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Synthesis of Linear and Star-Shaped Block Copolymers of Isobutylene and Methacrylates by Combination of Living Cationic and Anionic Polymerizations

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ABSTRACT: A new synthetic route for the preparation of polyisobutylene (PIB)-based linear and star-shaped block copolymers was developed by combining living carbocationic and anionic polymerizations. Living PIB chains were quantitatively endcapped with 1,1-diphenylethylene, leading to 1,1-diphenyl-1-methoxy (DPOMe) or 2,2-diphenylvinyl (DPV) termini, or both. Both the DPOMe- and DPV-terminated PIBs, and the mixtures of both endgroups were quantitatively metalated with K/Na alloy, Cs metal, or Li dispersion in THF at room temperature. The resulting stable macrocarbanion obtained by metalation with K/Na alloy was used to initiate living anionic polymerization of *tert*-butyl methacrylate (tBMA) yielding PIB-*b*-PtBMA block copolymers with nearly quantitative blocking efficiency. Hydrolysis of the ester groups by HCl in dioxane resulted in amphiphilic polyisobutylene-*block*-poly(methacrylic acid) block copolymers. Replacing K^+ with Li^+ by excess LiCl gave a PIB macroinitiator suitable for anionic polymerization of methyl methacrylate (MMA). A series of linear PMMA-*b*-PIB-*b*-PMMA block copolymers and of star-shaped PIB-*b*-(PMMA)$_3$ block copolymers were successfully synthesized by telechelic PIB macroanions with high blocking efficiencies. Characterizations of these new thermoplastic elastomers were carried out by SEC, DSC, dynamic−mechanical, and stress−strain measurements.

Introduction

Living polymerizations provide the most versatile synthetic routes for the preparation of a wide variety of well-defined polymer structures. Macromonomers and telechelic polymers are usually obtained by quantitative end-quenching of living chain ends and, sometimes, by further end-functionalization of end-quenched polymer chains. Sequential addition of different monomers yields block copolymers which are also of great scientific and commercial importance. Since specific living polymerization methods (e.g., living anionic and carbocationic polymerizations) are applicable only to a limited number of monomers, the combination of different living polymerization techniques is expected to lead to new and unique, otherwise unavailable, polymer architectures.

In recent years, there have been significant developments in the field of living carbocationic polymerization (LCCP) of vinyl monomers, such as isobutylene (IB), styrene and its derivatives, and vinyl ethers, leading to a wide variety of functional polymers (for recent reviews, see refs 1−4). Due to the attractive properties of polyisobutylene (PIB), available only by carbocationic polymerization, coupling this hydrophobic and thermally, oxidatively, and hydrolytically stable polymer, with a low T_g, to a variety of other chain segments is expected to result in new and useful products. For instance, methacrylate-telechelic PIB (MA-PIB-MA), obtained by LCCP and subsequent chain end derivatization, has been successfully used to synthesize novel amphiphilic networks by radical copolymerization of MA-PIB-MA with a variety of monomers, such as *N*,*N*-dimethylacrylamide and 2-[(trimethylsilyl)oxy]ethyl methacrylate, a protected 2-hydroxyethyl methacrylate (HEMA).[1,5−7]

Several attempts have also been made to obtain block copolymers by utilization of end-functionalized PIBs as macroinitiators for living anionic polymerization in order to synthesize new and useful thermoplastic elastomers (TPEs). One attempt used isobutyrate-telechelic PIB, which was prepared by the following reaction sequence: Living polymerization of isobutylene yielded *tert*-chlorine-telechelic PIB (ref 1 and references therein), and then the *tert*-chlorine chain ends were quantitatively converted to isobutenyl endgroups by quantitative dehydrochlorination[8] or, alternatively, allyl-telechelic PIB was prepared by direct end-quenching of LCCP of isobutylene by allyltrimethylsilane.[9] Both olefin termini can be quantitatively converted to primary hydroxyl chain ends by hydroboration followed by oxidation.[9,10] Reacting hydroxyl-telechelic PIB with isobutyroyl chloride gave isobutyrate-telechelic PIB.[11,12] Lithiation of these isobutyrate-telechelic PIBs with lithium diisopropylamide (LDA)[11,12] was reported to lead to initiation of methyl methacrylate (MMA) polymerization for the synthesis of PMMA-*b*-PIB-*b*-PMMA block copolymers. The isobutyrate endgroups were also converted to silyl ketene acetal chain ends, which subsequently were used to initiate group transfer polymerization of MMA.[13]

In another approach,[14] lithiation of tolyl-telechelic PIB, obtained by Friedel−Crafts alkylation of *tert*-chlorine-ended PIB[15] and subsequent addition of 1,1-diphenylethylene (DPE) to the metalated chain ends, was applied to initiate the polymerization of MMA. Living PMMA chains were also attached to PIB containing short endblocks of poly(*p*-vinylbenzyl bromide).[16] Although detailed characterization of the products is not available, this method is expected to yield PMMA branches at the PIB termini.

Metalated PIB, obtained by one-pot dehydrochlorination−metalation of *tert*-chlorine-ended PIB by potassium *tert*-amylate/nBuLi and tBuOK/nBuLi mixtures, was used to initiate the anionic polymerization of

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butadiene resulting PIB–polybutadiene block copolymers.[17]

All these methods have several disadvantages: multistep endgroup derivatizations are required for the synthesis of the telechelic PIB initiator precursor, and lithiation and, thus, subsequent initiation of anionic polymerization is not quantitative or requires extreme conditions. As a consequence of less than 100% initiating efficiency, these methods yielded mixtures of homopolymers and block copolymers. This is indicated by the fact that it was claimed that PMMA-*b*-PIB-*b*-PMMA was obtained only by selective extraction.[11–14]

It has been recently found that one-pot end-quenching of LCCP with DPE, a nonhomopolymerizable olefin in cationic polymerization, may yield either 1-methoxy-1,1-diphenylethyl (DPOMe)[18] or 2,2-diphenylvinyl (DPV)[19,20] chain ends, depending on the polymerization conditions.

