Synthesis and Characterization of Polyisoprene−Poly(methyl methacrylate) AB Diblock and A_2B_2 Heteroarm Star Copolymers

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ABSTRACT: The synthesis of A_2B_2 heteroarm stars, where A is polyisoprene (PI) and B is poly(methyl methacrylate) (PMMA) has been achieved using living anionic polymerization. A divinyl coupling agent 1,1-(1,2-ethandiyl)bis(4-(1-phenylethenyl)benzene) (EPEB) was used to link together polyisoprenyllithium chains and create a dianion from which methyl methacrylate (MMA) polymerization could be initiated and thus form a four-armed star. PI−PMMA diblocks were synthesized by sequential anionic polymerization. Characterization was performed using size exclusion chromatography (SEC), ^{1}H NMR, and membrane osmometry. Hydrogenation of the polymers using toluenesulfonyl hydrazide yielded the corresponding poly(ethylene-*alt*-propylene)−PMMA stars and diblocks.

Introduction

Block copolymers have been the subject of intense experimental and theoretical interest for more than two decades because of their practical applications as adhesives, surfactants, compatibilisers, and thermoplastic elastomers. Anionic polymerization has been the preeminent technique for the synthesis of such materials because of the ability it can offer to control the molecular weight, the molecular weight distribution, composition and the mode of enchainment—albeit of a limited range of monomers. In general, chemically different blocks are incompatible, but being covalently connected, phase separation is on a molecular scale and is geometrically regular. A wide variety of morphologies have been observed including spheres on a body-centered cubic lattice, hexagonally packed rods, and lamellae. The principal factors determining the morphology are the overall degree of polymerization, the relative volume fractions of the blocks, and the Flory−Huggins segment−segment interaction parameter χ.[1] In turn, the morphology has a profound effect upon the mechanical properties of these materials.[2]

Recently, attention has been focused upon nonlinear architectures such as heteroarmed stars and graft copolymers; a review is available.[3] The formation of star homopolymers by coupling anionic living polymers by reaction with chlorosilanes is a tried and trusted procedure.[4] Such condensations are generally free from competing side reactions and stars having up to 128 arms have been prepared.[5] Heteroarmed stars A_xB_y can be formed in a similar way using an appropriate chlorosilane to successively link x arms of polymer A and y of polymer B to a central core. Ensuring that all the stars have uniquely the chosen values of x and y (rather than merely average values) can present difficulties, but these can be overcome in favorable cases by exploiting steric effects[6] or by operating at subambient temperatures.[7] The diversity of chemically different compositions accessible by this route is, however, limited by the requirement to have polymers which remain living long enough at a temperature high enough to enable the subsequent condensation reaction to proceed to completion. PMMA fails to meet this criterion.

Reaction with divinylbenzene provides an alternative means of linking certain living polymers (A) into star architecture, although control over the number of arms is less precise.[8] Because the anionic charges are preserved intact on the oligomeric divinylbenzene at the center of the star, it is possible to transform this homopolymeric star into an A_xB_y hetero-armed star (where $y = x$) by using it to initiate the polymerization of a second monomer (B).[9] A variant on this theme is, for example, to couple two polystyryllithium chains with the nonpolymerizable “double diphenylethylene” linker 1,3-bis(1-phenylethenyl) benzene and then to grow two polybutadiene chains from the product—thereby forming an A_2B_2 heteroarmed star.[10]

The use of PMMA as a block offers the attraction of it being already an industrially important polymer and also the attraction that the syndiotactic form has quite a high T_g (120 °C). The polymerization of MMA using organolithium initiators in polar solvents such as THF at −78 °C results in monomodal and relatively narrow distributions and predominantly syndiotactic enchainment. Near-monodispersity can be achieved if certain coordinating ligands are present during the polymerization. These include μ-types such as aluminum alkyls,[11] alkali metal alkoxides[12] and lithium chloride,[13] σ-types, e.g., crown ethers,[14] and σ,μ-types such as polyether metal alkoxides.[15]

