The synthesis of block copolymers: 3. The use of functionalized polystyrene as a macroinitiator for free-radical polymerization

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This paper extends previous work on the use of polystyrene terminally functionalized with bromine as a macroinitiator for free-radical polymerization. The use of this macroinitiator for copolymer synthesis is demonstrated for several free-radically polymerizable monomers. Gel permeation chromatography is used to confirm formation of block copolymers.

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

INTRODUCTION

The requirement for block copolymers both as macromolecules for extensive physicochemical studies and as materials with diverse mechanical properties maintains interest in the synthesis of copolymers having different combinations of chemical components and molecular weight distributions. Because of practical limitations on synthesizing different copolymers using a single type of propagating species, Richards[1] and others developed the 'transformation' approach in which a polymer A, prepared by one mechanism, is terminally functionalized, isolated and used to initiate the polymerization of a second monomer, by a different mechanism, to form blocks of polymer B attached to the A blocks. That is, the preformed polymer A is used as a macroinitiator for polymer B. Indirectly one polymerization mechanism is transformed into another in order to incorporate into the copolymer combinations of blocks that cannot be prepared by a single mechanism.

We previously used the transformation approach[2] to demonstrate the feasibility of producing block copolymers by a combination of anionic and free-radical polymerizations using metal carbonyl plus organic halide redox reactions to initiate free-radical polymerization of methyl methacrylate (MMA) from terminally brominated polystyrene (PSt–Br); the PSt–Br was prepared by anionic polymerization of styrene (St). More recently we demonstrated the use of the same approach to prepare block copolymers of the same components by a combination of group transfer and free-radical polymerizations[3]; terminally brominated poly(methyl methacrylate) (PMMA), prepared by group transfer polymerization, was used as a free-radical macroinitiator.

This paper describes the extension of the anionic to free-radical transformation we described previously and illustrates its general applicability to the synthesis of B blocks by free-radical polymerization.

We report the use of dual-detection gel permeation chromatography (g.p.c.) to establish copolymer formation and to provide a preliminary characterization of the copolymers. We propose to present a more detailed paper on block copolymer characterization using a novel treatment of g.p.c. data, in a subsequent publication.

EXPERIMENTAL

Materials

Monomers. Inhibitor was removed from styrene and various acrylate and methyacrylate esters (all supplied by BDH) either by washing with dilute aqueous sodium hydroxide solution or by passing through a column of neutral alumina. In the former case monomers were then washed with distilled water and dried over molecular sieves (type 4A). Monomers were fractionally distilled under a nitrogen atmosphere at reduced pressure: styrene at 45°C, 20 mmHg; methyl methacrylate at 42°C, 80 mmHg; n-butyl methacrylate at 57°C, 12 mmHg; methyl acrylate at 32°C, 140 mmHg; ethyl acrylate at 35°C, 80 mmHg; and n-butyl methacrylate at 48°C, 12 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 then distilled under vacuum. For anionic polymerizations under high vacuum, samples of styrene were further purified by purging with dibutylmagnesium.

Chloroprene (BP Chemicals), supplied as a 50% (v/v) solution in xylene with added inhibitor, was purified by distillation under a nitrogen atmosphere, collecting the fraction boiling at 60°C. Three-quarters of that distillate was distilled under vacuum, washed with 10–20% (w/v) aqueous sodium hydroxide solution and then with deionized water; washings were performed under a nitrogen atmosphere. After drying over calcium hydride the monomer was transferred to a vessel with a break-seal in a side arm. The monomer was degassed and sealed under vacuum and stored at −70°C. Prior to use, the storage vessel was attached to the vacuum system, via the side arm, and the monomer was prepolymerized

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photochemically and then distilled (under vacuum) into the reaction vessels, through the break-seal, via a calibrated tube.

Solvents. Benzene was dried and stored over calcium hydride and was distilled under vacuum prior to use. Other solvents (AR grade when available) were used without further purification.

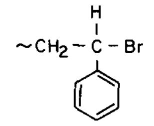
Initiators. Dimanganese decacarbonyl $Mn_2(CO)_{10}$ was purified by vacuum sublimation and stored in a refrigerator. Azobisisobutyronitrile (AIBN) was crystallized twice from methanol. 1-Bromoethylbenzene (Eastman Kodak) was used as supplied. n-Butyllithium, obtained as a 15% (w/w) solution in hexane, was used as supplied.

Terminating agents. 1,2-Dibromoethane (Fluka) was dried over calcium hydride and distilled at atmospheric pressure, collecting the fraction boiling at 130°C. α,α′-Dibromo-*m*-xylene (Fluka) was recrystallized from petroleum spirit and stored in a desiccator.

To form the PSt–Br macroinitiator, living anionically polymerized St was functionalized with bromine via a Grignard intermediate[4]. To form the intermediate, a freshly prepared suspension of magnesium bromide was prepared by reacting freshly washed magnesium turnings (16 g) with 1,2-dibromoethane (37 g) in tetrahydrofuran (350 ml) under a nitrogen atmosphere. The mixture was refluxed for 1 h and while hot was filtered and transferred to a clean vessel under nitrogen pressure.