The relatively stable, highly ionized cationic chain end formed by DPE addition was reacted with living PMMA chains carrying silyl ketene acetal endgroups obtained by group transfer polymerization, resulting in PIB-*b*-PMMA block copolymer.[21] However, the major disadvantage of this method is its applicability only under very specific conditions and precise stoichiometry. In addition to this, the titanium compounds (most likely $Ti(OR)_xCl_{4-x}$) present in this system cleave the coupled blocks by forming PMMA with titanium enolate endgroups and, thereby, decrease the blocking efficiency.

Both the 2,2-diphenylvinyl and the 1-methoxy-1,1-diphenylethyl chain ends are potential endgroups for the anionic polymerization of a variety of monomers by metalation. Our earlier results indicate that quantitative metalation of the 2,2-diphenylvinyl endgroups with alkyllithium cannot be achieved, most likely because of steric hindrance.[20] However, as described recently,[22] the ether cleavage of 1-methoxy-1,1-diphenyl-3,3,5,5-tetramethylhexane or electron transfer to 3,3,5,5-tetramethyl-1,1-diphenylhex-1-ene by K/Na alloy, Cs, or Li led to quantitative metalation, resulting in nearly quantitative initiation of the polymerization of methacrylic monomers. Both precursors led to identical macroinitiators. These compounds can be considered as models of PIB chain ends formed by LCCP of IB and subsequent end-capping with DPE. The present study deals with the application of this method to the synthesis of different AB and ABA block copolymers by the combination of LCCP and anionic polymerization.

Experimental Section

Materials. $TiCl_4$ (Aldrich, 99.9%), BCl_3 (Aldrich, 1 M in CH_2Cl_2), 1,1–diphenylethylene (DPE) (Aldrich, 97%), *N*,*N*-dimethylacetamide (DMA) (Aldrich, 99+%, <0.005% water), 2,6-di-*tert*-butylpyridine (DtBP) (Aldrich, 97%), and cesium (Merck) were used as received. LiCl (Merck, >99%) was dried for 48 h at 200 °C under vacuum and stored under nitrogen. Isobutylene (IB) (BASF) was passed through a drying column (Labclear filter; Aldrich, containing $CaSO_4$ and no. 13 molecular sieves). Methyl methacrylate (MMA) and *tert*-butyl methacrylate (tBMA) (Röhm GmbH) were fractionated by distillation and then stored over CaH_2 in a refrigerator. Both monomers were distilled under reduced pressure before use. *n*-Hexane (Aldrich) used for cationic and anionic polymerizations was refluxed over concentrated sulfuric acid for 48 h in order to remove olefins. The organic layer was washed with distilled water (pH $\approx$ 7), dried with $MgSO_4$, and stored over CaH_2. It was distilled under dry N_2 atmosphere before use. *n*-Hexane used for anionic polymerizations was additionally destilled from K/Na alloy. CH_2Cl_2 (Riedel deHaen, 99,8%) was dried and distilled over CaH_2 under dry nitrogen. Tetrahydrofuran (THF) was first distilled from potassium and stored over K/Na alloy on a vacuum line. Potassium (Merck, >98% in paraffin oil) and sodium (Merck, >99% in paraffin oil) (3:1–5:1) were melted in vacuo, resulting in an alloy. 5-*tert*-Butyl-1,3-dicumyl chloride was prepared by hydrochlorination of 5-*tert*-butyl-1,3-dicumyl alcohol[23] with HCl gas at 0 °C in CH_2Cl_2. The crude product was recrystallized twice in *n*-hexane. The pure product was stored in a refrigerator. 2-Chloro-2,4,4-trimethylpentane (TMPCl) was synthesized from 2,4,4-trimethyl-1-pentene (Aldrich, 99%) by hydrochlorination with HCl gas at 0 °C. The product was dried over $CaCl_2$ (stored in a refrigerator) and distilled under reduced pressure before use.

Synthesis of Diphenylmethoxy-Ended PIB. Living polymerizations of IB with 2-chloro-2,4,4-trimethylpentane initiator were carried out by a simple laboratory process.[24,25] When a combined $BCl_3/TiCl_4$ coinitiator system was used, the following procedure was carried out for IB polymerization: To a three-necked flask (reactor) equipped with a septum, a mechanical stirrer, and a nitrogen inlet were added of 18 mL CH_2Cl_2, 0.08 mL of *N*,*N*-dimethylacetamide (DMA), and 128 mg of TMPCl, and then the mixture was cooled to −78 °C. Two milliliters of IB was charged to the reactor by a syringe. After 5 min of stirring, 18 mL of BCl_3 (1 M in CH_2Cl_2) was transferred to the reactor by a transfer needle. After 10 min, 0.5 mL of $TiCl_4$ in 54 mL of *n*-hexane (olefin-free) containing 0.03 mL of 2,6-di-*tert*-butylpyridine (DtBP) was added. Subsequently, an additional 4 mL of IB was charged to the polymer solution. Ten minutes later a solution containing 0.76 mL of DPE (5 times excess relative to the living chain ends), 3 mL of *n*-hexane, and 2 mL of CH_2Cl_2 was added. The color of the solution changed from slightly yellow to orange. DPE was allowed to react with the living chain ends for 25 min. Finally, the reaction was quenched by addition of 30 mL of prechilled methanol. Two minutes later, a mixture of 40 mL of NH_3(aq) and 160 mL of methanol was added in order to obtain pH > 8, thus avoiding elimination of methanol.

When only $TiCl_4$ was used as a coinitiator, to a three-necked flask equipped with a septum, a mechanical stirrer, and a nitrogen inlet were added 80 mL of CH_2Cl_2, 80 mL of *n*-hexane (olefin-free), 0.28 mL of DMA, and 450 mg of TMPCl, and then the mixture was cooled to −78 °C. Ten milliliters of IB was charged to the reactor by a syringe. After 5 min of stirring, a stock solution of $TiCl_4$ (40 mL of CH_2Cl_2, 100 mL of *n*-hexane, 6.6 mL of $TiCl_4$, and 0.1 mL of DtBP) was transferred to the reactor by a transfer needle. After 10 min, a second addition of 11 mL of IB followed. Ten minutes later, a solution of DPE (2.65 mL of DPE, 6 mL of *n*-hexane, and 4 mL of CH_2Cl_2) was added to the polymerization system (the color of the solution changed from slightly yellow to dark red). DPE was allowed to react with the living chain ends for 20 min. Finally, the reaction was quenched by addition of 30 mL of prechilled methanol. Two minutes later, a mixture of 100 mL of NH_3(aq) and 400 mL of methanol was added.

