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Synthesis of Laterally Linked Poly(tetrahydrofuran)−Poly(methyl methacrylate) Block Copolymers via Use of a “Jekyll and Hyde” Comonomer

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ABSTRACT: Glycidyl methacrylate (GMA) is an example of a heterobifunctional monomer, a so-called “Jekyll and Hyde” monomer, in that one functional group can be polymerized via conventional free radical polymerization and the other via cationic ring-opening polymerization. Laterally linked diblock copolymers differ from conventional linear diblock copolymers in that the blocks are not linked via their termini but at a point some way along each chain. This architecture has therefore some of the characteristics of a graft copolymer. Free radical copolymerization of a low level of GMA with methyl methacrylate (MMA) yields MMA/GMA copolymers with a few pendent epoxide groups. Likewise cationic ring-opening copolymerization of low levels of GMA with tetrahydrofuran (THF) yields THF/GMA copolymers with a few pendent methacrylate groups. Subsequent cationic polymerization of the first copolymer type with THF, and subsequent free radical polymerization of the second copolymer type with MMA, yields laterally linked block copolymers of MMA and THF. The two strategies are complementary but the polymerization of the THF block first followed by the MMA block is more efficient and leads to good incorporation of both of these monomer segments. Typically mole ratios of THF/MMA segments approaching 1/1 are achievable with copolymer recoveries up to ∼60% and overall M_w values up to 125 kDa. While the products are significantly more heterogeneous in terms of the molar mass distributions of the blocks and the backbone architecture than are conventionally produced diblock copolymers, we believe that they are complementary to, rather than competitive with, conventional diblocks and that this new synthetic strategy and ease of synthesis offers potential for the exploitation of these materials.

Introduction

Methodologies for the synthesis of block copolymers are well developed.[1−4] Current procedures focus on the use of “living” polymerization techniques with the aim of producing structurally “pure” copolymers with precisely controlled monomer compositions and block lengths. Physicochemical characterization of these materials has been extensive and unique, potentially useful, behavior has been demonstrated in the solid state, in blends with homopolymers, and in the solution state. Despite these valuable properties however relatively few materials have emerged as useful and successful products. One of the reasons for this is that the value added in potential products has not been sufficiently high to off-set the relatively high cost associated with the production procedures which tend to be very demanding. Interestingly though while some potential applications do indeed require structurally “pure” block copolymers there are others that are not so demanding in this respect, e.g., blend compatibilizers, polymeric surfactants, etc. Indeed if more direct and more cost-effective routes to block copolymers could be developed, if necessary associated with compromise in terms of structural and compositional purity, then a far broader evaluation of physical properties and potential for exploitation could be undertaken. Developing such methodologies therefore remains a key challenge for academic polymer chemists as well as technologists. With this background we have been trying to evolve new procedures for the synthesis of architecturally complex copolymers,[5] including block copolymers,[6] via methodologies that might facilitate scale-up and reduce costs. In the context of the present work heterobifunctional *initiators*[7−15] have been used to synthesize linear diblock and triblock copolymers via orthogonal polymerization with each of the two initiator functions being chosen to generate specifically a different reactive intermediate and hence the possibility of initiating chain growth of two different monomers. Indeed Howdle et al. have even achieved an orthogonal and simultaneous copolymerization to form a diblock copolymer using a heterobifunctional initiator that induces an enzymic ring-opening polymerization and a controlled free radical polymerization in supercritical CO_2.[16] Furthermore, heterobifunctional monomers in which one functional group is a polymerizable species and one is an initiator were employed first by Frechet et al.[17] to generate branched homopolymers in a one-pot reaction via a so-called “self-condensing polymerization”. Subsequently such bifunctional monomer/initiator species have also been used to synthesize graft copolymers[18] and cross-linked network copolymers.[19] We wondered whether a heterobifunctional *polymerizable monomer* (a “Jekyll and Hyde” monomer), i.e., a monomer with two different functional groups polymerizable via two different reactive intermediates, might be exploited in the relatively facile

Scheme 1. Idealized Copolymerization of “Jekyll and Hyde” Monomer Sequentially with Monomers M_1 and M_2 Using Different Reactive Intermediates To Form Laterally Linked Diblock Copolymers

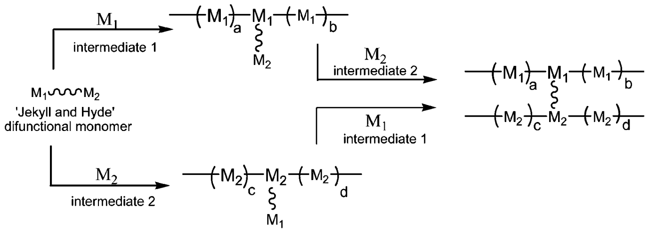

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Table 1. Analytical Data for PTHF/GM 1−6 Precursor Polymers