The literature reports relatively few syntheses of diene−alkyl methacrylate block copolymers. High 1,4-enchainment of the diene block requires the use of a nonpolar solvent. PI−PMMA diblocks have been prepared by first polymerizing isoprene in hexane using *sec*-BuLi as initiator, then adding benzene and pyridine, and finally adding MMA at −45 °C (Scheme 1).[16] PB−PMMA diblocks have been made by polymerizing butadiene in benzene, adding THF, and adding the MMA at −78 °C after capping the chains with 4-vinylpyridine.[17] Using a difunctional initiator formed from 1,3-bis(phenylethenyl)benzene (PEB) and *sec*-BuLi, ABA triblocks of polyisoprene and *tert*-butyl methacrylate

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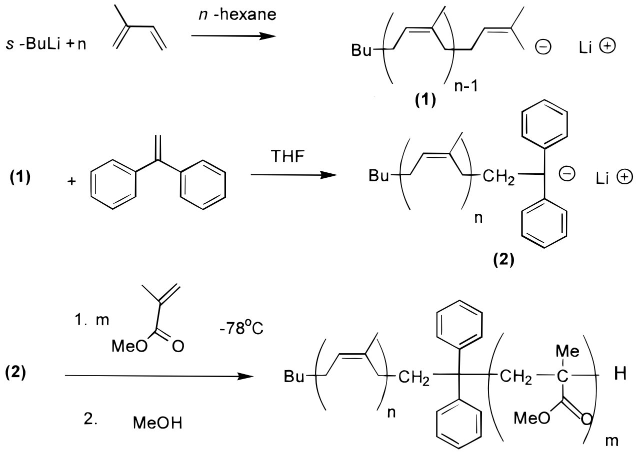
Scheme 1. Synthesis of a PI−PMMA Diblock Copolymer



have been synthesized, a polar solvent being added after the diene polymerization has been completed.[18] ABA triblocks of butadiene and MMA have been made using the difunctional adduct of *t*-BuLi and PEB; increased 1,2-enchainment of the butadiene resulted from the presence of diethyl ether.[19] The relatively straighforward synthesis of diene−methacrylate block copolymers, where high 1,2-enchainment of the diene is acceptable, is accomplished by polymerizing both blocks in a polar solvent such as THF. PB−PMMA diblocks[20] and polystyrene (PS) PS−PB−PMMA[21,22] triblocks have been made by sequential polymerization with monofunctional initiators and PMMA−PB−PMMA triblocks[23] and PMMA−PS−PB−PS−PB−PMMA pentablocks[24,25] using difunctional initiators. PI−PMMA diblocks have also been synthesized in polar media.[26,27]

The aim of the present work was to synthesize the hitherto unknown A_2B_2 star polymers of PI and PMMA and to derive from them the corresponding poly(ethylene-*alt*-propylene)-PMMA stars by hydrogenation of the PI blocks as a prelude to a detailed study of their rheology and morphology.

Experimental Section

Preparation and Purification of Reagents. *n*-Hexane and cyclohexane were first dried over sodium−potassium alloy and then over *n*-butyllithium. Tetrahydrofuran (THF) was stirred over sodium/potassium in the presence of a little benzophenone until a deep purple color was observed and finally distilled onto polystyryllithium prior to use in polymerizations. Isoprene (Fluka) was dried over dibutylmagnesium and then stirred over solvent-free *n*-butyllithium at −20 °C for 30 min immediately before use. Methyl methacrylate (Aldrich) was dried over calcium hydride, distilled onto triethylaluminum, and finally sealed in a glass ampule as a solution in THF. *sec*-Butyllithium (*sec*-BuLi) (Aldrich) was distilled in a short path length apparatus, dissolved in cyclohexane, and ampulized after the molarity of the solution had been determined by titration of a hydrolyzed sample with standard HCl. Lithium chloride (LiCl) (Fisons) was dried under high vacuum at 120 °C and then sealed in an ampule as a suspension in THF. 1,1-Diphenylethylene (DPE) (Aldrich) was titrated with 0.25 M *n*-butyllithium solution in hexanes until a permanent red color was generated, distilled under high-vacuum, and ampulized. 1,1-(1,2-Ethanediyl)bis(4-(1-phenylethenyl)benzene was synthesized using a literature procedure[28] and ampulized as a solution in THF. Toluenesulfonyl hydrazide (Lancaster) was used as received. *o*-Xylene was filtered through basic alumina prior to use.

