polymer communications

Formation of polystyrene–poly(methyl methacrylate) block copolymers by anion to free radical transformation

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This paper describes a new route for the synthesis of linear block copolymers using a combination of anionic and radical propagation reactions. Free radical polymerization of methyl methacrylate is initiated from halogen-containing end-groups incorporated into the terminal units of polystyrene produced by anionic polymerization. Gel-permeation chromatography is used to establish copolymer formation.

Keywords Anionic; block copolymer; free radical; methyl methacrylate; polymerization; styrene

Introduction

Attempts have been made to increase the number of combinations of monomers which can be incorporated into linear block copolymers by transforming one mode of chain propagation into another and simultaneously changing the polymerizable monomer[1]. In some cases this objective has been achieved by terminating the polymerization of the first monomer with a suitable reagent to incorporate a functional end-group capable of acting as an initiating site for the second mode of polymerization. An earlier paper[1] mentioned that we were attempting to synthesize block copolymers using such a transformation from anion to free-radical propagation and this communication demonstrates that the selected route is indeed feasible.

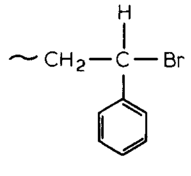
It is known that free radicals can be generated from certain organic halides by reaction with transition metal carbonyls or their derivatives[2]. The overall reaction mechanism is summarized by the equation

$$\mathrm{Me(O)} + \mathrm{R-X} \rightarrow \mathrm{R\cdot} + \mathrm{Me(I)X} \qquad (1)$$

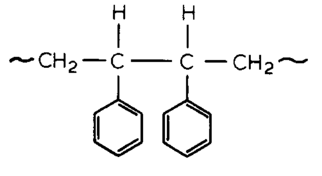
where Me(O) is the transition metal in its zeroth oxidation state and X is a halogen. In the presence of a suitable monomer, radical R· initiates polymerization. Detailed reaction mechanisms are described in ref. 2. We have used this reaction to synthesize non-linear block copolymers from preformed polymers having a halogen in side groups[3]. Similarly, using a preformed polymer, derived from monomer A, with halogen-containing end-groups, we may synthesize linear block copolymers. Radical formation in such a system produces a macroradical capable of initiating polymerization of a monomer B to form propagating AB block copolymer species. We have now examined the possibility of synthesizing polystyrene (PSt)–poly(methyl methacrylate) (PMMA) block copolymers by this procedure using a functionalized, anionically-prepared PSt as polymer A and as the source of radicals to initiate polymerization of MMA.

Synthetic procedure

PSt of molecular weight 2000 g mol^{-1} and with a narrow molecular weight distribution was prepared by anionic polymerization using lithium butyl as initiator and tetrahydrofuran as the solvent. Polymerization was terminated by bromine, *via* a Grignard intermediate, to produce PSt with a terminal benzylic bromine atom (structure I), designated Br–PSt[4]. Small amounts of PSt of molecular weight 4000 (see *Figure 2*) were formed through coupling of the PSt chains on termination; it is believed that these species (structure II) contain no bromine.



(I)



(II)

Although it is possible that some chains of molecular weight 2000 containing no bromine may have been formed, it is known that termination to form structure I is at least 60% efficient[4]. The Br–PSt was purified by several reprecipitations from benzene into pure methanol.

Under vacuum, Br–PSt in conjunction with dimanganese decacarbonyl is an effective photoinitiating system ($\lambda = 436$ nm) for the polymerization of methyl methacrylate (MMA). *Figure 1* shows that the rate of MMA polymerization is independent of [Br–PSt], down to low values of [Br–PSt], at constant light intensity and [carbonyl]. The kinetic behaviour in *Figure 1* is typical of metal carbonyl–organic halide initiating systems and demonstrates that the polymeric halide Br–PSt behaves in the same manner as reactive low molecular weight halides[3].