Similar experiments were performed with the 5-*tert*-butyl-1,3-dicumyl chloride (tBuDiCumCl) and 1,3,5-tricumyl chloride (TriCumCl) initiators in order to obtain di- and trifunctional polyisobutylenes. After the polymerizations were quenched, the crude mixture was filtered in order to remove the titanium complexes. During filtration, additional *n*-hexane was added. Then, the *n*-hexane phase was isolated and washed once with NH_3(aq) and subsequently with water until neutral. The organic layer was separated and dried over $MgSO_4$ for about 2 h. Subsequently, the solution was filtered, and the solvent was removed on a rotary evaporator. Then, the polymer was redissolved in a small amount of *n*-hexane and precipitated two or three times into acetone in order to remove excess DPE.

Synthesis of PIB-*b*-PtBMA and PIB-*b*-PMAA Block Copolymers A 1.0 g portion of DPOMe-capped PIB (M_n = 5800) was dissolved in THF and dried over CaH_2 for more than 24 h. The solution was filtered in a glovebox. THF was then removed under high vacuum (48 h at room temperature). Metalation was performed in 60 mL of THF with 2 g of K/Na alloy. The UV-vis spectrum was recorded a glass cuvette (10 × 10 mm^2) equipped with a 9.8 × 9.8 mm^2 spacer attached to a glass reactor, in which the metalation was carried out. After constant absorbence was observed at $\lambda_{max} = 480$ nm, the suspension was filtered into a flamed reactor in a glovebox. On a vacuum line, the solution was cooled to −78 °C. tBMA was added in bulk to the initiator solution during 10−20 s, and after 90 min the polymerization was quenched with methanol.

Hydrolysis of PIB-*b*-PtBMA leading to poly(isobutylene-*block*-methacrylic acid) (PIB-*b*-PMAA) was carried out in refluxing dioxane (~10 wt % polymer solution) containing 5 times excess water relative to tBMA units in the form of a HCl solution (32 wt % HCl) for 24 h. In order to remove colored impurities and unreacted PIB, nearly all of the dioxane was removed by rotary evaporation, and then the polymer was stirred with diethyl ether (PIB with $M_n < 10\,000$ is soluble in Et_2O) for more than 24 h. Finally, the ether suspension was centrifuged. The precipitated polymer was separated by decantation and dried in a vacuum oven at room temperature.

Synthesis of PMMA-*b*-PIB-*b*-PMMA and PIB-*b*-(PMMA)$_3$ Block Copolymers. After reaching constant absorption in the UV−visible spectrum of telechelic DPOMe- or DPV-ended PIB metalated with K/Na alloy, the reaction mixture was filtered, LiCl (10 times excess) was added, and the mixture was stirred for 20 min. The polymerization of MMA was carried out at −78 °C and quenched with methanol after 90 min. Then the solvents were removed by rotary evaporation. The polymer was subsequently dissolved in about 20 mL of THF and precipitated into 300 mL of CH_3OH in order to remove inorganic salts. The polymer was separated by filtration and dried in a vacuum oven at 40 °C.

Characterizations. The molecular weight distributions (MWDs) were determined by SEC calibrated with PIB, PMMA, and PtBMA standards (for the block copolymers, a weighted average of the homopolymer calibration curves were used): eluent, THF; detectors, two JASCO-UVIDEC 100 III with variable wavelength, Bischoff RI detector 8110; columns, PSS SDV-gel 5 μm, 60 cm, 1× linear (10^2−10^5 Å), 1 × 100 Å. ^{1}H NMR spectra, e.g., for endgroup analysis, were recorded on a Bruker AC-200 spectrometer in $CDCl_3$. For the dynamic−mechanic and stress−strain analyses, films were prepared by casting a 10 wt % toluene solution of the block copolymers into a Teflon mold (THF solutions led to macrophase-separated films). After 1 day of evaporation in a hood, the film was placed in a vacuum oven for 1 day at room temperature for a further 2 days at 50 °C, and finally for 3 h at 140 °C for annealing. Dynamic−mechanical measurements were carried out with a RSAII-Rheometrics instrument (1 °C/min). Stress−strain analysis was done with an HBM Hütting-Baldwin Messtechnik apparatus. DSC was performed with a Mettler apparatus using a heating rate of 20 °C/min (the curves correspond to the second heating).

Results and Discussion

Effect of the Reaction Conditions on the End-Capping with DPE. Two procedures were investigated for the synthesis of PIB macroinitiators by living carbocationic polymerization (LCCP) of isobutylene (IB) and for the subsequent end-capping with DPE: a two-step system[25] with sequential polarity change and addition of two different coinitiators, BCl_3 and $TiCl_4$, and a one-step polymerization in which only $TiCl_4$ was used as coinitiator. The reason for using the two-step system was based on earlier experience,[25] according to which narrow molecular weight distributions (MWDs) can be reached in the range $3000 \leq M_n \leq 8000$ with this polymerization system rather than with that coinitiated by $TiCl_4$ alone.

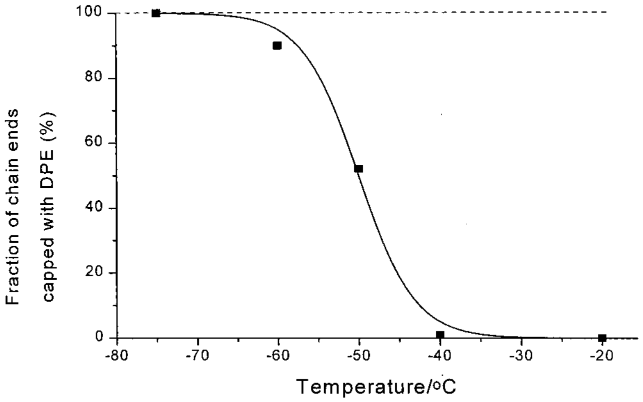
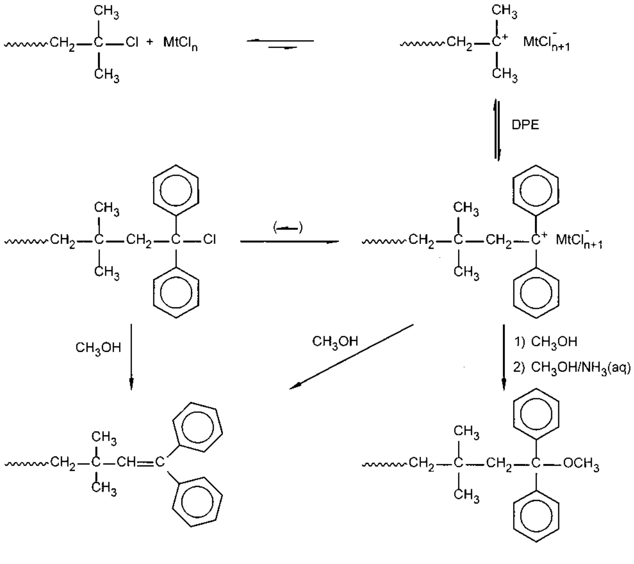