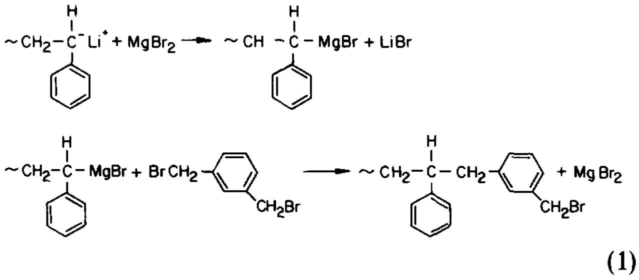
Synthesis of PSt–Br macroinitiator

Samples of PSt–Br were prepared by anionic polymerization. One sample (PSt–Br 1), used in our preliminary study (molecular weight 2000 g mol^{-1}), was prepared under vacuum by the late Dr D. H. Richards. This polymer was prepared by terminating the anionic polymerization, via a Grignard intermediate, with bromine to give terminal group (I):



(I)

Other samples (PSt–Br 2, etc.) were prepared similarly, either under a nitrogen atmosphere or under high vacuum; the latter conditions were used to prepare materials of higher molecular weight. Anionic polymerization of styrene in benzene solution was initiated by n-butyllithium with a little tetrahydrofuran added. To incorporate the terminal bromine, through reaction sequence (1):



(1)

the living polymer was first reacted with the magnesium bromide, referred to above, and then with α,α′-dibromo-*m*-xylene. This procedure, using the Grignard intermediate, minimizes coupling of the PSt chains, which otherwise occurs on direct termination with bromine or other reagents[4]. Polymers were isolated by precipitation into methanol.

In our previous study we found that the PSt–Br used contained a retarder for free-radical polymerization[2]. The same problem was again experienced and was more serious with materials prepared under a nitrogen atmosphere. The retarder was effectively removed by reprecipitating at least four times into methanol from dichloromethane solution, each time filtering the solution through a 0.2 μm Millipore filter.

Free-radical polymerizations

Free-radical polymerizations, either homopolymerizations or in forming block copolymers, were performed under vacuum using standard dilatometric or gravimetric techniques. All initiations were photochemical using either azobisisobutyronitrile ($\lambda = 365$ nm) or systems based on dimanganese decacarbonyl with organic halides ($\lambda = 436$ 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 or, in the case of butadiene and chloroprene, in benzene solution; for methyl acrylate polymerizations, toluene was used as solvent to reduce the Norrish–Tromsdorff effect[5]. Polymers were isolated by precipitation into an appropriate non-solvent.

Gel permeation chromatography

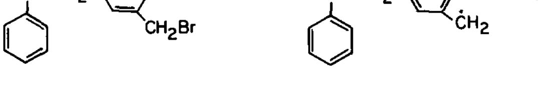
Polymers were characterized by g.p.c. The equipment consisted of a du Pont pumping system, column compartment and bimodal columns packed with silanized glass beads. Detectors were a Waters refractive index (RI) detector and a Kratos-Schoeffel variable-wavelength ultraviolet (u.v.) detector, used at a wavelength of 260 nm. The flow rate was 1 ml min^{-1} and the solvent was tetrahydrofuran. PSt standards were obtained from Waters Associates and samples of PMMA used as standards were obtained from Röhm GmbH[6].

WARNING. In using g.p.c. for quantitative polymer characterization, it is important that the chromatograms truly represent the polymer concentration in the eluant and are not distorted by instrumental factors. For copolymer analysis, even qualitative, the same requirement is essential. That is, if a pure low-molecular-weight substance is examined by g.p.c. the shapes of the chromatograms from the two detectors should be identical. This requirement is not always achieved in commercial equipment. We have found that some RI detectors distort the chromatograms, reducing the apparent concentration of solute with increasing elution volume through the solute peak.

RESULTS

Kinetics of MMA polymerization initiated by PSt–Br

To initiate free-radical polymerization from PSt–Br, we made use of reaction (2):



(2)

in the presence of a monomer[7]. M(0) represents an active manganese species in its zeroth oxidation state and produced on photolysis of $Mn_2(CO)_{10}$. The radical generated in (2) initiates polymerization of the monomer present. The characteristic kinetic feature of this initiating system, using either polymeric or small-molecule halides as components of the initiating system, is that at very low halide concentration the rates of initiation and polymerization increase with halide concentration and become independent of halide concentration at high halide concentration. Examples of this behaviour, using PSt–Br 1 as halide, are shown in *Figure 1*. Under conditions of high halide concentration, rates of initiation, R_i, are given by:

$$R_i = k[Mn_2(CO)_{10}]I \qquad (3)$$

where I is the light intensity. In synthesizing block copolymers we normally use conditions of high halide concentration.

We have mentioned previously[2] and above that PSt–Br as prepared contained a retarder. Without multiple reprecipitations, rates of polymerization did not behave as depicted in *Figure 1* but increased to a maximum and then decreased with increasing halide concentration in the same concentration range. Slopes of dilatometer plots, for nominally identical polymerizations, increased with the number of times the PSt–Br had been reprecipitated; approximately identical rates of polymerization were achieved after about six reprecipitations.