Synthesis of Diblocks. High vacuum conditions were used throughout the procedure and reagents were transferred using glass break-seals. *sec*-BuLi-initiated polymerization of isoprene in *n*-hexane was allowed to proceed for 24 h to ensure completion. The *n*-hexane was removed under vacuum and replaced with THF prior to the addition of DPE, in 3 times molar excess with respect to initiator, together with LiCl (5 times excess). After dissolution of LiCl, the reaction mixture was cooled to −90 °C, and similarly cooled MMA was added. The reaction was allowed to proceed at that temperature for 20 min before termination with degassed methanol. Any residual polyisoprene homopolymer was removed by Soxhlet extraction with 60/80 petroleum ether.

Synthesis of A_2B_2 Stars. 1,4-Polyisoprenyllithium was synthesized in the manner described above for the diblock copolymers. A solution of EPEB in THF was added dropwise until an amount some 30% in excess of that required to link all the PI chains in pairs had been added. LiCl was added with stirring until completely dissolved. The reaction mixture was cooled to −90 °C, cold MMA was added and the reaction allowed to proceed in a dry ice bath at −78 °C for 45 min. The reaction was terminated by the addition of degassed methanol. The star polymer was fractionated using toluene/petroleum ether (1:2) as the solvent and ethanol as nonsolvent (Scheme 2).

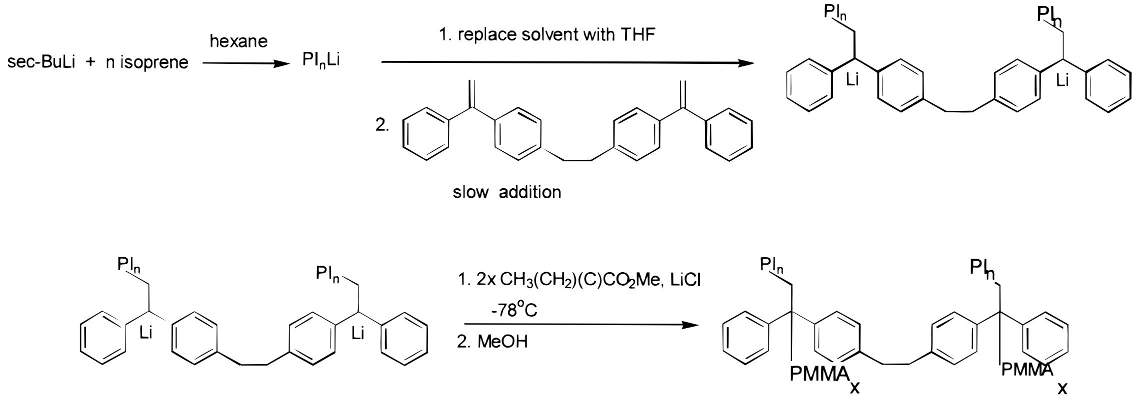
Hydrogenation of Copolymers. The copolymer was dissolved in *o*-xylene under nitrogen at room temperature to give a 1% solution. Toluenesulfonyl hydrazide (2 molar equiv with respect to diene unsaturated bonds) was added to the flask, and the mixture was refluxed at 135 °C under nitrogen for 4 h, with stirring. The solid formed was immediately filtered and the filtrate allowed to cool. The polymer was precipitated in methanol, filtered off, and dried. It was then redissolved in boiling *o*-xylene and reprecipitated in methanol.

Characterization of Materials. SEC experiments were carried out using a GBC LC1110 pump and an ERC 7512 differential refractometer together with three 60 cm Phenomenex 5 μm mixed gel columns. In all experiments the eluant was THF and the flow rate was 1 mL/min. Sample compositions were determined by ^{1}H NMR in $CDCl_3$ at 30 °C using a 300 MHz Varian spectrometer. Membrane osmometry was performed using a Wescan model 230 with toluene as solvent.

