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The Synthesis of Diene - Alkyl Methacrylate Diblock and Heteroarm Star Copolymers

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SUMMARY: The synthesis of A_2B_2 heteroarm stars, where A is either polyisoprene (PI) or polybutadiene (PB) and B is either poly(methyl methacrylate) (PMMA) or poly(butyl methacrylate) (PBMA) has been achieved using living anionic polymerization. Following polymerization of the diene in hexane by *sec*-BuLi, the solvent was changed to THF and the living chains were linked in pairs - without loss of anionic reactivity - using 1,2-bis[4-(1-phenylethenyl)]ethane (EPEB). Star synthesis was completed by the addition of MMA or BMA monomer at -78 °C. The diblocks were prepared by sequential polymerization. The resulting stereochemistries were those of greatest interest from a practical standpoint, i.e., PI or PB with a high 1,4-content (which is highly elastic) and syndiotactic PMMA (which has a high T_g).

Introduction

Block copolymers have been the focus of intense experimental and theoretical interest in recent years because of their practical applications as adhesives, surfactants, compatibilisers and thermoplastic elastomers. The synthesis of the majority of such polymers has predominantly exploited anionic polymerization because of the ability it can offer to control the molecular weight, the polydispersity, 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 geometrically regular[1]. A wide variety of mesophase arrangements has been observed using SAXS and TEM including spheres on a body-centred 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[1] χ. In turn, the morphology has a profound effect upon the mechanical properties of these materials[2].

Recently, attention has been focussed upon non-linear architectures such as hetero-armed stars and graft copolymers; several recent reviews are available[3-6]. The use of chlorosilanes to form star homopolymers by coupling anionic living polymers by condensation is generally free from

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competing side reactions and stars having up to 128 arms have been prepared[7]. Hetero-armed 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 favourable cases by exploiting steric effects[8] or by operating at sub-ambient temperatures[9]. 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.

An alternative means of linking certain living polymers (A) into stars is through reaction with divinylbenzene although control over the number of arms is limited[10]. Because the anionic charges are preserved intact on the oligomeric divinylbenzene core 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)[11-13]. In an extension of this principle, two polystyrene-lithium chains were coupled using the non-polymerizable "double diphenylethene" linker 1,3-bis(1-phenylethenyl)benzene and two polybutadiene chains were grown from the product thereby forming an A_2B_2 hetero-armed star[14,15].

Methacrylates have the attraction of being used industrially on a very large scale for the manufacture of thermoplastics. For many purposes, radical polymerisation provides a satisfactory and expedient route to the polymer although so-called group transfer polymerization is used for some specialised applications. The polymerization of MMA using organolithium initiators in polar solvents such as THF at -78 °C results in unimodal 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-type ligands such as alkylaluminiums[16], alkali metal alkoxides[17] and lithium chloride[18], σ-type, e.g., crown ethers[19] and σ,μ-type such as polyether metal alkoxides[20]. This fine control of the polymerization and the high T_g (120 °C) of the predominantly syndiotactic enchainment raise the possibility of interesting applications for copolymers containing blocks of PMMA.

The literature reports a rather small number of methacrylate-diene block copolymers. Doubtless part of the cause of this is the very different conditions required for the formation of the most useful forms of the different blocks. Elastomeric polybutadiene and polyisoprene are only obtained when the enchainment is predominantly in a 1,4-sense, which demands the use of organolithium initiation in a nonpolar solvent. Under such conditions, PMMA is generally formed with a very broad or multimodal distribution that reflects the occurrence of termination reactions and the presence of more than one kind of propagating species. Most previous work entails either the acceptance of high-vinyl polydienes or involves the addition of a polar modifier to the reaction mixture before the polymerisation of the methacrylate. Long et al. polymerized isoprene in cyclohexane using the difunctional initiator formed by the addition of two moles of *tert*-BuLi to 1,3-bis(1-phenylethenyl)benzene and diluted the reaction mixture with THF before adding *tert*-butyl methacrylate to form the triblock copolymer[21]. Auschra and Stadler polymerized butadiene in THF but capped the chains with DPE before introducing MMA monomer[22]. Yu et al. used the difunctional initiator formed from diisopropenylbenzene and *tert*-BuLi in cyclohexane/diethyl ether to prepare PB having about 45% 1,2-enchainment; the active chain ends were capped with DPE and THF was added prior to the introduction of a second monomer - MMA, ethyl or *tert*-butyl methacrylate[23,24]. Fayt and Teyssié polymerized butadiene by *sec*-BuLi in benzene; the living polymer solution was diluted with THF, cooled to -78 °C and capped with 4-vinylpyridine prior to adding MMA[25].