Figure 1. Effect of temperature on the equilibrium addition of DPE to living PIB chain ends (solvent, 60:40 *n*-hexane/CH_2Cl_2, $TiCl_4$, $n_{initiator} = n_{DMA} = n_{DPE}$).

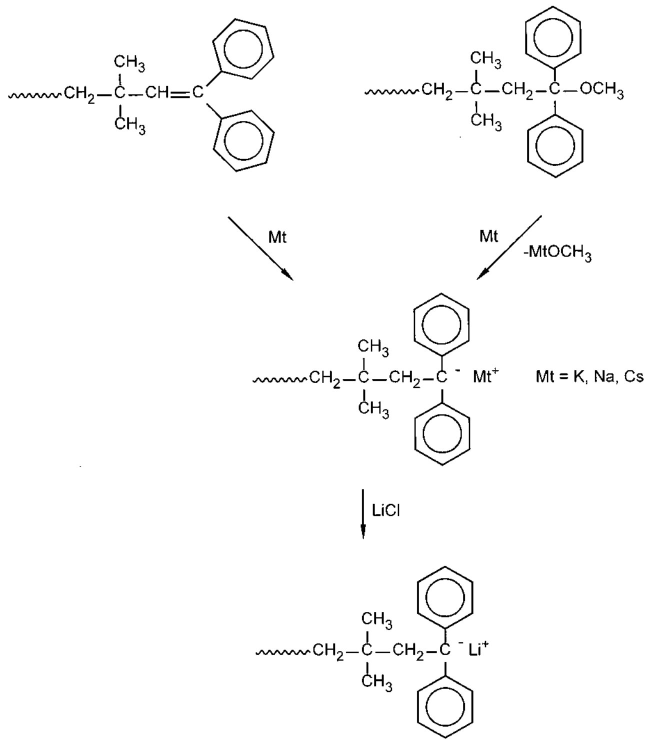
Scheme 1. Functionalization of Living PIB Chain Ends with DPE



The major processes occurring in the course of end-capping of living PIB with DPE are shown in Scheme 1. Quenching the DPE-capped living polymers with methanol−ammonia led to quantitative formation (>98%, verified by ^{1}H NMR) of 1,1-diphenyl-1-methoxy (DPOMe) endgroups when only $TiCl_4$ was used. 2,2-Diphenylvinyl (DPV) chain ends were obtained quantitatively when only methanol was used as quenching agent. and the quenched polymer solution was left for more than 4 h before further purification. The formation of DPV termini is due to the acidic nature of the solution, leading to elimination of methanol from the DPOMe termini formed initially. In some cases, dissolution of the polymer in $CHCl_3$ containing traces of HCl provided quantitative elimination. When only BCl_3 was used as coinitiator, less than quantitative capping (<10% at −80 °C) was found in the CH_3Cl/*n*-hexane (40:60 v/v) solvent mixture, since the DPE addition is an equilibrium reaction.[26] However, in the two-step procedure, >96% capping efficiency was reached for an equimolar ratio of the two Lewis acids in the CH_2Cl_2/*n*-hexane (40:60 v/v) mixture.

The choice of not only Lewis acid, solvents, and quenching conditions but also the reaction temperature is important for obtaining precursors suitable for subsequent metalation.[26] In an experiment carried out in the usual way at −78 °C (CH_2Cl_2/*n*-hexane and $TiCl_4$/DMA), the polymerization system was allowed to warm up slowly, and samples were withdrawn at different temperatures. The yield of DPE-capped product is shown as a function of temperature in Figure 1. While quantitative endcapping is observed at −78 °C, the

Scheme 2. Metalation of DPOME- and DPV-Ended with Alkali Metals/Alloys



capping yield rapidly decreases with increasing temperature. ^{1}H NMR spectra show 90% DPE capping (-$CH{=}C(Ph)_2$, 6.1 ppm and -OCH_3, 3.00 ppm) and 10% *tert*-chlorine (-CH_2-$C(CH_3)_2Cl$, 1.96 ppm) endgroups at −60 °C and no DPE-capping at −40 °C. These results are in good agreement with those obtained by Faust et al.[26]

In order to further investigate this phenomenon, DPOMe-ended PIB was prepared, purified, and then dissolved in CH_2Cl_2/*n*-hexane solvent mixture (40/60 v/v) and then cooled to −78 °C, and polymerization conditions were created by adding DMA and $TiCl_4$. This system was also allowed to warm up, and samples were withdrawn at diffeent temperatures. Results identical to those of the experiment shown in Figure 1 were observed, indicating that retroaddition of DPE takes place from the DPOMe-ended PIB in the presence of coinitiator.

In conclusion, the polymerization temperature should be kept below −75 °C in order to reach quantitative endcapping under the conditions used in this work (*n*-hexane/CH_2Cl_2, 60:40, $[I] \approx 10^{-2}$ M, $[DMA] \approx 10^{-2}$ M, $[TiCl_4] \approx 10^{-1}$ M, and $[DPE] \approx 5 \times 10^{-2}$ M).