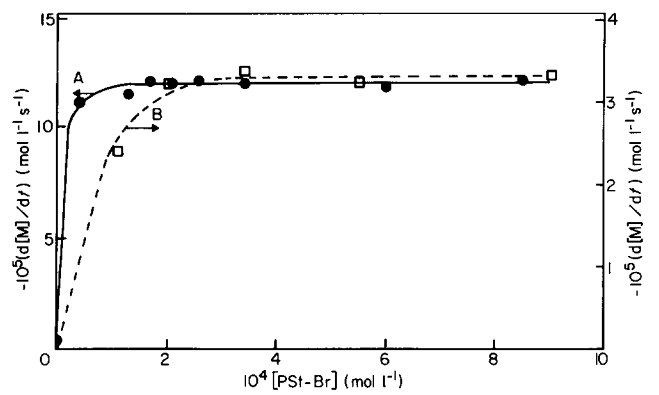


Figure 1 Variations in rate of photoinitiated polymerization ($\lambda = 436$ nm) of MMA ($[Mn_2(CO)_{10}] = 2.1 \times 10^{-4}$ mol l^{-1}; curve A) and chloroprene ($[Mn_2(CO)_{10}] = 2.56 \times 10^{-4}$ mol l^{-1}; curve B) with concentration of PSt–Br 1

The presence of a retarder in the initial PSt–Br was confirmed by adding it to polymerizations of MMA photoinitiated by AIBN when the rate of polymerization decreased with increasing PSt–Br concentration. In addition, values of $k_p/k_t^{1/2}$ (k_p and k_t are, respectively, the rate coefficients for propagation and termination in the free-radical polymerization of a monomer) were determined for polymerizations of MMA initiated by $Mn_2(CO)_{10}$ in conjunction with various halides. *Table 1* gives the apparent values of $k_p/k_t^{1/2}$ for various systems; these values were calculated using molecular weights determined by g.p.c. with PMMA standards. The values can be compared with a literature value of 0.055 $l^{1/2}$ mol$^{-1/2}$ s$^{-1/2}$ for MMA[8] obtained using a similar initiating system with molecular weights determined osmometrically. After about six reprecipitations the value of $k_p/k_t^{1/2}$ became approximately constant and rates of polymerization were proportional to the square root of the light intensity. Only when these conditions were achieved was the PSt–Br used in block copolymer synthesis. We described previously how dual-detection g.p.c. provided qualitative evidence for formation of PSt–PMMA block copolymers in this system[2]. The reaction products gave two peaks in the chromatograms using u.v. or RI detection; the low-molecular-weight peak arose from unreacted PSt–Br (which was usually only reacted to low conversion) and the higher-molecular-weight peak arose from the products formed by free-radical polymerization. The shapes of the high-molecular-weight peaks were not identical and were consistent with decreasing PMMA content with elution volume. *Figure 2a* shows a pair of such chromatograms for a sample prepared from PSt–Br 1, which had been reprecipitated from hexane to remove most of the unreacted low-molecular-weight PSt–Br ($M_n = 2000$ g mol^{-1}). Using appropriate response factors for PSt and for PMMA in the two detectors, the variation in composition of eluant with elution volume can be determined quantitatively and two examples for reaction products from PSt–Br/PMMA systems are presented in *Figure 3*. Weight fractions of, say, component B in an A,B

Table 1 Kinetic parameters for free-radical polymerization

		Values of $k_p/k_t^{1/2}$			
Monomer[a]	[M] (v/v)	Expt. (homopolym.)[b]	Expt. (copolym.)[c]	Lit.	Ref.
MMA	1	0.053	0.048[d] 0.039[e]	0.055	8
nBMA	1	0.110	0.085	0.099–0.11	10
	0.5	0.093	0.099		
	0.3	0.089			
MA	0.2	0.23	0.23	0.21–0.227	13
EA	0.2	0.23	0.19, 0.24	0.24	13
nBA	0.2	0.25	0.22	0.13–0.72	10, 13

[a] MMA, methyl methacrylate; nBMA, n-butyl methacrylate; MA, methyl acrylate; EA, ethyl acrylate; nBA, n-butyl acrylate

[b] Homopolymerization initiated by 1-bromoethylbenzene

[c] Copolymerization initiated by PSt–Br

[d] Identical results were obtained using PSt–Br 1 and PSt–Br prepared under vacuum after several reprecipitations

[e] PSt–Br prepared under nitrogen atmosphere and not repeatedly reprecipitated

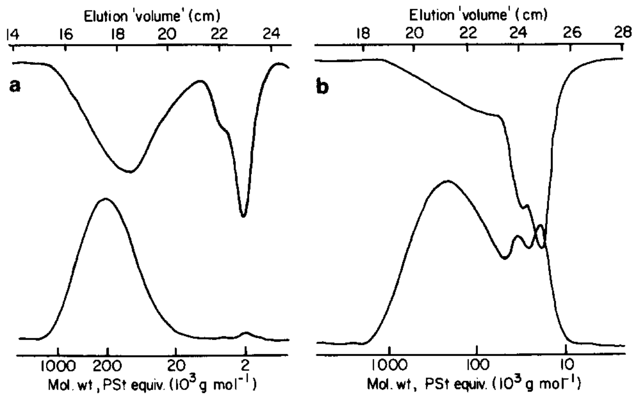


Figure 2 Gel permeation chromatograms of reaction products from initiating polymerization of MMA from PSt–Br 1: (a) PSt–Br molecular weight 2000 g mol^{-1}, product isolated by precipitation into hexane: (b) PSt–Br molecular weight 19 000 g mol^{-1}, total reaction product. Upper and lower chromatograms are from u.v. and RI detection, respectively

