

Synthesis of block copolymers: 4. Polytetrahydrofuran as a macroinitiator for free-radical polymerization

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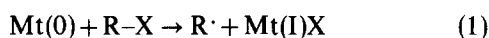
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Polytetrahydrofuran with a narrow molecular-weight distribution and terminal bromine atom was prepared by cationic polymerization. This polymer was used as a macroinitiator for the free-radical polymerization of styrene and methyl methacrylate to produce block copolymers. A block terpolymer was prepared by using terminally functionalized polystyrene, prepared by anionic polymerization, as a macroinitiator for cationic polymerization of tetrahydrofuran and to form a block copolymer. This polymer was terminally functionalized and used as a macroinitiator for the free-radical polymerization of methyl methacrylate. In each case gel permeation chromatography was used to establish block copolymer formation.

(Keywords: block copolymer; synthesis; characterization; cationic polymerization; free-radical polymerization)

INTRODUCTION

Previous papers in this series reported the synthesis of block copolymers using terminally functionalized preformed polymers as macroinitiators. In part 1¹ we reported the use of anionically prepared polystyrene as a macroinitiator for methyl methacrylate (MMA) polymerization and in part 2² the use of poly(methyl methacrylate) prepared by group transfer polymerization as a macroinitiator for styrene (St) polymerization; in both cases the macroinitiator carried a terminal bromine atom. Polymerization was initiated by use of the redox reaction between metal carbonyls and organic halides:



(where Mt is the metal in the carbonyl and RX is the halide with reactive halogen atom X) to create a radical R· in the presence of the monomer³. In the previous examples R was a preformed polymer chain (the macroinitiator), X was the terminal bromine atom and R· was a macroradical⁴. Radical formation was achieved photochemically ($\lambda = 436 \text{ nm}$) with dimanganese decacarbonyl⁵.

These procedures are examples of the general procedure of using combinations of different polymerization mechanisms to synthesize block copolymers in which a stable preformed polymer prepared by one mechanism is used as a macroinitiator for polymerization by a second mechanism. This procedure is sometimes referred to as the 'transformation' approach, several examples of which have been reviewed elsewhere⁶. In part 3 of the same series we extended the anionic to free-radical transformation used in part 1 to a variety of monomers polymerizable by free-radical polymerization⁷ and used gel permeation chromatography (g.p.c.) to establish copolymer formation. We now report the extension of this concept to the use of cationically prepared terminally brominated polytetrahydrofuran (PTHF-Br) as a macroinitiator for free-radical polymerization. Gel permeation

chromatography was used to confirm block copolymer formation.

EXPERIMENTAL

Materials

Monomers. Inhibitor was removed from St and MMA (BDH) by washing with dilute aqueous sodium hydroxide solution. Monomers were then washed with distilled water and dried over molecular sieve (type 4A) and were fractionally distilled under a nitrogen atmosphere at reduced pressure: St at 45°C, 20 mmHg; MMA at 42°C, 80 mmHg. Monomers were dried over calcium hydride and stored at -20°C under a nitrogen atmosphere. Prior to use, samples were prepolymerized by heating and were distilled under vacuum.

Tetrahydrofuran (THF), used as a monomer, was dried over molecular sieve and then dried further and freed from inhibitors by standing over sodium wire in the presence of a little naphthalene and under a nitrogen atmosphere, until a dark green colour persisted. The monomer was distilled under nitrogen immediately prior to use.

Initiators. Dimanganese decacarbonyl was purified by vacuum sublimation and stored in a refrigerator. Silver hexafluorophosphate and hexafluoroantimonate were stored in a desiccator under a nitrogen atmosphere and used without further purification. *p*-Methylbenzyl bromide was used as supplied.

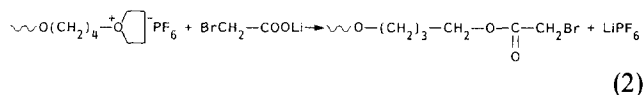
Terminating agents. Lithium bromoacetate was prepared from bromoacetic acid and *n*-butyl lithium. Bromoacetic acid was purified by fractional distillation, collecting the fraction distilling at 208°C. A 10% (w/v) solution of bromoacetic acid in diethyl ether was repeatedly dried with calcium sulphate. The dried solution was filtered and was added dropwise to a vigorously stirred solution of butyl lithium (15% w/w) in hexane until the acid was in excess. Insoluble lithium bromoacetate was filtered off, dried and stored in a vacuum desiccator.