		GMA content (mole %)		MALS/SEC data			
PTHF/GMA	yield (%)	feed	ex ^{1}H NMR	M_n	DP_n	M_w	PDI
1	51	10	5.3	10 300	143	14 500	1.4
2	60	5	2.5	5200	72	9900	1.9
3	48	2	3.1	4500	62	8400	1.9
4	61	2	5.1	5200	72	18 500	3.6
5	77	2	2.8	3600	46	7900	2.8
6	58	4	2.6	3300	50	9500	2.2

synthesis of *branched* diblock copolymers (Scheme 1) where the two blocks are linked laterally rather than terminally. (Note: we have knowingly used the term "block copolymer" loosely since the IUPAC Compendium of Macromolecular Nomenclature specifically defines block copolymers as being linear. However we feel that the targeted species are structurally more closely related to diblock copolymers than they are to graft copolymers which generally possess many grafted chains.) Right at the outset, we appreciated that this approach would be unlikely to yield structurally and compositionally homogeneous copolymers but *the intention was to synthesize as easily as possible* complex and interesting block copolymers that might be complementary to, but not competetive with, their more structually "pure" analogues. Some years ago Haas and Simon[20] used the difunctional species β-vinyloxyethyl methacrylate to form a cross-linkable network and Chan et al.[21] similarly used an acrylamide and an acrylate containing difunctional monomer to control cross-linking in their networks. Most recently Hirao et al.[22] have demonstrated the ability to polymerize the styrene function selectively via anionic intermediates in a difunctional monomer also containing an α-methylstyrene functional group. As far as we aware, however, there are no earlier reports of the use of a "Jekyll and Hyde" comonomer in the premeditated synthesis of soluble block copolymers upon which we now report.

Experimental Section

Materials. MMA, THF, THF (HPLC grade), AIBN, and triethyloxonium hexachloroantimonate were from the Aldrich Chemical Co. GMA was from the Dow Chemical Co. Toluene, DCM and hexane were from Strathclyde Chemicals. All materials were used as received except for the THF and DCM which were dried using a "Pure Solv" system from Innovative Technologies Inc.

Synthesis of PMMA/GMA Precursors. MMA (4 g, 40 mmol) and GMA (1 mol %) were dissolved in toluene (20 mL) in one of the glass flasks in a Radley's Carousel Reactor Station (Radley Discovery Technology, U.K.). The solution was deoxygenated by bubbling with nitrogen gas for 15 min and then heated to 85 °C. Finally for **PMMA/GMA1** 1 wt % AIBN (0.04 g) (for **PMMA/GMA2** 5 wt %) was added and the reaction stirred under N_2 at 85 °C for 5 h. The crude yield of each polymer was determined following evaporation of the toluene. The initial product was then dissolved in toluene and the polymer precipitated by pouring into an excess (~10/1) of cold hexane. The resulting polymer was filtered off and dried at 40 °C in a vacuum oven for 4 days. The final products were recovered as white powders (yields 78 and 94%) and the elemental microanalytical data (C%, H%) show good agreement with the values based on the feed of MMA and GMA.

Anal. Calcd (1% GMA feed): C, 59.8; H, 8.0. Found for **PMMA/GMA1**: C, 60.2; H, 8.3. Found for **PMMA/GMA2:** C, 60.3; H, 8.2.

^{1}H-NMR ($CDCl_3$) δ (ppm):

H^a 0.85-1.0

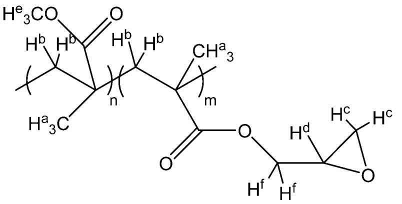
H^b 1.4-1.9

H^c 2.85, 2.65

H^d 3.2

H^e 3.6

H^f 4.3,3.8



Synthesis of PMMA/GMA-b-PTHF. Two Schlenk flasks were dried and the air replaced by dry nitrogen using three cycles of evacuation and nitrogen purge. **PMMA/GMA** precursor polymer (≡60 mmol MMA) was introduced into one graduated (5 mL) flask followed by dry THF (~5 mL, 4.45 g, ~60 mmol) directly from the drying system (see Materials section). To reduce the viscosity of the resulting solution a small quantity of dry DCM was also added and then the flask stored under nitrogen. The cationic ring-opening polymerization (CROP) initiator, $Et_3O^+SbCl_6^-$(1 mol %) was weighed into the other flask and kept under nitrogen in an ice bath. The THF solution was then added through a canula to the initiator solution. The reaction mixture was stirred under nitrogen at room temperature or 0 °C until gelation occurred, generally after 40−50 min. The physical gel was easily dissolved by addition of 2−3 mL of DCM and a few drops of MeOH were added to obtain methoxy-terminated polymer chains. Any residual THF and DCM were then evaporated off and the yield of crude product obtained. This was usually a yellowish oil which was dissolved in DCM, washed with $NaOH_{aq}$ (0.05 M) and the polymer extracted 2−3 times with fresh DCM. Addition of brine and/or ethanol facilitated the separation of the organic phase from the aqueous phase. The organic phases were combined together and dried over magnesium sulfate ($MgSO_4$). Finally, after filtering off the $MgSO_{4,}$ the polymer was isolated by evaporation of the DCM before drying in a 40 °C vacuum oven for 4 days. Usually a white oil was formed which solidified in ~1 h at room temperature (yields 40 and 31%) and the elemental microanalytical data (% C; % H) are in reasonable agreement with the values based on the equimolar feed of MMA and THF. In practice the ^{1}H NMR data (see later text) indicate a lower content of THF residues in the block copolymers than expected from the feed, and the lower than expected C% reflects this (PMMA % C = 60.0; PTHF % C ~ 66.6). In addition all PTHF containing products are isolated as oils or waxes from an aqueous workup procedure and may contain varying levels of moisture.