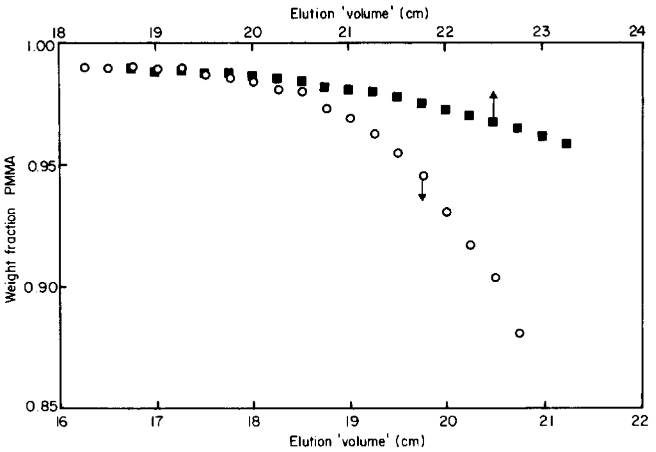


Figure 3 Variations in weight fractions of PMMA in the eluant with elution volume for polymers responsible for high-molecular-weight components of chromatograms in *Figure 2a* (○) and chromatograms in *Figure 2b* (■)

copolymer as a function of elution volume V are calculated from:

$$W_{\mathrm{B}}(V)=\frac{h_{\mathrm{ri}}(V)K_{\mathrm{uvA}}-h_{\mathrm{uv}}(V)K_{\mathrm{riA}}}{K_{\mathrm{uvA}}k_{\mathrm{riB}}-K_{\mathrm{riA}}K_{\mathrm{uvB}}} \tag{4}$$

where $h_{\mathrm{ri}}(V)$ and $h_{\mathrm{uv}}(V)$ are the responses of the RI and u.v. detectors at V, and K_{ri} etc. are the factors relating detector response to concentrations of pure A and B polymers in the respective detectors. The high-molecular-weight peak arises primarily from PMMA formed by free-radical polymerization. The PSt present at low elution volume (which must originate from low-molecular-weight PSt–Br) and its increasing content with increasing elution volume are all consistent with formation of PSt–PMMA block copolymers. In view of previous studies, which indicate that propagating PMMA radicals terminate predominantly by disproportionation[9], we anticipate that the products are about 67% ABA and 33% AB (by weight) block copolymers (A = PSt, B = PMMA).

The conversion of elution volume to molecular weight is a continuing problem in copolymer analysis. We have recently used a novel approach to this problem and will discuss its basis and application separately[3]. However, during this study we had available low-molecular-weight PSt–Br ($\bar{M}_n = 2000$ g mol^{-1}) and a series of PMMAs with narrow molecular weight distribution[6]. Because the molecular weight of the PSt end-block in the presumed copolymer was trivial compared with that of the PMMA eluting over most of the elution range, we converted elution volume to molecular weight using a PMMA calibration. Using standard procedures we then converted the chromatograms to a weight fraction distribution for PMMA, in terms of PMMA molecular weight. An example of the results is given in *Figure 4*.

Superimposed on the experimental weight fraction distribution for PMMA in *Figure 4* is a theoretical weight fraction distribution (curve B) calculated assuming a probability of propagation of 0.99845 and 33% combination termination. Also included in *Figure 4* is the experimental variation in weight fraction of PSt in the eluant with elution volume. Superimposed on the experimental data is a curve (A) of the weight fraction of PSt in PMMA chains calculated assuming that PSt blocks are incorporated as end-groups on initiating PMMA chains. That is w_{A} is given by:

$$w_{\mathrm{A}}=\frac{M_{\mathrm{A}}}{M_{\mathrm{A}}+rM_{\mathrm{B},0}}\times(\text{number of ends per PMMA chain}) \tag{5}$$

where M_{A} is the molecular weight of the PSt–Br, $M_{\mathrm{B},0}$ is the molecular weight of MMA and r is its degree of polymerization. In calculating the number of ends per PMMA chain (which is a function of degree of polymerization), we used the same probability of propagation and fraction of combination termination as in calculating the theoretical weight fraction distribution in curve B. There is a little scatter and some small discrepancies between the experimental data and theoretical curves, especially at low molecular weight where the PSt content becomes relatively large and the high-molecular-weight peak starts to overlap with that from unreacted PSt–Br. The general agreement between the experimental and theoretical data provides strong confirmation for the formation of block copolymers.