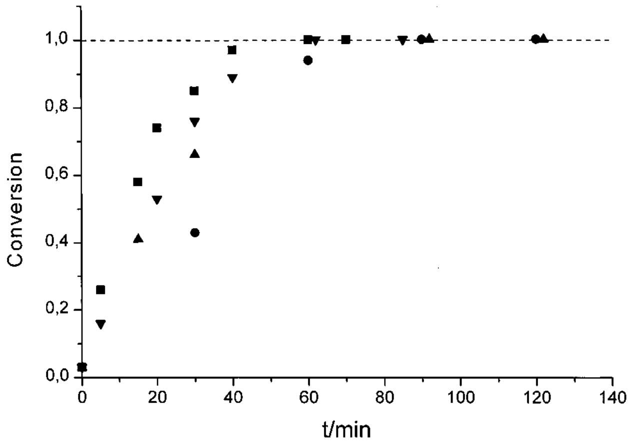


Figure 2. Time−conversion plots for metalation of DPE-capped PIBs with K/Na alloy as followed by UV−vis absorbence at $\lambda_{max} = 480$ nm ($\epsilon \approx 2 \times 10^4$ mole^{-1}·L·cm^{-1}), $M_n = 150$ (■), 5000 (●), 17 500 (▲), 32 000 (▼).

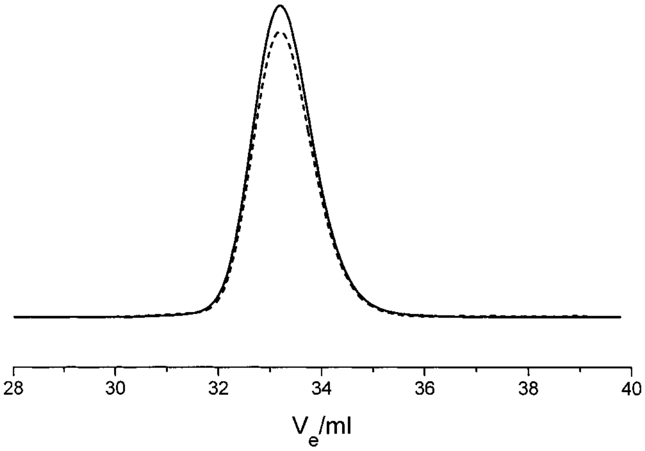


Figure 3. SEC eluograms (RI signal) of a DPV-ended PIB precursor before (- - -) and after (—) metalation.

Metalation of Diphenylmethoxy- and Diphenylvinyl-Ended PIB. As we reported recently,[22] metalation of model compounds of the corresponding PIB chain ends, i.e., 1-methoxy-1,1-diphenyl-3,3,5,5-tetramethylhexane and 1,1-diphenyl-3,3,5,5-tetrametylhex-1-ene, is quantitative with K/Na alloy, Cs, Na, and Li suspension. The resulting carbanions led to a living anionic polymerization of methacrylic monomers with ~100% initiating efficiency.[22] In order to prepare the desired block copolymers, it was of interest whether the quantitative metalation results obtained with the model compounds can be converted to the PIB macroprecursors within a broad range of molecular weights. Schemes 1 and 2 outline the chemical transformations in the course of endcapping of living PIB chains with DPE and the subsequent formation of the carbanionic macroinitiator upon metalation, respectively. Figure 2 summarizes the time−conversion plots obtained by UV−visible spectroscopy for PIB samples, with the degree of polymerization in the range of $2 \leq P_n \leq 570$. As shown in this figure, the molecular weight has no significant effect on the rate of metalation. Quantitative metalation of DPE-capped PIBs can be achieved within 60 min (constant absorbence). From the UV absorbance, an absorption coefficient of $\epsilon \approx 2 \times 10^4$ mol^{-1}·L·cm^{-1} is calculated. This value is in good agreement with literature data on comparable compounds.[27] The metalation products were further analyzed by ^{1}H NMR. In all cases, 100% metalation was observed (see, e.g., ref 22).

As it is known from the literature,[28] electron transfer to DPE with K/Na alloy at room temperature yields a radical anion which recombines, leading to 1,1,4,4-tetraphenylbutyl dianion, which is a difunctional initiator. Therefore, coupling could also be expected when metalating DPV-ended PIB. However, as shown in Figure 3, the SEC eluograms of PIB with DPV endgroups before and after 60−420 min of metalation are identical, indicating the absence of coupling upon metalation. This confirms results obtained with the corresponding model compound.[22] The absence of coupling during metalation of DPV-ended PIB can be explained by the steric hindrance caused by the two methyl groups adjacent to the radical carbon. The stability of the

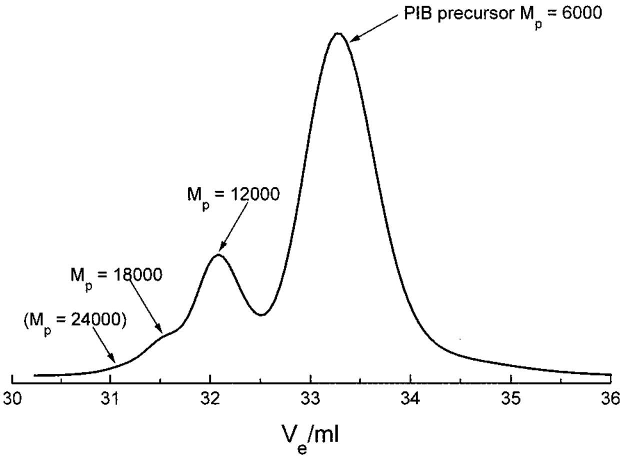
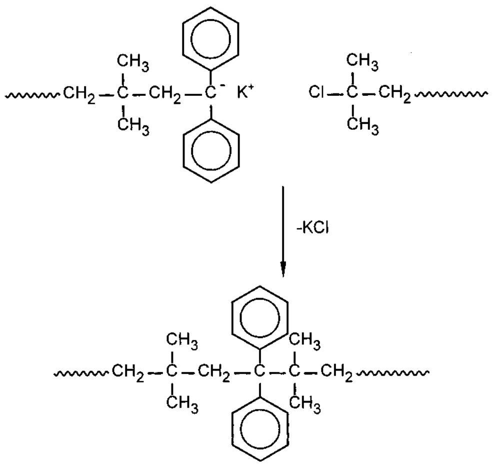


Figure 4. SEC eluogram (RI signal) of a difunctional PIB sample containing 85% DPV and 15% Cl^t endgroups after 60 min of metalation with K/Na alloy in THF at room temperature.