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Synthesis of PTHF-Br macroinitiator

Living polytetrahydrofuran was prepared by using silver hexafluorophosphate or hexafluoroantimonate as co-initiator with (4-bromomethyl)xylene^{8,9}. Polymerizations were performed at 10°C under a nitrogen atmosphere. To incorporate a terminal bromine function, polymerization was terminated by addition of lithium bromoacetate:



The solution was filtered and solvent removed. The polymer was dissolved in ether, washed to remove excess lithium salt and then dried. Polymer was isolated by removal of the solvent. The molecular weight of the PTHF-Br was controlled by varying the polymerization time.

Free-radical polymerization

Free-radical polymerizations, either homopolymerizations or formation of block copolymers, were performed under vacuum using standard dilatometric or gravimetric techniques. All initiations were photochemical using systems based on dimanganese decacarbonyl with organic halides ($\lambda = 436 \text{ nm}$). Light intensities were varied using neutral density filters and experiments were performed in a laboratory illuminated with sodium light. Polymerizations were performed in bulk monomer. Polymers were isolated by precipitation into an appropriate non-solvent.

Gel permeation chromatography (g.p.c.)

Polymers were characterized by g.p.c. The equipment consisted of a du Pont pumping system, column compartment and bimodal columns packed with silanized glass beads. Detectors were a Waters refractometer (r.i.) and a Kratos-Schoeffel variable-wavelength ultra-violet (u.v.) spectrophotometer, used at a wavelength of 260 nm. The flow rate was 1 ml min^{-1} ; the solvent was fresh unstabilized tetrahydrofuran (Fisons). PSt standards were obtained from Waters Associates and samples of PMMA used as standards were obtained from Röhm GmbH¹⁰.

RESULTS

Synthesis of block copolymers

Bromomethyl groups activated by proximity to a carbonyl group are reactive in free-radical formation using metal carbonyl plus halide systems³ and were used to effect a transformation from cation to free-radical propagation. PTHF-Br prepared by cationic polymerization of tetrahydrofuran and termination with lithium bromoacetate was shown to be an effective macroinitiator in conjunction with photolysed $\text{Mn}_2(\text{CO})_{10}$. Figure 1 shows that rates of polymerization of MMA initiated with this system vary with [PTHF-Br] in a manner characteristic of the carbonyl-halide initiating systems: rates of polymerization (and initiation) vary with [halide] at 'low' [halide] and become independent of [halide] at 'high' [halide]^{3,7}. In addition, rates of polymerization varied linearly with $I^{1/2}$ (I is the incident light intensity) and conversions were linear with time (observed dilatometrically at low conversions).

Relative rates of polymerization of St and MMA under

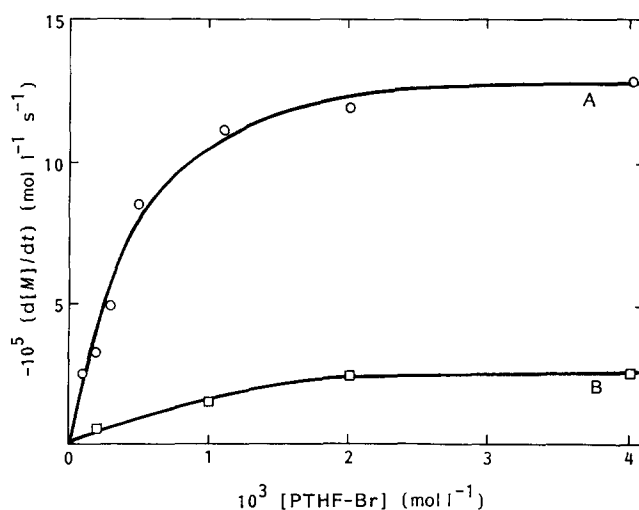


Figure 1 Variation in rates of polymerization with concentration of terminally brominated polytetrahydrofuran (PTHF-Br): curve A, methyl methacrylate monomer, $[\text{Mn}_2(\text{CO})_{10}] = 2.5 \times 10^{-4} \text{ mol l}^{-1}$, $I_{\text{abs}} = 5.9 \times 10^{-8} \text{ einstein l}^{-1} \text{ s}^{-1}$, rates determined dilatometrically; curve B, styrene monomer, $[\text{Mn}_2(\text{CO})_{10}] = 2.3 \times 10^{-4} \text{ mol l}^{-1}$, $I_{\text{abs}} = 5.36 \times 10^{-8} \text{ einstein l}^{-1} \text{ s}^{-1}$, rates determined gravimetrically