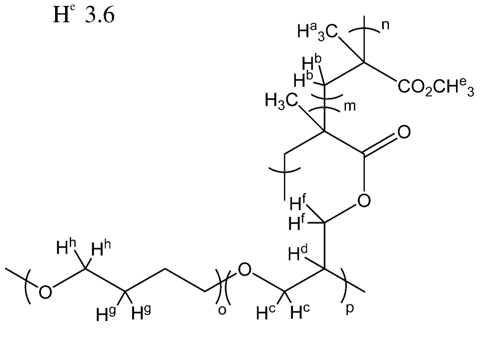
^{1}H NMR ($CDCl_3$) δ (ppm):

H^a 0.84-1.22

H^b 1.4-1.9 (overlapped with H^g)

H^c 3.4 (overlapped with H^d, H^f and H^h)

H^e 3.6



Anal. Calcd: C, 63.2; H, 9.5. Found for **PMMA/GMA-*b*-PTHF1**: C, 60.0; H, 8.2. Found for for **PMMA/GMA-*b*-PTHF2**: C, 63.0; H, 8.0.

Synthesis of PTHF/GMA Precursors. These were synthesized by CROP using the same procedure as indicated above but without

Table 2. Analytical Data for PTHF/GMA-*b*-PMMA1−6

precursor **PTHF/GMA** polymer	**PTHF/GMA-*b*-PMMA**	yield (%) crude	yield (%) purified	THF/MMA mole ratio[a] (ex ^{1}H NMR)	MALS/SEC data M_n	MALS/SEC data M_w	MALS/SEC data PDI
1	**1**	76	61	1/1.0	29 200	128 500	4.4
2	**2**	81	45	1/1.4	15 700	47 200	3.0
3	**3**	71	26	1/1.4	11 400	34 900	3.0
4	**4**	63	49	1/0.9	23 200	99 400	4.3
5	**5**	58	46	1/0.5	3700	13 900	3.7
6	**6**	65	53	1/0.7	5600	19 700	3.5

[a] Feed value 1/1 in all cases.

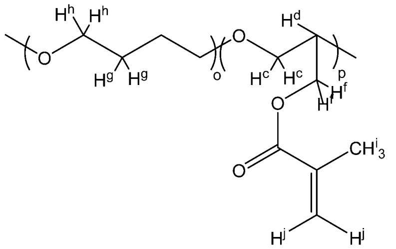
the addition of any DCM solvent. The yields obtained are shown in Table 1. The elemental microanalytical data all show lower % C contents than the values calculated from the corresponding THF/GMA feed ratios and the most likely reason for this is residual trapped water from the aqueous workup procedure.

^{1}H NMR ($CDCl_3$) δ (ppm):

H^c 3.4 (overlapped with H^d,H^f and $H^{h)}$

H^g 1.6

H^i 1.9



Anal. Calcd (samples with targetted $DP_N = 100$).

PTHF/GMA1 Calcd: C, 65.1; H, 10.4. Found: C, 61.0; H, 10.7.

PTHF/GMA2 Calcd: C, 65.9; H, 10.7. Found: C, 61.3; H, 10.6.

PTHF/GMA3 Calcd: C, 66.2; H, 10.9. Found: C, 62.5; H, 9.9.

PTHF/GMA4 Calcd: C, 66.2; H, 10.9. Found: C, 63.9; H, 10.4.

Synthesis of PTHF/GMA-b-PMMA. These were synthesized using conventional free radical polymerization as described above using a THF/MMA mole feed of 1/1. The yields obtained are shown in Table 2 and as before the found % C values are somewhat below the expected value for an equimolar composition PMMA/PTHF and most likely reflect moisture content.

^{1}H NMR ($CDCl_3$) δ (ppm): See entry for **PMMA/GMA-*b*-PTHF** above.

Anal. Calcd: C, 63.2; H, 9.5 for equimolar composition PMMA/PTHF.

Found for **PTHF/GMA-*b*-PMMA1**: C, 60.6; H, 9.6.

Found for **PTHF/GMA-*b*-PMMA2**: C, 60.3; H, 9.3.