The slight discrepancies between the experimental and theoretical weight fraction distributions could arise for a variety of reasons including inapplicability of the simple

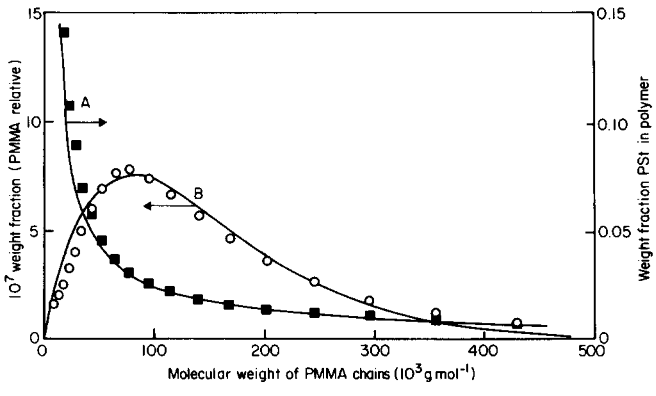


Figure 4 Weight fraction distributions of PMMA chains in PSt–PMMA block copolymer: (○) experimental points derived from data in *Figure 2a* with theoretical curve (B) calculated for 33% bimolecular termination by combination and probability of propagation 0.99845; (■) experimental weight fractions of PSt in copolymer as a function of molecular weight of PMMA chains with calculated curve (A) using the same conditions as for curve A and a PSt molecular weight of 2000 g mol^{-1}

and idealized model for free-radical polymerization used to calculate the theoretical curve (no transfer, no primary radical termination, etc.) or errors in calibration. *Figure 5* compares experimental weight fraction distributions for PMMA homopolymer and for PMMA chains in PSt–PMMA block copolymers. The two polymers were prepared using identical rates of initiation (i.e. identical $Mn_2(CO)_{10}$ concentrations and light intensities) and conditions of high halide concentration, using the low-molecular-weight halide (bromoethylbenzene) to form the PMMA homopolymer. The identity of the two data sets, irrespective of any errors in calibration or inadequacy of the theoretical model, confirms that the PSt–Br acts as a simple initiator for free-radical polymerization in these systems.

Efficiency of copolymer formation

Figure 6 presents chromatograms of reaction products obtained at different irradiation times. The data show a gradual build-up of high-molecular-weight copolymer relative to the intensity of unreacted PSt–Br. The latter peak decreases with respect to the small peak at twice the molecular weight of the PSt–Br; this small peak arises from PSt produced by coupling on terminating anionic polymerization[4]. This PSt is unreactive as a macroinitiator and acts as a reference marker.

It is difficult to determine the ultimate efficiency of initiation from PSt produced anionically to form copolymer because of problems in ensuring complete consumption of the PSt–Br and accurately determining the number of copolymer chains formed. In most of our studies the conversion of PSt–Br to copolymer was kept low to minimize kinetic complications and distortions of molecular weight distributions. However, one kinetic feature of the initiating systems used, referred to earlier, is that the rate of polymerization is independent of halide concentration until halide concentration falls below some critical value (see *Figure 1*). Below the critical value, rates of polymerization decrease rapidly with decreasing halide concentration. We used this feature to assess the efficiency of the transformation from anionic to free-radical polymerization. Dilatometric experiments were performed using $[Mn_2(CO)_{10}] > [PSt–Br]$, so that in a polymerization reaction PSt–Br concentration fell below the critical value before consumption of $Mn_2(CO)_{10}$ became significant. *Figure 7* (curve A), which presents the change in meniscus height with time, shows an approximately constant rate of polymerization for approximately 4 h, after which reaction essentially ceased. A corresponding reaction with $[PSt–Br] > [Mn_2(CO)_{10}]$ (*Figure 7*, curve B) did not show this cessation at corresponding reaction times, demonstrating that the effect was not a result of $Mn_2(CO)_{10}$ consumption; there is some evidence in *Figure 7* (curve B) of acceleration at long reaction times, probably due to the Norrish–Tromsdorff effect[5]. From data of the type in *Figure 7* (curve A), rates of initiation were calculated and hence the total number of initiations in the reaction time were estimated. Cessation of polymerization was assumed to correspond approximately to reduction of halide concentration to the critical value. On this basis the potential yield of copolymer from anionically prepared PSt was assessed as at least 70%. This efficiency compares favourably with other anion to free-radical transformations[1].

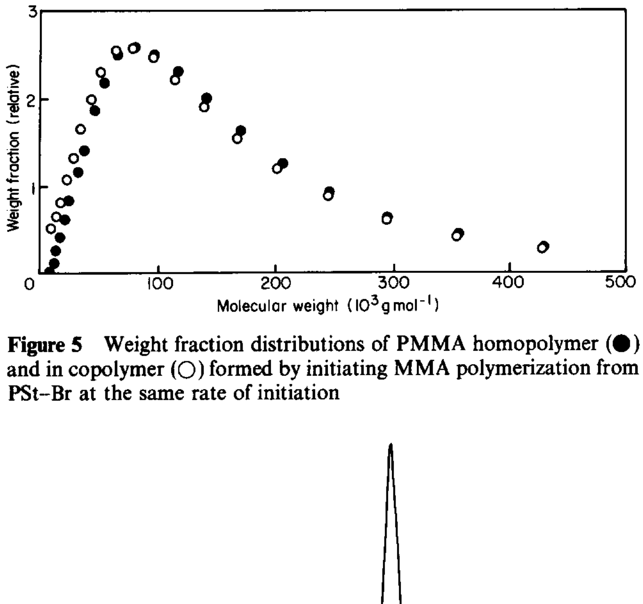


Figure 5 Weight fraction distributions of PMMA homopolymer (●) and in copolymer (○) formed by initiating MMA polymerization from PSt–Br at the same rate of initiation