Scheme 3. Side Reaction Caused by Nonquantitative DPE-Capped PIB, Leading to Partial Coupling of PIB Chains



PIB–DPE$^-$ K$^+$ ion pair was also tested. It was found that the intensity of the UV–visible absorption at 480 nm did not change, even after 10 days, indicating the high stability of this macroinitiator in THF at room temperature.

The effect of nonquantitative endcapping on the metalation process was also investigated. A difunctional PIB sample having 85% DPV and 15% *tert*-chlorine chain ends was metalated with K/Na alloy as described in the Experimental Section. After 60 min, the reaction was quenched with methanol, and the resulting material was analyzed by SEC. As shown in Figure 4, coupling occurs between the carbanion and the *tert*-chlorine-containing endgroups. This reaction is shown in Scheme 3. Since the precursor PIB is difunctional, multiple coupling occurs, resulting in a multimodal MWD with peak maxima corresponding to multiples of the molecular weight of the precursor. There are two important consequences of these findings: The endcapping reaction with DPE should be quantitative during LCCP of IB, on one hand. The absence of coupling during metalation of the DPE-capped PIB is an indirect proof for quantitative endcapping, on the other hand. Since even relatively low amounts of coupling can be detected by SEC, this can be utilized for testing the yield of DPE capping for high-molecular-weight PIBs (M_n > 10 000) when ^{1}H NMR or UV–vis spectroscopies cannot be used for reliable endgroup analysis.

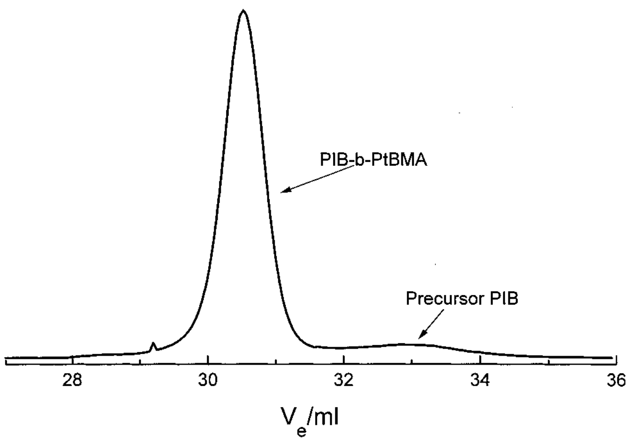


Figure 5. SEC eluogram (UV signal at 260 nm) of PIB-*b*-PtBMA ($M_n \approx$ 32 000, $M_w/M_n \approx$ 1.05) obtained from a PIB precursor with M_n = 5800.

Synthesis and Characterization of Block Copolymers. Polyisobutylene-*block*-poly(tert-butyl methacrylate) (PIB-*b*-PtBMA) block copolymers were synthesized by using the PIB-DPE$^-$ K$^+$ macroanion as initiator for the polymerization of tBMA.

First, an experiment was carried out for investigating the blocking efficiency. Therefore, the block lengths were chosen in such a way that the peaks of the PIB precursor and the PIB-*b*-PtBMA block copolymer in the SEC eluogram are separated from each other. Figure 5 shows the SEC eluogram (UV signal at 260 nm) for such a block copolymer. It can be seen that only a small peak appears for the unreacted PIB. Since only the aromatic rings absorb at this wavelength, integration allows us to estimate the blocking efficiency, which is higher than 95%. The resulting block copolymer has narrow MWD, with M_w/M_n = 1.06.

At the start of these series of blocking experiments, the effect of the PIB endgroup structure was also investigated. To one reactor, a DPOMe-capped PIB was added, and to another was added a 50:50 mixture of DPOMe- and DPV-capped PIB. After metalation with K/Na alloy, tBMA was charged to both reactors. In both cases, nearly identical blocking efficiencies were obtained, which proves that the metalation and the subsequent polymerization are not influenced by the ratio of the two chain ends. The independence of the metalation and anionic polymerization on the ratio of the diphenylvinyl and diphenylmethoxy endgroups is a very important finding. This means that it is not necessary at all to consider the chain end composition of the DPE-capped PIB in the course of its preparation by LCCP. Both the DPOMe- and DPV-capped PIB chains in a mixture yield the same macroanion (Scheme 2) and lead to the same block copolymer by anionic polymerization.

Polyisobutylene-*block*-poly(methacrylic acid) (PIB-*b*-PMAA) was prepared by hydrolysis of the ester group under acidic conditions, using HCl(aq) in dioxane. After hydrolysis, a new amphiphilic diblock copolymer is formed, as shown in Scheme 4. The resulting amphiphilic block copolymers form stable emulsions in dioxane and in water at pH = 12. Detailed investigations will be published elsewhere.

Scheme 4. Synthesis of Amphiphilic PIB-*b*-PMAA Block Copolymer

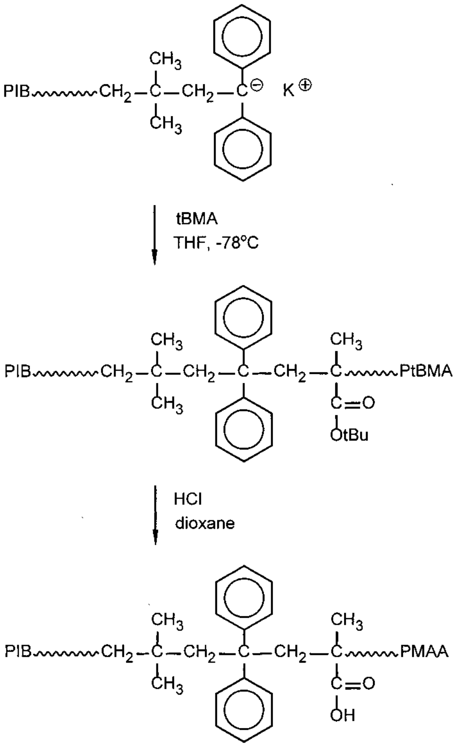


Table 1. M_n of the PIB Midsegment and the PMMA Outer Blocks, the Blocking Efficiency (f_{block}), and the Polydispersity of the Resulting Block Copolymer Obtained by Anionic Polymerization of MMA Using Different Difunctional DPOMe-PIB-DPOMe Precursors in THF at −78 °C (Gegenion, Li$^+$)

	M_n			
sample	PIB	PMMA[a]	f_{block}[b]	M_w/M_n[b]
ABA1	6300	6400	>0.95	1.13
TPE32	17 500	2200	>0.95	1.10
TPE31	17 500	3200	>0.95	1.09
TPE33	17 500	5800	>0.95	1.11
TPE44	32 000	9000	>0.95	1.13
TPE45	32 000	6900	>0.95	1.13
TPE46	32 000	4500	>0.95	1.12

[a] Per block. [b] Crude polymer, no extraction.