Found for **PTHF/GMA-*b*-PMMA3**: C, 59.6; H, 9.4.

Found for **PTHF/GMA-*b*-PMMA4**: C, 61.3; H, 9.5.

Analytical Methods. ^{1}H NMR spectra were recorded on a 400 MHz Bruker DPX-400 spectrometer using deuterated solvents ($CDCl_3$, DMSO-d_6) in 5 mm NMR tubes. All the spectra were calibrated using the signal of the deuterated solvent as a reference (i.e.: 7.3 ppm for $CDCl_3$ or 2.5 ppm for DMSO-d_6).

Elemental microanalyses were carried out by the microanalytical service available within the Department of Pure and Applied Chemistry at the University of Strathclyde.

Polymer molar mass data were evaluated using a multiangle light scattering (MALS) in combination with size exclusion chromatography (SEC). The instrument package was supplied by Optokem and comprised the following equipment: (i) a Jones Chromatography 7600 Series Solvent D-Gasser; (ii) a Waters 515 HPLC pump operating at room temperature; (iii) a Jasco AS-950 autosampler with 50 position sample racks, (iv) a Shimadzu CTO-6A column oven; (v) a set of three Styragel HR 2, HR 4 and HR 6 designation 7.8 × 300 mm GPC columns; (vi) two detectors connected in a serial configuration, a multiangle light scattering detector (mini-Dawn) operating at 690 nm supplied by Wyatt Technology, and an interferometer refractometer detector (Optilab DSP) supplied by Wyatt Technology. THF was the mobile phase, the column oven temperature was set to 40 °C, and the flow rate was 1 mL/min. The samples were prepared for injection by dissolving approximately 20 mg of polymer in 4 mL of HPLC grade THF; 0.2 mL of this mixture was then injected, and data were collected for 40 min. The wavelength used was 690 nm. ASTRA for Windows (Wyatt technology, version 4.73.04) was used to collect and process the signals transmitted from the detectors to the computer and to produce the molar mass distribution and molar mass vs elution volume plots. Refractive index increments (d*n*/d*c*) were found in the literature[23] (0.089 for PMMA in THF and 0.066 for PTHF in THF). For the copolymers of MMA and THF, an average value was calculated from the mass ratio MMA/THF in the samples. For example, if a copolymer is composed of 60 wt % THF and 40 wt % MMA, the d*n*/d*c* of the copolymer was calculated as: $0.6 \times 0.066 + 0.4 \times 0.089 = 0.0752$. This value was assumed to be valid across the whole of the molar mass distribution.

Differential scanning calorimetry (DSC) was performed using a TA Instruments DSC Q1000, with all data being processed with TA Instruments Universal Analysis 200 software. The experimental procedure was a follows. Each sample (ca. 10−15 mg), was weighed into a crimped aluminum pan and the analysis was performed under a flow of nitrogen (20 mL/min) in the following steps: (1) equilibrate at 25.0 °C; (2) isothermal for 1.00 min; (3) ramp 10.0 °C/min to 120.0 °C; (4) end of cycle 1; (5) isothermal for 1.00 min; (6) ramp 10.0 °C/min to −90.0 °C; (7) end of cycle 2; (8) isothermal for 10.00 min; (9) ramp 10.0 °C/min to 200.0 °C; (10) end of cycle 3; (11) end of method. For the PTHF component the crystallization temperature, T_C, was taken as the temperature at the peak maximum of the crystallization peak of the sample upon cooling from +120 to −90 °C at a cooling rate of 10 °C/min. The melting points, T_M, were obtained on the subsequent heating step and were also taken as the peak maximum at a heating rate of 10 °C/min. The glass transition temperature, $T_{G,}$ of the PMMA component was taken as the midpoint of the incline associated with the change in heat flow for this transition on the heating step at a rate of 10 °C/min.

Results and Discussion

Glycidyl methacrylate (GMA) was selected as a potential “Jekyll and Hyde” monomer with the intention of sequentially copolymerizing the methacrylate function with methyl methacrylate (MMA) via free radical intermediates and then the epoxide function with tetrahydrofuran (THF) via oxonium ion intermediates or vice versa. (Scheme 2). Thus, in our first approach, GMA (1 mol %) and MMA were copolymerized under N_2 in toluene at 85 °C for 5 h using conventional free radical polymerization initiated using azobis(isobutyronitrile) (AIBN, 1 and 5 wt %). The two polymers (PMMA/GMA1 and PMMA/GMA2) were precipitated in *n*-hexane and recovered in 78 and 94% yield respectively. The ^{1}H NMR spectroscopic