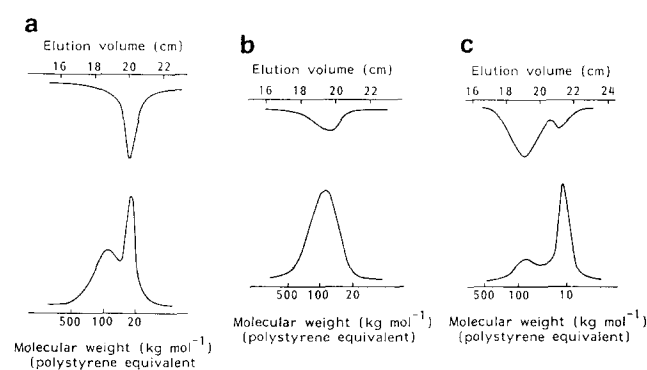


Figure 2 Gel permeation chromatograms of reaction products as described in text; upper chromatograms, u.v. detection; lower chromatograms, r.i. detection

identical reaction conditions were consistent with known values of $k_p/k_t^{1/2}$ for the two monomers^{5,11} and the previously determined quantum efficiencies for radical formation in solutions of the two monomers^{5,11}. The kinetic data establish that PTHF-Br behaves as a conventional halide in these initiating systems. (Some samples of PTHF-Br appeared to contain an impurity, introduced on synthesis, capable of photoinitiating styrene polymerization without the aid of carbonyl.)

Similar conditions were used to initiate polymerization from PTHF-Br as were reported for the preparation of block copolymers from terminally functionalized PSt⁷. Figure 2 presents chromatograms of the reaction products formed by initiating polymerization of MMA and St from PTHF-Br. In the u.v. traces the responses from unreacted PTHF-Br and the high-molecular-weight products from MMA polymerizations must arise from the phenyl groups incorporated into PTHF-Br on initiating cationic polymerization of THF by (4-bromomethyl)xylene. In such cases the appearance of a u.v. absorption at high molecular weight is a strong indicator of block copolymer formation. Figures 2a and 2b show, respectively, chromatograms for products from MMA polymerization after removal of all volatiles and after precipitation from dichloromethane into hexane, respectively. Precipitation

into hexane removes most of the unreacted low-molecular-weight PTHF-Br ($\sim 10 \text{ kg mol}^{-1}$) from the reaction products. (Note that it has been established previously¹² that at a specific elution volume molecular weights of PSt (M_{PSt}) and PTHF (M_{PTHF}) which elute are related by $M_{\text{PTHF}} = 0.56 \times M_{\text{PSt}}$.) The presence of PTHF end-groups in the copolymer is not clearly established in Figure 2a but is more clearly demonstrated in Figure 2b, since an ill-defined shoulder in the u.v. chromatogram of Figure 2a is seen as a clear peak in Figure 2b where the peak is at greater elution volume than that in the r.i. chromatogram, consistent with the greater weight fraction of phenyl end-groups in low-molecular-weight polymer. Separate chromatograms of the hexane-soluble fraction are almost identical to those of unreacted PTHF-Br, but it cannot be guaranteed that precipitation into hexane does not fractionate the low-molecular-weight copolymer species to some extent.

Further confirmation of block copolymer formation is provided by the variations in composition with elution volume (Figure 3) through the chromatograms of the hexane-insoluble fraction, which appears to contain all or most of the possible copolymer species. The variation in composition with elution volume, determined from the heights of the chromatograms and response factors for the two polymers in each detector⁷, is qualitatively consistent with block copolymer formation. Because PMMA propagating radicals terminate by combination (33%) and disproportionation (67%)¹³, it is expected that the product will be mainly AB block copolymer with some ABA block copolymer.

Products from the polymerization of St initiated by PTHF-Br and $\text{Mn}_2(\text{CO})_{10}$ were isolated by removal of volatiles. Because of the relative response factors of PSt and PTHF in the two detectors, formation of block copolymer in this system cannot be established from Figure 2c by inspection, although there is qualitative evidence because the high-molecular-weight peak does not extend to such low molecular weights as would be anticipated if the major reaction product was PSt homopolymer; elution volumes of copolymer must be less than that of the end-block while homopolymer elution volumes would extend to larger values. A plot corresponding to that in Figure 3 shows a small variation in composition with elution volume as expected for copolymer with high-molecular-weight polystyrene blocks. Polystyrene propagating radicals terminate by combination¹³ and the product is expected to be ABA block copolymer.

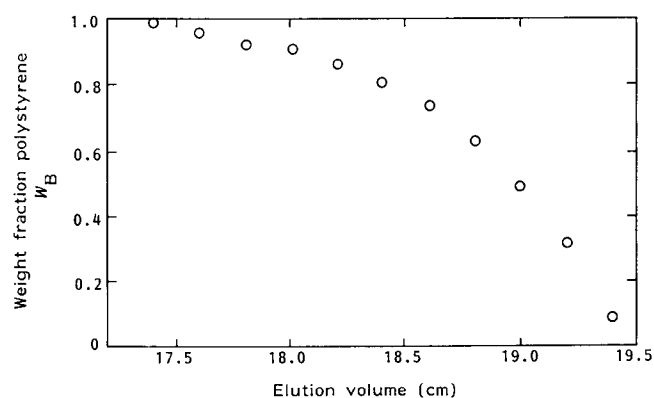


Figure 3 Variation in weight fraction of polystyrene with elution volume for high-molecular-weight component in Figure 2c

