) were insoluble in acetone as well as in hexane. As a matter of fact, acetone extraction removes not only PMMA homopolymers, but also *st*-PMMA-*b*-PIB-*b*-*st*-PMMA triblocks with very short PIB middle segment. These kinds of structures are derived from low molecular weight prepolymers which account for the low molecular weight tail of the GPC plot (Figure 3). Visual inspection showed that Samples 1 and 2 were, unlike the starting prepolymer, rubbery and non-sticky products, whereas Sample 3 was a white, brittle powder.

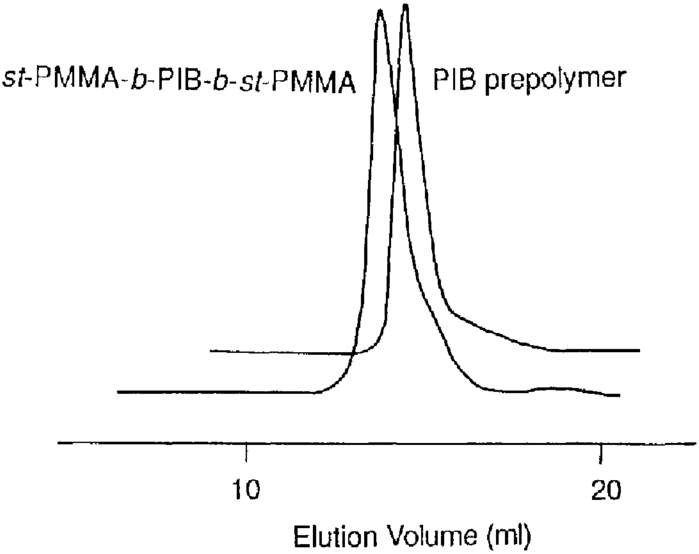

Figure 3 GPC curves of *st*-PMMA-*b*-PIB-*b*-*st*-PMMA triblock copolymer (Sample 2) and the starting poly[(*p*-bromomethyl)styrene]-*b*-PIB-*b*-poly[(*p*-bromomethyl)styrene] (PIB prepolymer)

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