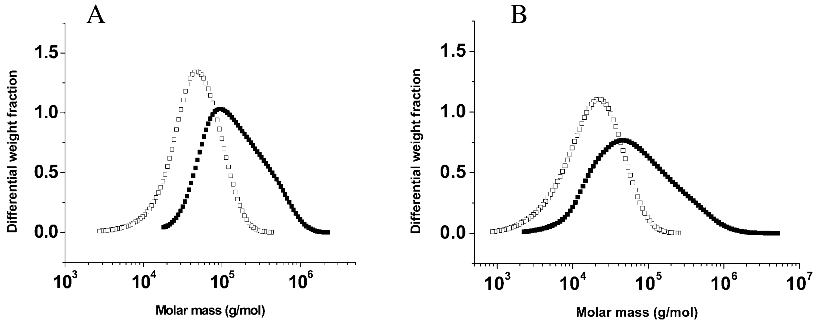
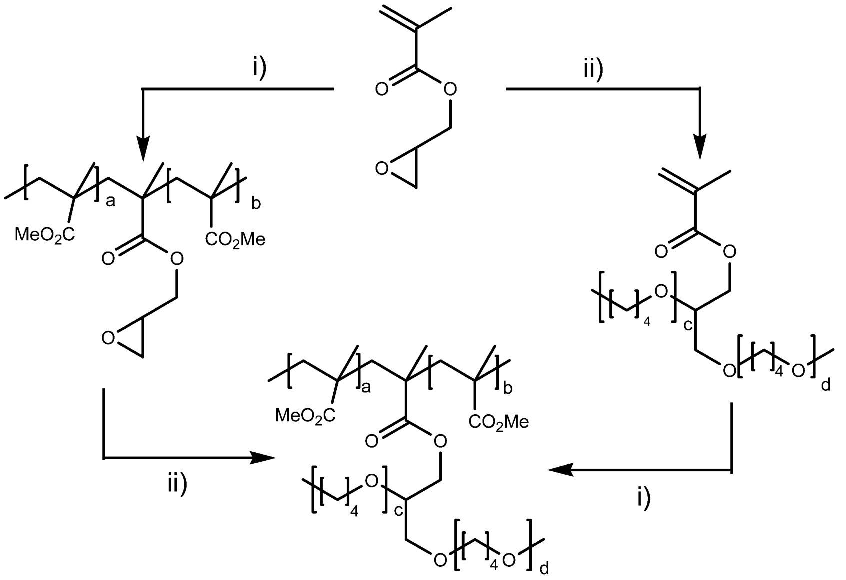


Figure 1. MALS/SEC molar mass distribution curves: (A) □, **PMMA/GMA1**; ■, **PMMA/GMA-*b*-PTHF1**; (B) □, **PMMA/GMA2**; ■, **PMMA/GMA-*b*-PTHF2**.

Scheme 2. Idealized Strategy for the Use of GMA as a "Jekyll and Hyde" Comonomer in the Synthesis of PTHF−PMMA Diblock Copolymers: (i) MMA/AIBN; (ii) THF/EtO$^+$SbCl$_6$$^-$



analysis showed the GMA content to be ~1.4 and 0.8 mol % and the multiangle light scattering/size exclusion chromatographic (MALS/SEC) analysis yielded values of M_n, M_w, and the polydispersity index (PDI) of 30.7 kDa, 55.1 kDa, and 1.8 and 10.6 kDa, 23.6 kDa, and 2.2 respectively. Figure 1 shows the corresponding molar mass distribution curves which display shapes and breadths typical of polymers prepared via conventional free radical polymerization. Each linear MMA/GMA copolymer was then copolymerized at 0 °C with dry THF (MMA/THF mole ratio 1/1), in a small amount of dry dichloromethane (DCM) to reduce the viscosity, under N_2 using triethyloxonium hexachloroantimonate ($Et_3O^+SbCl_6$, 1 mol %)) as the cationic ring-opening polymerization (CROP) initiator. The resulting physical gels (crude yields 62 and 75% respectively) were dissolved in dichloromethane (DCM) and washed with NaOH(aq) before drying ($MgSO_4$) and the copolymers (**PMMA/GMA-*b*-PTHF1** and **PMMA/GMA-*b*-PTHF2**) were isolated by evaporation of the solvent. The resulting white viscous oils solidified on cooling to room temperature with recoveries of 40 and 31% respectively. The ^{1}H NMR spectroscopic analysis indicated the MMA/THF ratio to be ~1/0.1 and 1/0.2, i.e., a rather poor incorporation of the THF component into each copolymer relative to the feed values. For **PMMA/GMA-*b*-PTHF1** and **PMMA/GMA-*b*-PTHF2** the MALS/SEC analysis yielded values of M_n, M_w and PDI of 102 kDa, 208 kDa, and 2.0 and 33.8 kDa, 130 kDa, and 3.9, respectively, and the corresponding molar mass distribution curves are shown in Figure 1. Though these are broader with more overlap than would be the case for the distributions for correponding materials synthesized via traditional living polymer procedures, the curves show quite clearly that the distributions of the two precursor PMMA polymers do broaden somewhat and shift to higher molar mass in the two PMMA-*b*-PTHF copolymers. Since the incorporation of the THF comonomer relative to the existing MMA content in the precursors is low (i.e., ~15% of the mass), and is reflected in the limited recoveries obtained, these shifts are significant and tend to confirm that block copolymers as opposed to two homopolymers have been formed. Had this not been the case the molar mass distribution curve for each PMMA precursor would have dominated the distributions in the products.