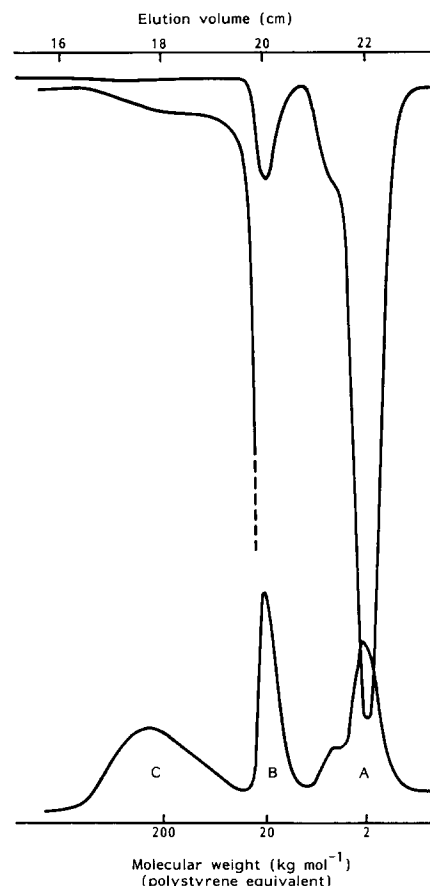


Figure 4 Gel permeation chromatograms of reaction product from series of reactions used to produce a PSt-PTHF-PMMA terpolymer. Upper chromatogram obtained using u.v. detection with portion of chromatogram obtained using high detector response; lower chromatogram obtained using r.i. detection

Synthesis of a triblock copolymer

In the preceding section and previous papers evidence for the formation of block copolymers using cation to radical and anion to radical transformations has been presented and the generality of the procedures, especially the latter, has been demonstrated. As a further generalization we used terminally brominated PSt (PSt-Br) ($M_n = 2 \text{ kg mol}^{-1}$), used in previous studies^{1,7}, as an initiator for the cationic polymerization of THF and prepared a PSt-PTHF block copolymer¹⁴. The living species was terminated with lithium bromoacetate to form PSt-PTHF-Br copolymer as described above. This latter species was used to initiate MMA polymerization and to effect the cation to radical transformation. Figure 4 shows the gel permeation chromatograms for the final product, including a portion of a u.v. chromatogram obtained using high detector sensitivity. Peak A arises from PSt with a terminal unsaturated group. This product is formed on initiation of cationic polymerization of THF by a process of β -elimination⁹; the anion to cation transformation is inefficient¹⁴. Peaks B and C arise, respectively, from PSt-PTHF-Br and high-molecular-weight products formed by the final free-radical polymerization. The u.v. absorption at molecular weights of about 200 kg mol^{-1} in products produced on polymerization of MMA must arise from the PSt in the initial PSt-Br and, almost certainly, from formation of a PSt-PTHF-PMMA terpolymer. Evidence that the high-molecular-weight product is a terpolymer is provided by

the shape of the corresponding peak, which does not extend to low molecular weight in the manner expected if the product was a homopolymer or diblock copolymer formed in some way from the PSt responsible for peak A. Also, the only u.v.-absorbing species present that could account for the u.v. absorption at high molecular weight is the polystyrene, which must have been incorporated into the copolymer as end-blocks from the PSt-PTHF-Br copolymer.

CONCLUSIONS

It has been demonstrated that terminally brominated PTHF (PTHF-Br), of molecular weight up to at least 20 kg mol^{-1} , can act as an effective macroinitiator in conjunction with dimanganese decacarbonyl (photolysed at 436 nm), and that the kinetics of polymerization for St and MMA are closely similar to those for initiation from low-molecular-weight initiators. A potential complication is that the PTHF-Br prepared by cationic polymerization contains unidentified impurities that affect free-radical polymerizations; extensive purification of the preformed polymers may be required prior to use in well defined systems.

As a result of g.p.c. analysis of the reaction products it is concluded that the products formed by free-radical initiation from PTHF-Br (polymer A) in the presence of monomers B are block copolymers. Using a terminally functional PSt-PTHF-Br diblock copolymer as an initiator it has been demonstrated that the technique can be used to form triblock copolymers.

Radicals are formed from the A chains gradually and it is difficult to achieve the situation that all A chains are converted to copolymer. Thus the copolymers contain residual homopolymer. We conclude that this route is an effective means of incorporating PTHF blocks in block

copolymers with other components and in combinations that are not readily available by other means.

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