Results and Discussion

To obtain PMMA−PI block copolymers where the PI block is highly elastic and the PMMA block has a high glass transition temperature (T_g), it is necessary for the blocks to have the appropriate microstructure, viz. *cis*-1,4 PI and syndiotactic PMMA. These goals present conflicting solvent requirements. To obtain PI which is predominantly 1,4-enchained, a hydrocarbon solvent has to be employed; the use of polar solvents such as THF results in a high percentage of 3,4-enchainment. On the contrary, the polymerization of MMA will not proceed cleanly if a hydrocarbon solvent is used, and furthermore, the resulting isotactic polymer has a low T_g. However, the polymerization of MMA in THF at low temperature forms a near-monodisperse (largely syndiotactic) polymer having a high T_g. Diblocks of this type have been synthesized previously[29] by adding THF to the reaction mixture after the diene has been polymerized but before the MMA polymerization. We found that disproportionately large volumes of THF had to be added in order to enable the formation of near-monodisperse diblocks. A more manageable procedure was found to be the removal of hydrocarbon solvent under high vacuum and its replacement with THF; this was accomplished without detectable loss of anionic activity. An excess of 1,1-diphenylethylene was then added to ensure capping of the polyisoprene living chain ends which thereby minimizes the likelihood of nucleophilic attack on the carbonyl group of the MMA monomer leading to chain termination. Lithium chloride was also

Scheme 2. Synthesis of a PI−PMMA A_2B_2 Star Copolymer



added to aid the control of the MMA polymerization; by modifying the living chain end with the lithium salt, the occurrence of side reactions is reduced and the molecular weight distribution narrowed. The resulting copolymers were often contaminated with small amounts of homopolyisoprene which either arose from chain termination by impurities contained in LiCl, DPE, THF, or MMA or by reaction of the living polyisoprene with MMA monomer. The contaminant was cleanly removed by Soxhlet extraction. A minimum yield of 90% was obtained using this method of purification.

The synthesis of the A_2B_2 stars involves coupling of living PI by EPEB. Clearly, if the amount of linking agent employed is less than that required by stoichiometry, the residual unlinked PI would result in the formation of AB diblock contaminating the desired A_2B_2 star on the subsequent addition of MMA. The consequences of introducing excess amounts of EPEB depend on the rate at which this happens. If mixed all at one time, both olefinic double bonds of some EPEB molecules would add a PI chain whereas only one would react in the remaining molecules; the final outcome would be the formation of a mixture of diblock and star. However, if EPEB is added very slowly as in a titration, PI is in excess over EPEB right up to the end point, thereby ensuring perfect coupling. Excess EPEB added beyond the end point plays no further role in the synthesis because the propagating center derived from MMA is insufficiently nucleophilic to react with it. In order for this strategy to be successful, the coupling reaction must be reasonably rapid. Tests made using a reactor with an optical cuvette attached to it enabled visible spectrophotometry to be employed, which showed that the reaction of PI with EPEB in THF to form the diphenylmethyl anion chromophore absorbing at around 450−550 nm is almost instantaneous.

Polyisoprenyllithium was synthesized in *n*-hexane, and ^{1}H NMR spectroscopy showed that the monomer was 92% 1,4-enchained. The hexane was removed under vacuum and replaced by THF before the addition of the EPEB. The coupling agent was added dropwise via a greaseless stopcock as a solution in THF, the solution becoming gradually deep red in color; the reservoir containing it was calibrated so that the point at which stoichiometric equivalence should be achieved was known. Lithium chloride was added to the solution and dissolved prior to the addition of MMA. Initially, the temperature of the solution was taken below −78 °C and the temperature of the MMA ampule was lowered until the point at which incipient crystallization was observed whereupon the break-seal was ruptured. The red color of the EPEB-linked PI was discharged instantly. A polymerization reaction time of 45 min was employed, longer than the 20 min for the PMMA block of the corresponding diblock copolymer. The extended reaction time appeared to be necessary, along with a temperature no lower than −78 °C, in order for the MMA polymerization to proceed to completion. It is possible that this might be due to intramolecular association of the two PMMA terminal ion pairs. Such a phenomenon has been observed previously when MMA was polymerized using a difunctional organosodium initiator: dissociation of this species was observed to occur slowly but at a rate increasing with the increasing degree of polymerization.[30]

Small amounts of homopolyisoprene were successfully removed from the star copolymer by fractionation. Toluene, which is a good solvent for both polyisoprene and PMMA, was used to prepare a solution. Addition of petroleum ether did not induce precipitation despite being a nonsolvent for PMMA, but precipitation occurred on adding ethanol, a nonsolvent for both polymers. Using a single fractionation step, the yield of star free from homopolymer contamination would typically be in the region of 20%. Attempts to remove polyisoprene using Soxhlet extraction were partly successful but resulted in low molecular weight tailing being observed on SEC traces.