In an attempt to achieve a better balance in the PMMA−PTHF content of the final copolymers additional precursor GMA/MMA polymers were prepared with the feed of GMA increased to 2 and 10 mol %. The polymers were recovered in ~90% yield and ^{1}H NMR spectral analysis indicated the GMA content to be 4.5 and 13 mol % respectively. Unfortunately however when these samples were subsequently used in copolymerizations with THF the gelled products that resulted proved to be insoluble in DCM and were clearly cross-linked. It was concluded that the higher GMA content in the precursors yielded polymer chains with on average more than GMA residue per chain hence facilitating cross-linking on subsequent polymerization with THF.

As a second complementary block copolymer synthesis GMA was first copolymerized with THF again with $Et_3O^+SbCl_6$ as the CROP initiator using similar conditions to those used earlier but without the diluting DCM solvent. Since the cationic

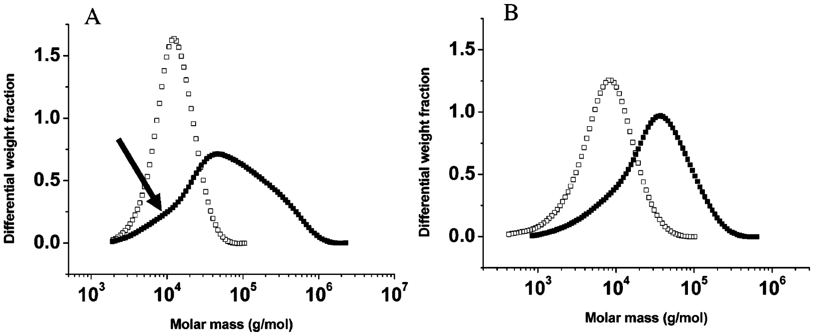


Figure 2. MALS/SEC molar mass distribution curves: (A) □, **PTHF/GMA1**; ■, **PTHF/GMA-*b*-PMMA1**; (B) □, **PTHF/GMA2**; ■, **PTHF/GMA-*b*-PMMA2**.

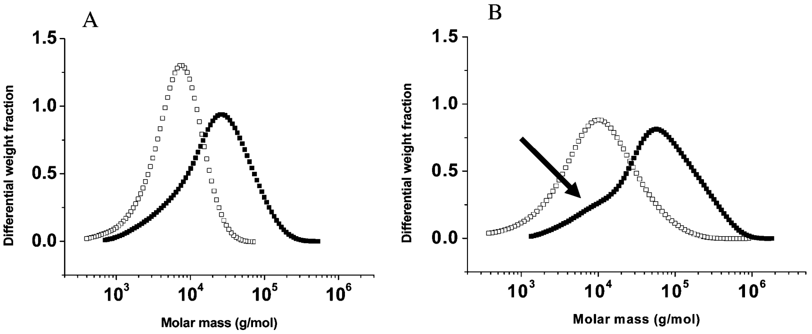


Figure 3. MALS/SEC molar mass distribution curves: (A) □, **PTHF/GMA3**; ■, **PTHF/GMA-*b*-PMMA3**; (B) □, **PTHF/GMA4**; ■, **PTHF/GMA-*b*-PMMA4**.

polymerization of THF can be living[24] then DP_n values of 100 and 50 were targeted by appropriate choice of the initiator/THF mole ratios. Also, since we were unsure as to how well the epoxide group in GMA would copolymerize with THF, GMA feed contents in THF of 10−2 mol % were investigated. The resultant polymers **PTHF/GMA1−6** were isolated as viscous oils when recovered from the DCM workup solvent and these solidified on standing at room temperature. To ensure that all unreacted GMA was removed each sample was extracted with *n*-hexane and then methanol. Analysis via ^1H NMR spectroscopy allowed the GMA content in each PTHF to be assessed and the absence of any significant GMA monomer residue to be confirmed. All the samples analyzed to be rather low in carbon (see Experimental section) and it is not clear why this so. The corresponding molar mass data were computed from the MALS/SEC analysis. The results are summarized in Table 1.