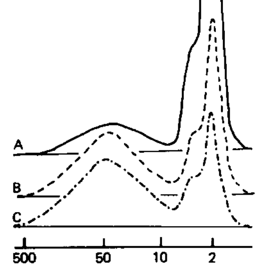


Figure 6 Gel permeation chromatograms of reaction products from initiating MMA polymerizations from PSt–Br for reaction times of 4 min (A), 8 min (B) and 20 min (C), with RI detection

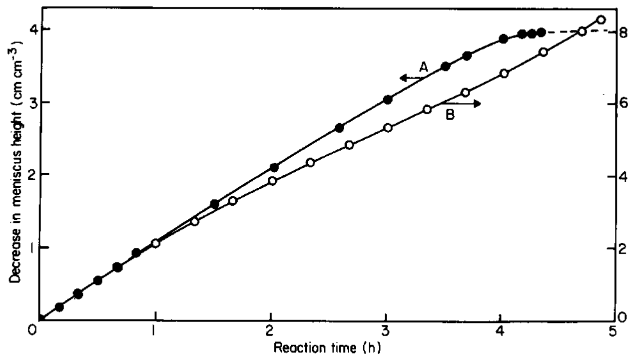


Figure 7 Variation in dilatometer meniscus heights with reaction time for polymerization of MMA initiated by PSt–Br: curve A (●), $[Mn_2(CO)_{10}] = 1.03 \times 10^{-3}$ mol l^{-1}, $[PSt–Br] = 5.1 \times 10^{-4}$ mol l^{-1}; curve B (○), $[Mn_2(CO)_{10}] = 1.04 \times 10^{-3}$ mol l^{-1}, $[PSt–Br] = 2.05 \times 10^{-3}$ mol l^{-1}

Generalization of copolymer formation

To make the anion to free-radical transformation potentially useful it is necessary to extend the procedure to incorporate free-radically prepared blocks other than PMMA. We have previously demonstrated that polymerizations of many monomers susceptible to free-radical polymerization are initiated by metal carbonyl plus organic halide systems and we have used the systems to prepare graft copolymers and to assess modes of free-radical termination[10,11]. These studies demonstrated that the conjugate radicals of most monomers, other than monomers having an α-methyl substituent, undergo termination almost exclusively by combination. This provides potential for the synthesis of ABA thermoplastic elastomers in which the B blocks are prepared by free-radical polymerization and are elastomeric, e.g. acrylates or chloroprene.

Figure 1 includes the variation in rate of polymerization of chloroprene with PSt–Br concentration, demonstrating that PSt–Br is an effective macroinitiator and that the characteristic kinetic features apply in this system. Similar data were obtained for other monomers.

Kinetic studies were used to confirm that, for several monomers used, rates of polymerization were proportional to $I^{1/2}$, at constant $Mn_2(CO)_{10}$ concentration, and that rates of polymerization were inversely proportional to the molecular weights of the polymers formed, as required by simple free-radical polymerization kinetics. In the absence of g.p.c. standards for most polymers, molecular weights were estimated using PMMA standards and the *Q*-factor method[12]; values of $k_p/k_t^{1/2}$ derived from these measurements are included in *Table 1*.

Figure 8 shows chromatograms* for the products of various polymerization reactions initiated by PSt–Br, which illustrates the formation of high-molecular-weight polymers. *Figure 9* shows corresponding composition–elution volume data for the high-molecular-weight components, and in each case data clearly demonstrate variations in composition with elution volume consistent with block copolymer formation.

Further examples and quantitative analyses will be presented in a future publication, but at this point a few qualitative observations are appropriate. As a result of initiation from PSt–primary radicals formed from PSt–Br, it is possible to form, as a result of combination termination, disproportionation termination or chain transfer to PSt–Br or monomer, either ABA and AB block copolymers or B homopolymers or a mixture; the consequence of each of these variations is different. Because the B chains are formed by free-radical polymerization, they are associated with broad molecular weight distributions.

ABA copolymers inevitably have distributions extending to higher molecular weights than $2M_A$ (where M_A is the molecular weight of the initial PSt–Br), AB copolymers will extend to high molecular weight from M_A, and homopolymer B will extend to very low molecular weight irrespective of the value of M_A.

It is clearly apparent from data in *Figures 2* and *8* that for the PSt–methacrylate copolymers there is considerable overlap of the broad high-molecular-weight peak from the reaction products and the unreacted PSt–Br, consistent with the tendency for propagating methacrylate radicals to undergo disproportionation termination and, hence, form AB block copolymers in addition to some ABA block copolymer; it is impossible to make any definitive statement on the extent of chain transfer. For copolymer formation using methyl and n-butyl acrylate monomers or chloroprene, there is little overlap of the high-molecular-weight peak with that of PSt–Br or of the PSt of molecular weight $2M_A$ (*Figure 8*). This observation is consistent with a predominance of combination termination of the propagating radicals and, under the reaction conditions employed, of little chain transfer.