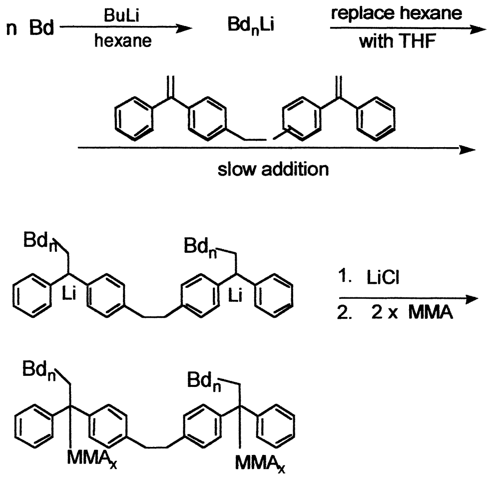
Experimental

n-Hexane and cyclohexane were first dried over sodium-potassium alloy, then over butyllithium. Tetrahydrofuran (THF) was stirred over sodium/potassium alloy in the presence of a little benzophenone and finally distilled from polystyryllithium immediately prior to use in polymerizations. Isoprene (Fluka) was dried over dibutylmagnesium and then stirred over solvent-free butyllithium at -20 °C for 30 min immediately before use. Butadiene (Aldrich) was treated with successive sodium mirrors and then finally with solvent-free butyllithium at -20 °C. MMA and BMA (Aldrich) were purified immediately prior to use to prevent loss by premature partial polymerization during storage. MMA was dried over calcium hydride, distilled onto triethylaluminium, and finally ampoulized as a solution in THF. BMA was only dried over calcium hydride as treatment with triethylaluminium caused the formation of polymer. *sec*-Butyllithium (Aldrich) was distilled in a short-pathlength apparatus, dissolved in cyclohexane and ampoulized 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, then sealed in an ampoule as a suspension in THF. 1,1-Diphenylethene (DPE) (Aldrich) was titrated with 0.25M butyllithium solution in hexane until a permanent red color was generated, distilled under high vacuum, and ampoulized. EPEB was synthesized as described[26] and ampoulized as a solution in THF.

Synthesis of AB diblock copolymers

The polymerization of butadiene or isoprene was initiated by *sec*-BuLi in *n*-hexane using standard high vacuum techniques. After 24 h, the hexane was removed and replaced by THF under vacuum and a small portion of the reaction mixture was isolated in a side arm behind a greaseless stopcock for subsequent analysis by SEC. DPE and LiCl were added in amounts to create, respectively, three and five times the active chain end concentration. When all of the LiCl had dissolved, the reaction mixture was cooled to -90 °C and similarly cooled MMA or BMA was added very rapidly from an ampoule having a domed breakseal. After 20 min, degassed methanol was added to inactivate the anionic chain ends. The polymer recovered was extracted in a Soxhlet thimble by 60/80 petroleum ether to remove any homopoly(diene) contaminant from the MMA blocks. This procedure could not be applied to the BMA blocks and attempts to fractionate them using the following solvent/precipitant combinations were met with only limited success: toluene/ethanol, toluene/methanol, toluene/petroleum ether, butan-2-one/water and THF/formic acid.

Scheme 1



Synthesis of A_2B_2 Stars

The synthetic route to the A_2B_2 stars is shown in Scheme 1. Butadiene (Bd) or isoprene was polymerised in *n*-hexane as in the preparation of the diblocks and a small quantity of the reaction mixture was isolated in a side arm behind a greaseless stopcock for subsequent analysis. A solution of 1,2-bis[4-(1-phenylethenyl)]ethane (EPEB) in THF was added slowly and dropwise until eventually in excess of that required to link all the chains in pairs. LiCl was then added with stirring until completely dissolved. A further sample of the reaction mixture was isolated behind a stopcock. The reaction mixture was cooled to -90 °C, cold MMA or BMA was added and the reaction was allowed to proceed for 45 min at -78 °C. The reaction was terminated by the addition of degassed methanol. The PMMA star polymers were purified by fractionation using toluene/petroleum ether (1:2 v/v) as the solvent and ethanol as non-solvent. The fractionation of the BMA stars encountered the same difficulties as the corresponding diblocks.

Characterization of Materials

Some SEC measurements were carried out using a GBC LC1110 pump and an ERC 7512 differential refractometer together with three 60 cm Phenomenex 5 micron mixed gel columns. Other SEC measurements employed a set of Waters Styragel HR columns in conjunction with a Waters 410 concentration detector and Viscotek Model T60 viscosity and light scattering detectors. In all experiments the eluant was THF and the flow rate was 1 ml/min. Sample compositions were determined by ^1H NMR in $CDCl_3$ at 30 °C using a 300 MHz Varian spectrometer. Membrane osmometry employed a Wescan 230 instrument and toluene as solvent.