Accurate determination of the GMA content was difficult because of the low signal intensity in the ^1H NMR spectra, but overall there is poor correlation with the feed data. In addition the average number of GMA segments (i.e., pendent vinyl groups) per precursor polymer chain is >1, which in principle poses the possibility of cross-linking occurring in the synthesis of the second MMA block, but nevertheless offers a good opportunity for the growing on of this block. The DP_n achieved in the case of **PTHF/GMA1−4** is ∼60−140 (targeted value 100) and ∼45−50 for **PTHF/GMA5** and **-6** (targeted value 50) and so the level of control achieved in the polymerizations is modest. In each case the polydispersity index also deviates from unity leaving scope for improvement if this were to be desirable Conventional free radical copolymerization of each of **PTHF/GMA1−6** with MMA in toluene under N_2 at 85 °C for 5 h using AIBN (1 mol %) as initiator was employed to grow on the second block. The THF/MMA feed mole ratio was 1/1 in each case. The products **PTHF/GMA-*b*-PMMA1−6** were precipitated in *n*-hexane and recovered as white powders. Dissolution of these in $CDCl_3$ for recording ^1H NMR spectra and in THF for MALS/SEC analysis indicated the presence of some cross-linked gel particles which most likely arise as anticipated because the average number of GMA segments per polymer chain in the precursor blocks **PTHF/GMA1−6** is >1. Separation of this small fraction caused loss of material and reduced the recoveries (Table 2). The ^1H NMR spectra of the diblock copolymer solutions indicated that the PMMA block had indeed been well incorporated with the THF/MMA mole ratios being in the range 1/0.5−1/1.4, reasonably close to the targeted figure of 1/1. A number of attempts were made to check for potential “homopolymer” fractions in the products using selective precipitation, but despite a number of possible solvent/precipitant combinations being explored no “homopolymer” fractions could be isolated. While it is tempting to conclude that this demonstrates the absence of any significant levels of “homopolymers” it is also possible that the degree of incompatibility of these with the block copolymers is too low to allow separation by this differential solvation process. Interestingly, with **PTHF/GMA1−4**, the GMA content of the PTHF/GMA block does not seem to have a significant influence on the efficiency with which the PMMA block is generated (Table 2), whereas the precursors with the lower DP_n, **PTHF/GMA5** and **-6**, seem to incorporate the PMMA block less effectively. Additional experimentation is needed to confirm this. The ^1H NMR spectra also show the presence of residual unused pendent vinyl groups. The level is ∼1−2 mol % which confirms the consumption of some of the original vinyl groups present in forming block copolymer. The MALS/SEC molar mass data (Table 2) also show clearly the growth in molar mass on polymerization of the second block though the increase in the case of **PTHF/GMA-*b*-PMMA5** and **-6** is lower than with the other four samples. Perhaps more importantly however the molar mass distribution curves for **PTHF/GMA-*b*-PMMA1−4** (Figures 2 and 3) shift significantly to higher molar mass across the whole of each mass distribution of the **PTHF/GMA1−4** precursors with **PTHF/GMA-*b*-PMMA1** and **PTHF/GMA-*b*-**

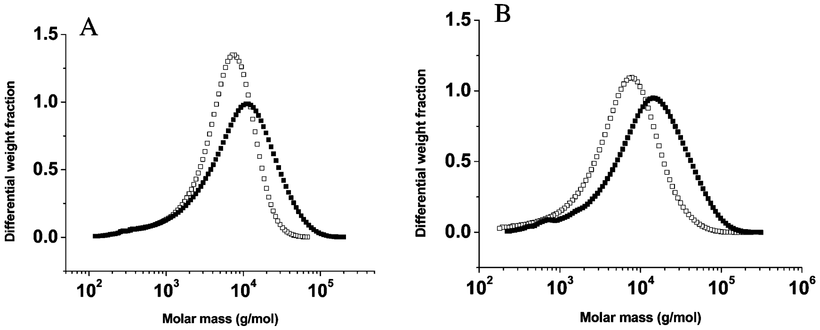


Figure 4. MALS/SEC molar mass distribution curves: (A) □, **PTHF/GMA5**; ■, **PTHF/GMA-*b*-PMMA5**; (B) □, **PTHF/GMA6**; ■, **PTHF/GMA-*b*-PMMA6**.

PMMA4 possibly showing a shoulder (Figures 2 and 3, indicated by arrow) at lower molar mass perhaps indicative of some residual **PTHF/GMA1** and **4** where blocking has failed. In the case of **PTHF/GMA-*b*-PMMA5** and **-6**, the MALS/SEC data Figure 4 is perhaps not so convincing regarding efficient blocking, and this seems to be related to the poorer growth of the PMMA block on the PTHF/GMA precursors referred to earlier.