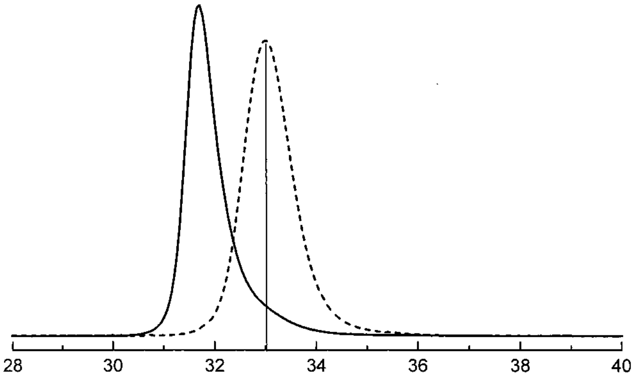


Figure 6. SEC eluograms (RI signal) of a difunctional PIB precursor (M_n = 6300, M_w/M_n = 1.12) (- - -) and the corresponding triblock copolymer ABA1 (—) after anionic polymerization of MMA (M_n = 18 000, M_w/M_n = 1.13).

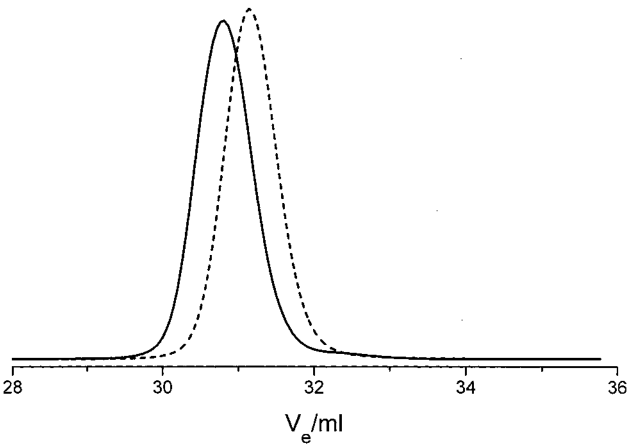


Figure 7. SEC eluograms (RI signal) of a difunctional PIB precursor (M_n = 17 500) (- - -) and the corresponding PMMA-*b*-PIB-*b*-PMMA with M_n(PMMA) = 3200 (—).

Synthesis of poly(methyl methacrylate)-*block*-polyisobutylene-*block*-poly(methyl methacrylate) (PMMA-*b*-PIB-*b*-PMMA) triblock copolymers was also performed (see Table 1). First, a series of DPE-telechelic PIBs were prepared by using a difunctional initiator (tBuDiCumCl) for LCCP of IB. In an orienting experiment, the molecular weight of the difunctional PIB macroinitiator was relatively small compared to that of the outer PMMA segments in order to obtain sufficient separation by SEC between the PIB precursor and the expected triblock in order to check the efficiency of this new system. As shown in Figure 6, the resulting block copolymer has unimodal narrow MWD. The SEC eluograms in this figure also indicate high blocking efficiency. Indeed, extraction by hexane removed only 4% PIB and small amounts of block copolymer after 1 month. These results clearly verify nearly quantitative blocking efficiency and the formation of the desired PMMA-*b*-PIB-*b*-PMMA block copolymer.

Since thermoplastic elastomers usually have a rubbery midsegment of 60−70 wt % and higher molecular weight, difunctional PIB precursors with M_n > 15 000 were also prepared. The SEC eluograms in Figure 7 show a uniform shift to higher molecular weights after block formation. Since the eluograms of the PIB precursor with M_n = 17 500 and the ABA block copolymer having outer PMMA segments with M_n = 3200 overlap, it is difficult to use SEC for the verification of quantitative blocking efficiency in this range of block copolymer composition. However, the resulting triblock has unimodal and narrow MWD (M_w/M_n = 1.10), which is a good indication for controlled synthesis of the desired triblock copolymer.

A second PIB precursor with M_n = 32 000 was used for the synthesis of another series of triblock copolymers. However, solubility problems arose during the polymerization of MMA since the precursor precipitated in THF below −55 °C. At −50 °C the polymerization of MMA with the high-molecular-weight PIB macroinitiator resulted in polymers with multimodal MWD due to uncontrolled polymerization of MMA. In order to increase the solubility of PIB at −78 °C, anionic polymerizations of MMA were performed in a 70:30 THF/*n*-hexane mixture. This process yielded PMMA-*b*-PIB-*b*-PMMA with unimodal MWD and low polydispersity (M_w/M_n = 1.10), indicating high blocking efficiency.

In experiments involving difunctional PIBs with M_n > 15 000, a temporary precipitation was observed right after the addition of MMA. The precipitate dissolves

Table 2. Weight Fraction and M_n of the PMMA Outer Blocks, Theoretical M_n of the Block Copolymer, M_n Measured by SEC, and Polydispersity of the Resulting Block Copolymer Obtained by Anionic Polymerization of MMA Using a Trifunctional PIB Precursor (M_n = 30 000, M_w/M_n = 1.07) in THF at −78 °C (Gegenion, Li$^+$)

sample	% PMMA	$M_{n,theor}$-(PMMA)[a]	$M_{n,theor}$-(block)[b]	$M_{n,SEC}$-(block)[c]	M_w/M_n[d]
TRI30_0	46	8 500	56 000	60 000	1.09
TRI30_1	37	5 900	48 000	51 000	1.07
TRI30_2	27	3 700	41 000	44 000	1.08

[a] Theoretical M_n of the PMMA blocks, expecting a block efficiency of 1. [b] Theoretical M_n of the block copolymer, expecting a block efficiency of 1. [c] M_n obtained by SEC using weighted PIB and PMMA calibration curves. [d] Crude polymer, no extraction.