SEC analysis of the progress of the synthesis of a PI−PMMA diblock copolymer CF22 is shown in Figure 1. A sample of polyisoprenyllithium was taken from the reaction vessel, prior to the introduction of MMA, and analyzed. The trace shown corresponds to a molecular weight of 12 100 and a dispersity of 1.02. The chromatogram of the crude material formed after the addition of the MMA shows a bimodal distribution with the main peak having a markedly decreased retention time from that of the polyisoprene block. The smaller peak at 48.6 min represents the termination of a proportion of the parent polyisoprenyllithium by some residual impurity. This contaminant was successfully removed from the diblock by extraction with petroleum ether. The copolymer had a molecular weight of 28 800.

The SEC traces of Figure 2 show the course of the synthesis of the A_2B_2 star CF50. The PI was successfully converted to the corresponding diadduct on the addition of EPEB and is represented by the elution peak at 47.2 min. A little of the parent homopolymer remains uncoupled and this can be attributed to the termination of some of the living polymer chains by impurities introduced after the polymerization of isoprene was complete. As a matter of experimental expediency, after

Table 1. Molecular Weight, Polydispersity, and Mole Fraction of Isoprene

copolymer	architecture	isoprene arm M_n[a]	copolymer M_n[b]	isoprene mole fraction (polymer[c])	dispersity[d]	isoprene arm M_n calcd[e]
CF22	diblock	12 100	28 800	0.47	1.01	10 800
CF26	diblock	12 500	15 700	0.75	1.02	10 500
CF29	diblock	4800	25 700	0.30	1.03	5800
CF48	star	11 100	58 900	0.50	1.03	11 900
CF50	star	7900	54 700	0.40	1.04	8500
CF61	star		49 700	0.52	1.04	11 500

[a] Determined using SEC. [b] Determined using membrane osmometry. [c] Calculated from ^{1}H NMR spectrum. [d] Calculated from SEC results for M_w/M_n relative to polystyrene standards. [e] Apparent molecular weight calculated from MO and ^{1}H NMR.

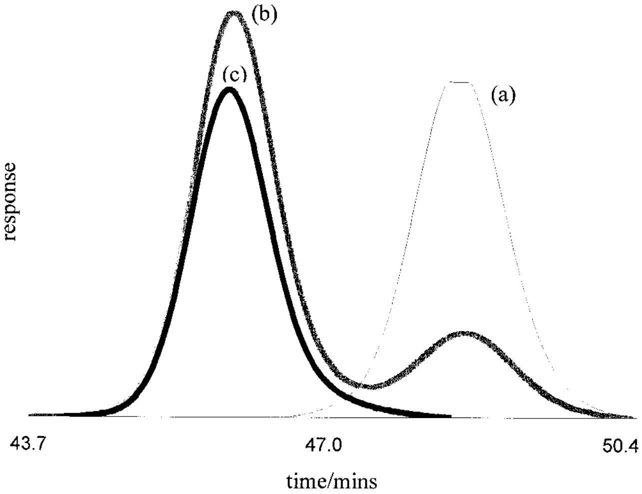


Figure 1. CF22–SEC results following the synthesis of a PI–PMMA diblock copolymer. Trace a is the polyisoprene block, trace b is the diblock prior to purification, and trace c is the diblock after Soxhlet extraction to remove homopolyisoprene.

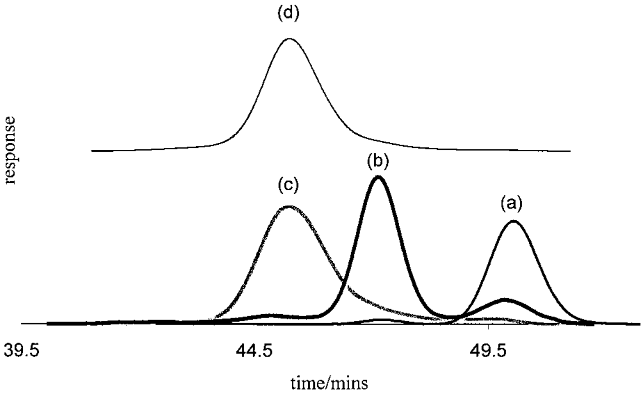


Figure 2. SEC results following the synthesis of CF50 A_2B_2 Star. Trace a is a single arm of polyisoprene, trace b is the polyisoprene diadduct, trace c is the star prior to fractionation, and trace d is the fractionated star.