A key physical feature of block copolymers can of course be their solid-state morphology which for compositionally and structurally well-defined species can be highly regular and microphase separated on a very small length scale. As a preliminary evaluation of the solid-state morphology of the present novel laterally linked diblock materials the two precursor **PTHF/GMA** and **PMMA/GMA** species along with the respective diblock materials derived from each of these were eaxamined by DSC. In all cases the samples were analyzed as recovered from their syntheses and the data discussed here was gathered following a pre-heat cycle on each sample. The solid-state phase behavior of PTHF−PMMA conventional diblocks and their blends with homoPTHF has been reported relatively recently.[25,26] An important characteristic is that on heating from below room temperature solid homoPTHF undergoes a crystalline melting transition, T_M, at ~ +25 °C and a crystallization transition, T_C, at ~ +5 °C on cooling from the melt. The corresponding glass transition temperature, $\mathrm{T_G}$, is vey low ~ −80 °C. This crystallization behavior of homoPTHF makes the phase behavior of of its block copolymers with PMMA rather complex and interesting. An important effect of the presence of the PMMA block is to reduce significantly both the T_C and the T_M of the PTHF block significantly by ~15 and ~ 10 °C, respectively. Our own PTHF precursors **PTHF/GMA1−4** have a T_M in range +22 to +25 °C and a T_C in the range ~ +7 to +10 °C. and two these show a very weak feature in the DSC traces at ~ −80 °C consistent with the latter being the $\mathrm{T_G}$. The PTHF−PMMA laterally linked diblocks **PTHF/GAMA-*b*-PMMA1−4** have a T_M in the range +11 to +18 °C and a T_C in the range −17 to − 23 °C, *i.e.* both the T_M and T_C of the PTHF block are reduced relative to those of homoPTHF in keeping with a diblock copolymer structure involving PMMA. Indeed the depression observed in both transition temperatures is greater than seen with conventional PTHF−PMMA diblocks.[25,26] This may well be a consequence of the lateral linkage between the two blocks which on the one hand inhibits crystallization to some extent, and on the other eases melting simply as a result of steric effects. HomoPMMA can have a $\mathrm{T_G}$ as high as +125 °C but samples produced by routine free radical polymerization methods are typically cited as having a $\mathrm{T_G}$ ~ +105 °C.[27] Interestingly this feature is not seen in the samples of **PTHF/GMA-*b*-PMMA1−4** dispite the mass ratio of PTHF to PMMA blocks being ~1/1. One possible explanation is that this transition is simply too weak to be seen on our instrument or there may be some plasticization effect from the molten PTHF block. Our precursors **PMMA/GMA1** and **PMMA/GMA2** do display a weak and broad transition at ~ +115 to 120 °C which we deduce is the $\mathrm{T_G}$. Furthermore, in the diblocks derived from these, **PMMA/GMA-*b*-PTHF1** and **PMMA/GMS-*b*-PMMA2,** what we assume is the same transition is seen at much lower temperatures, ~+85 and +108 °C respectively. Though the mass ratio of PMMA/PTHF is rather high in these samples (1/0.1 and 1/0.2), i.e., the PTHF content is low; nevertheless, the presence of the PTHF block does have a significant effect, and potentially a larger component of PTHF may have an even more profound effect on the PMMA transition as we have seen with the **PTHF/GMA-*b*-PMMA1−4** materials. Interestingly however no crystallization of the PTHF component can be seen in the samples of **PMMA/GMA-*b*-PTHF1** and **PMMA/GMA-*b*-PMMA2** and we can only speculate that this might be due the low content of PTHF in these samples or perhaps the PTHF block is more intimately associated with the PMMA block. If the latter were the case then it would be consistent with observed effect of the PTHF block on the PMMA block.

To give some further preliminary insight into the phase behavior of these materials samples were dissolved in THF and films cast from these solutions onto glass optical microscope slides. A control sample of an equal mass mixture of homoPTHF and homoPMMA was also examined. The latter formed a rough, highly opaque, grossly phased separated “film” . On the other hand, samples from each of homoPTHF and homoPMMA controls both formed smooth, glossy and transparent films. Likewise the films produced from samples of our precursor blocks, **PMMA/GMA** and **PTHF/GMA**, and the diblocks, **PMMA/GMA-*b*-PTHF** and **PTHF/GMA-*b*-PMMA**, derived from these all yielded smooth, glossy, and transparent films even when viewed under the optical microscope. The length scale of the phase separation that seems to be present is therefore too small to be readily observabe by eye, and so further work with other more sophistocated techniques is needed to evaluate the length scale involved, and how regular or otherwise the phase separation is.

Conclusions

The use of commercially available GMA as an example of a “Jekyll and Hyde” comonomer does indeed allow the fairly facile synthesis of *branched* diblock copolymers.[28] The latter are by no means narrow molar mass materials, neither in terms of the individual block lengths nor the overall molar mass, nor indeed is the backbone of a single well-defined architecture. Nevertheless the materials are interesting. They are complementary to analogues that might be made by more complex experimental procedures, and they are potentially useful because of their chemical composition, block structure, and backbone architecture. Furthermore, they are produced by a relatively straightforward synthetic procedure which is not particularly demanding neither in terms of manpower time and skills, and financial resource. This novel synthetic strategy might well be integrated into a high throughput synthesis system and certainly broadens the opportunity for synthesizing new materials for properties and applications evaluation. The possible combinations of polymerizable groups that could be embodied in “Jekyll and Hyde” monomer structures is large and these might be drawn from all monomers that undergo chain growth polymerization reactions. Indeed some such combinations are already available from commercial sources are many others might be readily synthesized. In this context Müller et al.[29] have recently reported the ring-opening polymerization of the thiirane ring in (thiiran-2-yl)methyl methacrylate) to yield a polythioether with pendent methacrylate groups which might then form the basis of a route to diblock copolymers as we have reported here.

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