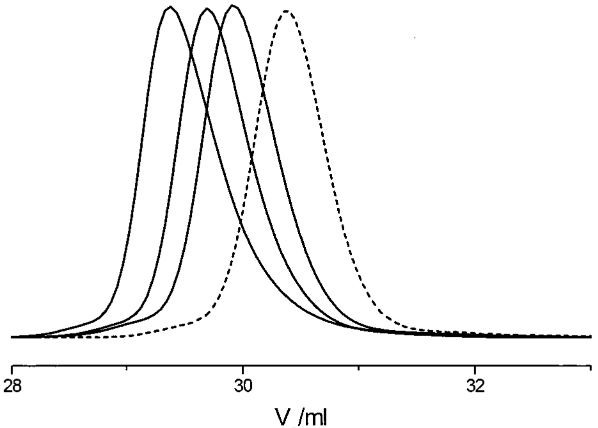


Figure 8. SEC eluograms (RI signal) of a trifunctional PIB precursor (M_n = 30 000) (- - -) and the corresponding PIB-*b*-(PMMA)$_3$ block copolymers (—) (see Table 2).

after about 10−15 min. The precipitation is most likely due to the aggregation of the lithiated chain ends surrounded by the non-polar PIB leading to the formation of a coordinative network which is redissolved after a certain length of the PMMA segments is reached.

Polyisobutylene-*block*-poly(methyl methacrylate) (PIB-*b*-(PMMA)$_3$) star-shaped block copolymers were also synthesized (see Table 2) by using a trifunctional initiator (TriCumCl) for LCCP of IB. The three-arm PIB precursor had M_n = 30 000. This value is apparent only since calibration was performed with linear PIB standards. A solvent mixture of THF and *n*-hexane (70:30) was also used here, in order to avoid solubility problems at low temperature (−78 °C). As shown in Figure 8, a series of block copolymers with 27−46 wt % MMA has been prepared with low polydispersity (M_w/M_n < 1.10). The investigation of the morphology and the thermoplastic properties is in progress.

Preliminary investigations were also carried out on the physical properties of the PMMA-*b*-PIB-*b*-PMMA block copolymers. A representative DSC curve is shown in Figure 9. As indicated in this figure and in Table 3, the block copolymers have two glass transitions corresponding to microphase separation of the two segments. Dynamic−mechanical analysis also verifies the presence of the transitions in the vicinity of −60 and 110 °C, as displayed in Figure 10. Stress−strain/dynamic−mechanical measurements were performed with solvent-cast films (from THF) of three triblock copolymers having the same PIB precursor but different PMMA chain lengths (see Table 3). Further mechanical studies and the synthesis of different thermoplastic elastomers are in progress.

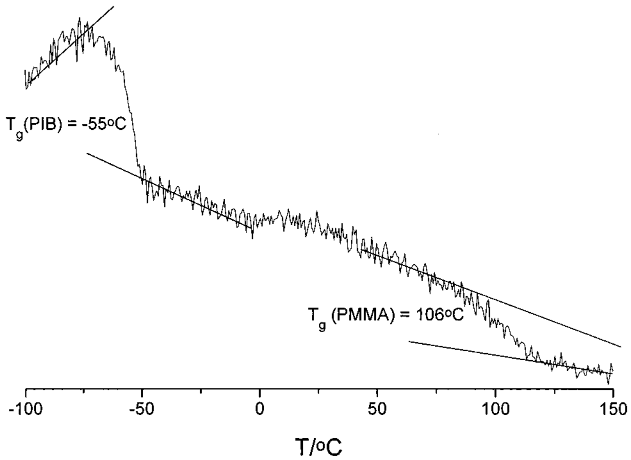


Figure 9. DSC curve of PMMA-*b*-PIB-*b*-PMMA (TPE31) (see Table 3) (second heating, 20 °C/min).

Table 3: Molecular Weight of PMMA Segments, Composition, Glass Transition Temperatures, Tensile Strength, and Elongation at Break of PMMA-*b*-PIB-*b*-PMMA Block Copolymers (Precursor, Difunctional PIB with M_n = 17 500)

sample	M_n PMMA[a]	PMMA %	T_g (°C) PIB	T_g (°C) PMMA	ultimate tensile strength (MPa)	elongation at break (%)
TPE32	2200	21	−55	94	1.7	150
TPE31	3200	27	−55	106	4.1	230
TPE33	5800	41	−56	110	8.1	310

[a] Per block.

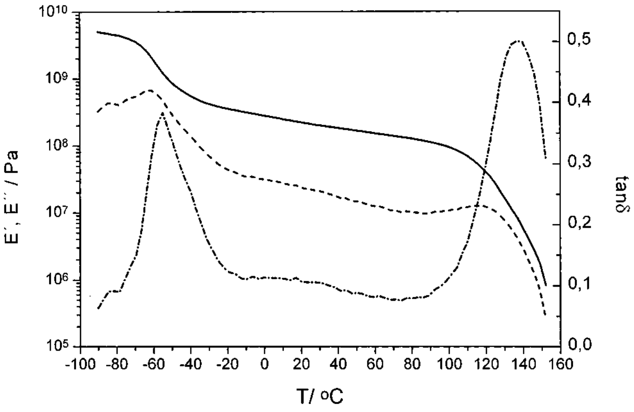


Figure 10. Dynamic−mechanical analysis of TPE31 (see Table 3): *E*′ (—), *E*″ (- - -), tan *δ* (−•−).

Conclusions

A new method for the synthesis of polyisobutylene-based linear and star-shaped block copolymers, involving living carbocationic polymerization of isobutylene and subsequent living anionic polymerization of methacrylic monomers, has been demonstrated. Linear di- and triblock copolymers and triarmed star block copolymers nearly free of PIB precursor and with narrow and unimodal MWD were synthesized under well-controlled conditions.

The PIB macroinitiators can also initiate living anionic polymerization of a wide variety of functional monomers, such as vinylpyridine, *N,N*-dimethylacrylamide, and a variety of protected monomers, such as silylated 2-hydroxyethyl methacrylate. Polymerization studies with these monomers are in progress. The resulting products are potential new thermoplastic elastomers, dispersing agents, blending compounds, emulsifiers, nonionic surfactants, biomaterials, etc.

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