Results and discussion

In order to form polybutadiene (PB) and polyisoprene (PI) which have high elasticity, it is necessary to use an organolithium initiator in a hydrocarbon solvent at ambient or elevated temperature. The presence of polar additives or solvents results instead in much 1,2- or 3,4-enchainment. In contrast, the polymerization of MMA to form a syndiotactic polymer of low dispersity demands the use of a polar solvent such as THF and temperatures at or below -70 °C to minimise competing reactions which lead to chain termination. A procedure for the synthesis of PI-PMMA diblocks has been described where THF was added to the reaction mixture after the diene was polymerised but before the MMA polymerization[23,24]. 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 the hydrocarbon solvent under high vacuum and its replacement by THF, which can be accomplished without loss of anionic activity. An excess of DPE was then added to convert the allylic living chain ends into diphenylmethyl anions which have a considerably reduced nucleophilicity, thereby minimising the likelihood of attack on the carbonyl group of the monomer which would lead to chain termination. Lithium chloride was also added at this stage since it has been demonstrated that when the living chain end is associated with this salt, the occurrence of side reactions is further reduced and the molecular weight distribution narrowed[18]. It was found, however, that the resulting copolymers were often contaminated with small amounts of homopoly(diene) which either arose from chain termination by residual impurities contained in LiCl, DPE, THF or the MMA or, possibly, by reaction of the living poly(diene) with the ester group of the MMA monomer if mixing was not sufficiently vigorous to prevent the development of localised "hot" spots. The contaminant was cleanly removed by Soxhlet extraction with petroleum ether.

Quirk et al. coupled polystyrene-lithium with the analogous linking agent 1,3-bis(1-phenylethenyl)benzene and initiated the polymerization of butadiene with the adduct[15]. However, the addition of a promoter such as THF or lithium butoxide is necessary to ensure rapid and complete initiation of the polymerization of the second monomer and this can lead to an increase in the vinyl mode of addition. Wright et al. reversed the sequence and coupled polybutadiene-lithium and then grew polystyrene arms: since the desired high 1,4-enchainment of the diene had already taken place, the addition of a little THF to ensure completeness of the linking had no deleterious effect on the subsequent polymerisation[8]. Whichever sequence of star construction is employed, it is vital that exactly one mole of EPEB be employed per pair of chains in the linking reaction: a deficit would lead to contamination by diblock and an excess to the formation of some more highly branched polymer. The requirement for exact stoichiometric equivalence is eased in the case of the stars with PMMA arms. Provided that the linking agent is added dropwise, there is an excess of poly(diene)-lithium present up to the end-point so ensuring perfect coupling. The presence of THF during this operation is highly beneficial to the subsequent polymerization of the methacrylate. The addition of further EPEB after the end-point has been reached is of no consequence since EPEB does not polymerize and since the propagating PMMA anion is insufficiently nucleophilic to react with EPEB.

The optimum reaction conditions for the formation of the PMMA arms from the EPEB-linked poly(diene)-lithium chains were found to differ from those found for the synthesis of the corresponding diblocks. Slightly higher temperatures (-78 °C) and an increased polymerization time of 45 min were found to be necessary. It has been reported that the polymerization of MMA using a disodium initiator results in the intramolecular association of the terminal ion pairs which suppresses their reactivity until, in due course, dissociation occurs[27,28]. It is possible that a similar phenomenon occurs with lithium-containing chain ends.

The quick disappearance of the red colour of the diphenylmethyl anion moieties of the EPEB-linked chains, together with the absence of PI_2PMMA three-armed stars, shows that the initiation of the polymerization of the MMA is rapid and complete. The simplest conclusion is that the two PMMA arms have the same molecular weight but there is no simple means of verifying this.

The syntheses of diblocks and stars with blocks of PB proceeded in an entirely analogous manner, as did those of PBMA with PI and PB.

Figure 1 shows the progress of the formation of a PB-PBMA diblock . The main peak in the SEC trace of the polybutadiene block (a) at 46.5 min corresponds to a polydispersity of 1.01. There is, however, a second much smaller peak at 43.9 min which is an artefact caused by terminating the activity of the sample withdrawn from the reactor by opening the sample tube in air before introducing methanol. Although expedient, particularly in terms of the complexity of the glassware, this technique resulted in coupling of radicals produced by electron transfer from the active centres to oxygen. It is important to note that the reactor contents were never exposed to air. SEC trace (b) is that of the crude diblock (PD 1.01 from SEC).