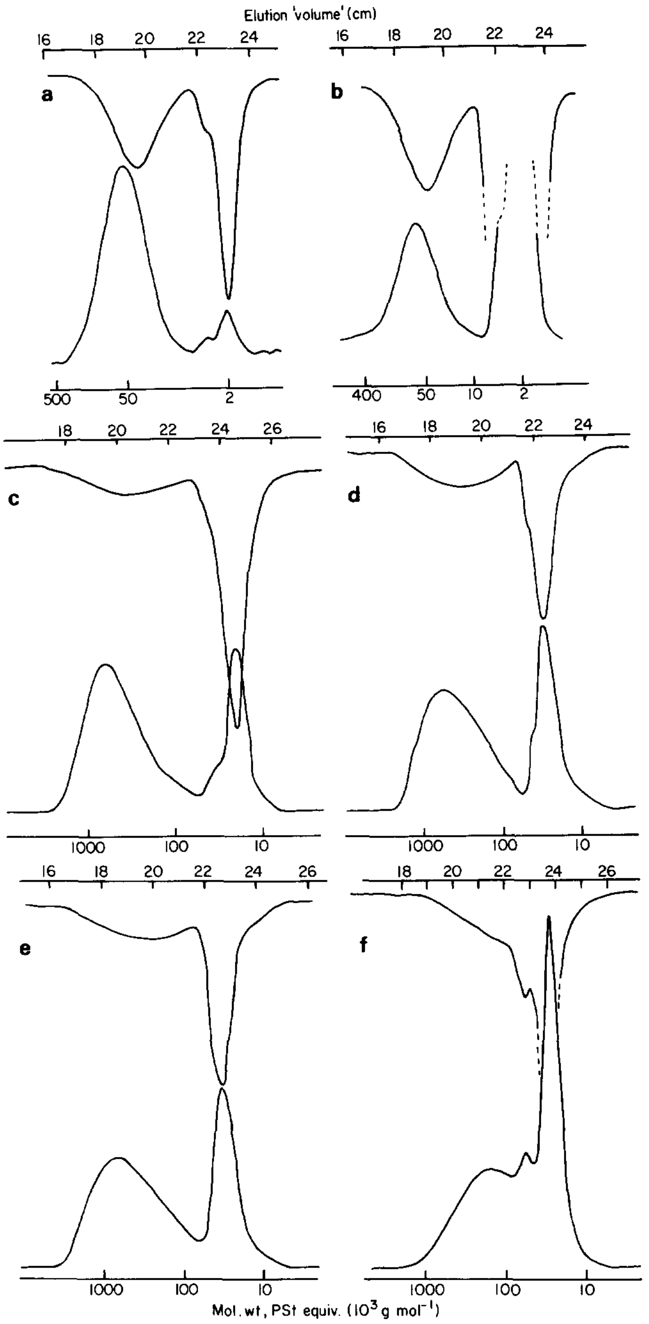


Figure 8 Gel permeation chromatograms for reaction products by initiating polymerizations of (a) chloroprene, (b) methyl acrylate (PSt–Br mol. wt 2000 g mol^{-1}), (c) methyl acrylate (PSt–Br mol. wt 19 000 g mol^{-1}), (d) ethyl acrylate, (e) n-butyl acrylate and (f) n-butyl methacrylate from PSt–Br; upper and lower chromatograms from u.v. and RI detection, respectively

Although it is well known that butadiene does not polymerize effectively by free-radical polymerization in solution, because of a high rate of bimolecular termination[5], we undertook some experiments using butadiene as monomer (0.15 M in toluene solution). *Figure 10a* (curve C) shows a chromatogram for the reaction products. Clearly a species with a molecular weight of about 5000 g mol^{-1} has been formed. To

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*Note that direct comparison of relative heights of u.v. and RI chromatograms and elution volumes for different samples is not valid as different detector settings and column sets were used in the course of this work

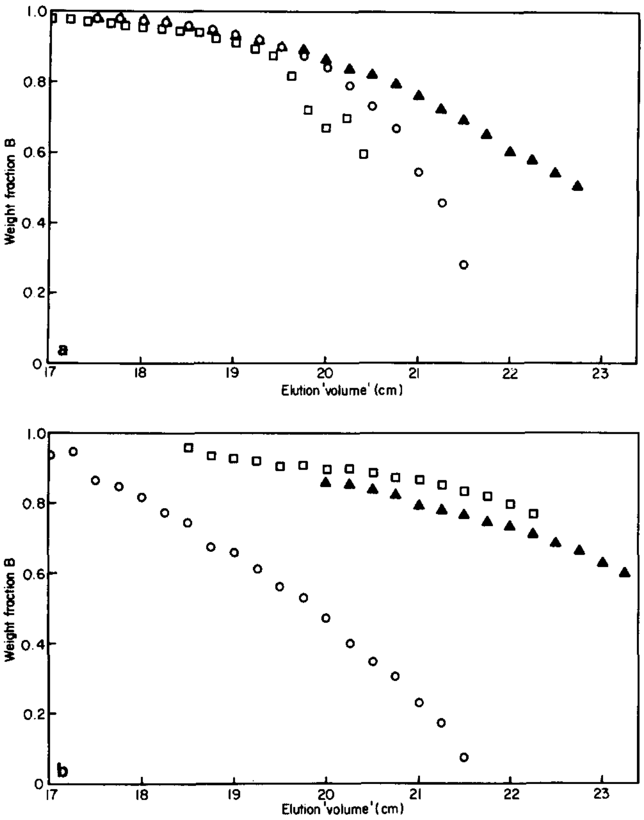

Figure 9 Variations of composition of reaction products from copolymerization reactions corresponding to chromatograms in *Figure 8*. B components are: (a) (○) chloroprene, (□) methyl acrylate (PSt–Br mol. wt 2000 g mol^{-1}), (▲) methyl acrylate (PSt–Br mol. wt 19000 g mol^{-1}); (b) (▲) ethyl acrylate, (○) n-butyl acrylate, (□) n-butyl methacrylate