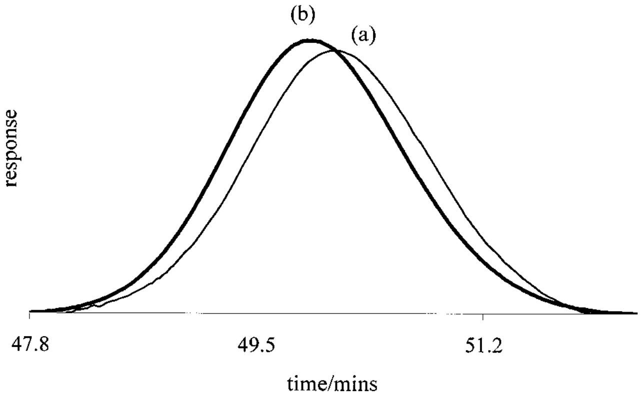


Figure 3. SEC results of CF29 before and after hydrogenation. Trace a shows the PI–PMMA diblock, and trace b shows the diblock after hydrogenation.

withdrawal, this sample was terminated under nonvacuum conditions. Electron transfer to atmospheric oxygen has resulted in the formation of a small amount of coupled chains which are responsible for the small peak at 44.8 min. The chromatogram of the crude star formed consequent to the addition of the MMA shows a peak broadened by a small tail on the low molecular weight side, the latter which most probably represents the presence of a small amount of star having two polyisoprene arms and only one PMMA arm. Such a species would be formed by destruction of one of the anionic centers of the PI diadduct by an impurity in the MMA monomer. The immediate loss of color on introducing the MMA shows that such a three-armed star does not arise from incomplete crossover. It is possible that termination reactions, e.g., "backbiting" reactions, occur during the polymerization of methyl methacrylate, especially at temperatures higher than −78 °C, leading to the broadening of the distribution of PMMA arm molecular weights. Fractionation resulted in a four-armed star having a symmetrical SEC elution peak and a polydispersity of 1.04.

Table 1 summarizes the results obtained for a series of diblocks and four-armed stars. In all cases, products with very satisfactory narrow molecular weight distributions were obtained after fractionation. In general, the compositions were close to those predicted. By way of illustration, reasonable agreement is obtained between the SEC molecular weight of the parent polyisoprene arm and the value calculated from a combination of the osmometric molecular weight of the copolymer and the composition determined by ^{1}H NMR spectroscopy.

Diimide reduction of polydienes was pioneered by Harwood[31] and Lenz.[32] They found that *cis*-1,4-polyisoprene could be reduced quantitatively using *p*-toluenesulfonyl hydrazide by refluxing in a high-boiling solvent, e.g., diglyme or xylene. However, Nang[33] found that such a method for reduction resulted in the depolymerization, decomposition and cyclization of PI which was attributed to the presence of toluenesulfonic acid produced as a byproduct of the reaction. The production of the acid could be suppressed using pyridine as a cosolvent, but this also had the effect of reducing the rate of hydrogenation. Hahn[34] found that tri-*n*-propylamine in the reaction mixture suppressed side reactions during the diimide hydrogenation of polybutadiene but found that incomplete hydrogenation and molecular weight degradation occurred when similar attempts to hydrogenate polyisoprene were made.

^{1}H NMR spectroscopy showed that hydrogenation of the polyisoprene in the diblock and star copolymers proceeded to completion using TSH in boiling xylene but was incomplete in boiling toluene—presumably because of the lower temperature employed for the latter. An amine such as tri-*n*-propylamine was not employed in the diimide hydrogenation of the PI−PMMA copolymers because no degradation was observed as a result of the method employed. Figure 3 shows the SEC traces of a diblock copolymer before and after hydrogenation. The ^{1}H NMR spectra of the hydrogenated copolymers showed the absence of any significant aromatic resonances due to the incorporation of tosyl derivatives.

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