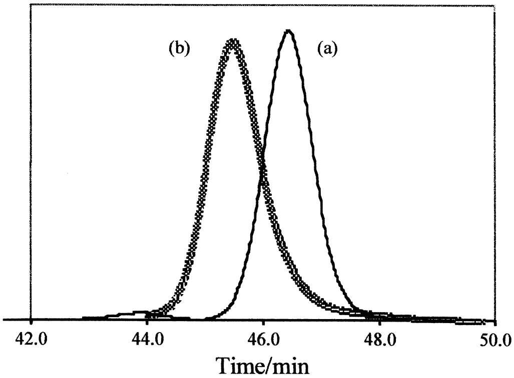


Figure 1: Synthesis of PB-PBMA diblock copolymer. SEC traces of (a) the PI block and (b) the crude diblock

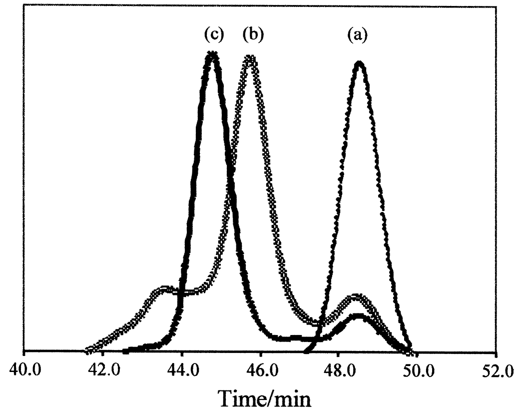


Figure 2: Synthesis of PI$_2$PBMA$_2$ star copolymer. SEC traces: (a) single PI arm, (b) EPEB-linked PI arms (c) crude star copolymer

Figure 2 shows the stepwise formation of a (PI)$_2$(PBMA)$_2$ star. Trace (a) shows the chromatogram of the PI arm which has a polydispersity of about 1.01. Trace (b) is that for a sample withdrawn from the reactor after the addition of EPEB. The peak for the diadduct is located at 45.8 min as expected for the doubling of the molecular weight. As with the synthesis of the diblock described above, some air was admitted to this sample after its withdrawal from the reactor, resulting in some oxidative dimerisation of the coupled arms which is responsible for the large shoulder at about 43.7 min. In addition, there is a peak at 48.6 min which represents the presence of some arm which has been terminated by residual impurities in the LiCl, EPEB or the THF. In consequence, this peak also appears in the chromatogram (c) of the unfractionated star. The dominant peak in trace (c) is that due to the star at 44.8 min and, since air never entered the reactor during synthesis, the artefact shoulder of trace (b) at 43.7 min is entirely absent.

Table 1 Molecular weights, polydispersity and diene mole fractions of copolymers

A	B	Architecture	$M_n \times 10^{-3}$ targeted	$M_n \times 10^{-3}$ observed	PD	Φ_{diene} feed	Φ_{diene} observed
PI	PMMA	block	22	28.8[a]	1.01[c]	0.57	0.58
PI	PMMA	block	22	25.7[a]	1.03[c]	0.30	0.31
PI	PMMA	star	46	58.9[a]	1.03[c]	0.60	0.62
PI	PMMA	star	41	49.7[a]	1.04[c]	0.60	0.57
PB	PMMA	block	24	18.4[b]	1.08[b]	0.69	0.69
PB	PMMA	star	43	43.9[b]	1.10[b]	0.45	0.40
PB	PMMA	star	38	38.6[b]	1.06[b]	0.57	0.53
PB	PBMA	block	22	-	1.01[c]	0.85	0.85
PI	PBMA	star	40	-	1.01[c]	0.79	0.80

[a] By membrane osmometry; [b] by SEC with triple detector; [c] by SEC with RI detector only.

Table 1 shows a summary of the results obtained. In general, the compositions of the copolymers determined by ^1H NMR analysis are very close to those of the monomer feeds. The molecular weight distributions of the PMMA-PB copolymers are narrow, as shown by analysis with triple detection by RI, viscosity and light scattering. SEC analysis of the PMMA-PI polymers was solely with an RI detector and the polydispersity shown in Table 1 was calculated on that basis. The measured molecular weights are in good agreement with expectation except for the PI-PMMA samples which are systematically about 25% higher, which may be due to an error in the titration of that batch of *sec*-BuLi. Attempts to fractionate the PBMA copolymers were unsuccessful as the solubilities of the two components were too similar in the solvent/precipitant combinations tried but SEC analysis with the system with only the RI detector showed that the molecular weight distributions of the copolymer peaks were very narrow.

Conclusion

Linking poly(diene)-lithium molecules in pairs with 1,2-bis[4-(1-phenylethenyl)]ethane proceeds without loss of anionic reactivity. The adduct so formed can initiate the polymerization of alkyl methacrylates to create A_2B_2 hetero-armed star copolymers with low polydispersity and controlled composition.

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