confirm the formation of copolymer a sample of PSt–Br 1 was irradiated, under comparable conditions, in the presence of $Mn_2(CO)_{10}$. Primary radicals derived from PSt–Br 1, identical with conventional PSt propagating radicals, are expected to undergo termination by combination and, hence, produce PSt of molecular weight $2M_A$. G.p.c. traces of the initial PSt–Br (curve A) and irradiated PSt–Br (curve B) are also shown in *Figure 10a*. From these data it is clear that the reaction products formed in the presence of butadiene have a slightly higher molecular weight than PSt of molecular weight $2M_A$ (4000 g mol^{-1}) formed by irradiation of PSt–Br 1, indicating that irradiation in the presence of butadiene caused formation of a low-molecular-weight copolymer. These results indicate a degree of polymerization for propagating butadiene chains of 10–20 monomer units. The reaction products were also examined by infra-red spectroscopy, when it was seen that the reaction products formed in the presence of butadiene (*Figure 10b*, curve B) had an absorption at 10.3 μm, characteristic of a *trans*-1,4 olefinic unit in polybutadiene, which was not present in PSt–Br (*Figure 10b*, curve A). These results supplement the former, obtained using various olefinic monomers, in establishing the general applicability of the anion to free-radical transformation route investigated to copolymer formation.

CONCLUSIONS

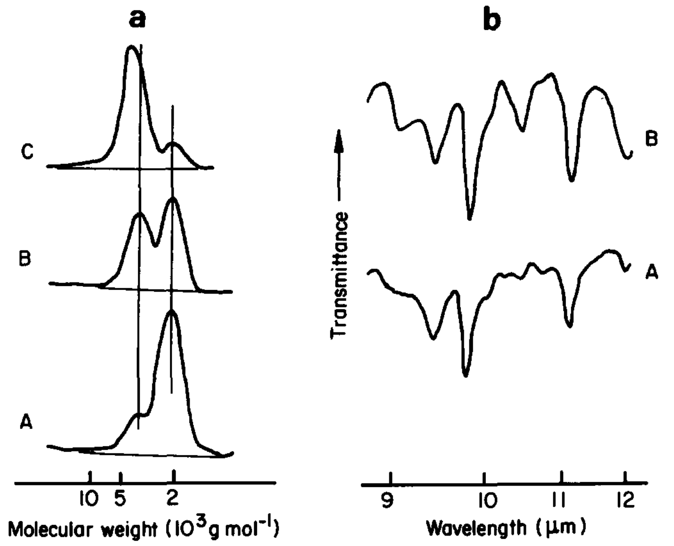

Figure 10 (a) Gel permeation chromatograms of PSt–Br (A), products of initiating radical formation from PSt–Br in the absence of a monomer (B) and the product of initiating polymerization of butadiene from PSt–Br for [butadiene] = 0.15 mol l^{-1} (C). (b) Infra-red spectra of PSt–Br (A) and the product of initiating polymerization of butadiene from PBt–Br (B). In each case $[Mn_2(CO)_{10}] = 2.3 \times 10^{-4}$ mol l^{-1}, $[PSt–Br] = 3.55 \times 10^{-4}$ mol l^{-1}

It has been demonstrated that terminally brominated PSt (PSt–Br), of molecular weight up to at least 20000 g mol^{-1}, can act as an effective macroinitiator, in conjunction with dimanganese decacarbonyl (photolysed at 436 nm), of free-radical polymerization and that the kinetics of polymerization for several monomers are closely similar to those for initiation from low-molecular-weight halide initiators. A potential complication is that the functional polymers, as prepared by anionic polymerization, contain unidentified impurities that retard free-radical polymerizations initiated by them; extensive purification of the preformed polymers may be required prior to use in well defined systems.

As a result of gel permeation chromatographic analysis of the reaction products, it is concluded that the products formed by free-radical initiation from PSt–Br (polymer A) in the presence of monomers B are block copolymers in which the molecular weight distribution of the B blocks, at least in some cases, approximates to those of B polymers formed by conventional free-radical polymerization. Whether AB or ABA block copolymers are formed is presumed to depend on the mechanism of mutual bimolecular termination of the propagating B radicals and the presence or absence of chain transfer.

Although the ultimate efficiency of block copolymer formation from PSt–Br was not determined, there is every reason to believe that every chain having a terminal bromine atom is a potential macroinitiator and that any limitation on efficiency is determined by the efficiency of functionalization of the ionically formed chain. A practical limitation of efficiency is that, to form block copolymers, radicals must be formed from the A chains gradually. It is therefore difficult to achieve the situation that all A chains are converted to copolymer, especially if control over reaction kinetics is desired throughout. The residual homopolymer may be an inconvenience if pure block copolymer is required but, for many purposes, some residual A chains would be no disadvantage. Thus, it is concluded that this route is an effective means of forming block copolymers with combinations of components that are not readily available by other means.

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