Because we have previously established that radical formation normally occurs by reaction as depicted in equation (1), we anticipated that, in this case, R· would be

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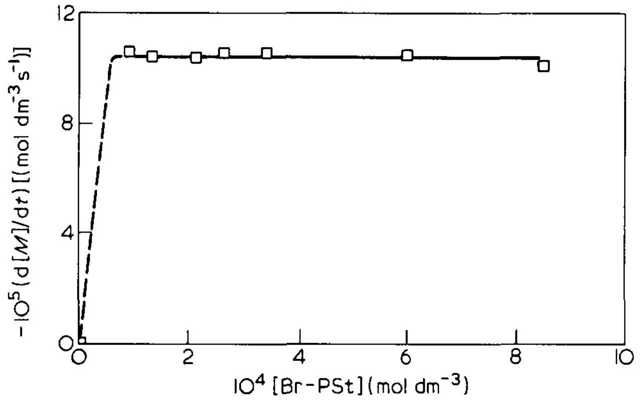

Figure 1 Variation in rate of polymerization of MMA with concentration of bromine-terminated polystyrene. Average rates (30 min reaction time) of polymerization were measured gravimetrically. $[Mn_2(CO)_{10}] = 2.1 \times 10^{-4}$ mol dm^{-3}, $I_{abs} = 4.9 \times 10^{-8}$ einsteins dm^{-3} s^{-1}

a PSt macroradical formed by removal of Br from Br–PSt. Thus, initiation of MMA polymerization by the PSt radical would lead to block copolymer formation and, since MMA propagating radicals terminate predominantly by disproportionation (70%) at 25°C[5], the reaction product would be expected to be primarily an AB block copolymer in which the A-block is derived from styrene and the B-block from MMA. Combination termination (30%) would lead to the simultaneous formation of some ABA block copolymer. Since all primary radicals are macroradicals the synthesis produces only minimal amounts of homopolymer of the second monomer.

Isolation and identification of reaction products

A typical reaction mixture consisted initially of $[\text{carbonyl}] = 5 \times 10^{-4}$ mol dm^{-3}, $[\text{Br–PSt}] \sim 10^{-3}$ mol dm^{-3} in bulk MMA. After photolysis (typically 30 min) polymers were isolated by precipitation into a large excess of methanol. The products were dissolved in tetrahydrofuran and 50 μl samples of 0.25% (w/v) solution (18 μl of 0.08% solution of Br–PSt) were injected into a Du Pont gel permeation chromatograph fitted with silanized glass bead columns; ultraviolet ($\lambda = 260$ nm) (Kratos–Schoeffel) and refractive index (Du Pont) detectors were employed simultaneously.

Compared with PSt, PMMA homopolymer is virtually transparent at 260 nm and, at the instrument settings used, the ultraviolet detector effectively responds to PSt only. The r.i. detector responds to both polymers but, because the reaction products consist largely of PMMA, typically 50–80% (w/w), the response is primarily from PMMA.

Figure 2 presents chromatograms of the total polymeric products isolated from a reaction mixture as described above. The traces from the two detectors have been shifted to make their molecular weight scales coincident. Also included in *Figure 2*, for comparative purposes, are traces for the initial Br–PSt. The latter traces show a major peak at a molecular weight of 2000 with a small shoulder at 4000; the latter feature arises from PSt chains which coupled on terminating the anionic polymerization.

The u.v. trace from the reaction products has an intense peak coincident with that of Br–PSt and arising from unreacted Br–PSt. This chromatogram also exhibits a less intense broad peak at high molecular weight. The refractive index trace from the same sample consists of a broad peak at high molecular weight (peak molecular weight (PSt equivalent) 170000 approximately). This latter peak undoubtedly arises primarily from PMMA in the copolymer produced by free-radical polymerization, as described above, and the molecular weight is consistent with the mean rate of MMA polymerization observed, 1.45×10^{-4} mol dm^{-3} s^{-1}.

Samples of the reaction products were redissolved, precipitated into petroleum spirit (hexane fraction) and re-examined by g.p.c. Chromatograms (*Figure 3*) show that reprecipitation removed most of the low molecular weight Br–PSt, leaving the high molecular weight products; traces of residual Br–PSt and PSt of 4000 molecular weight can be detected in the u.v. trace.

Comparison of the chromatograms obtained using dual detection (*Figure 3*) provides strong evidence for the

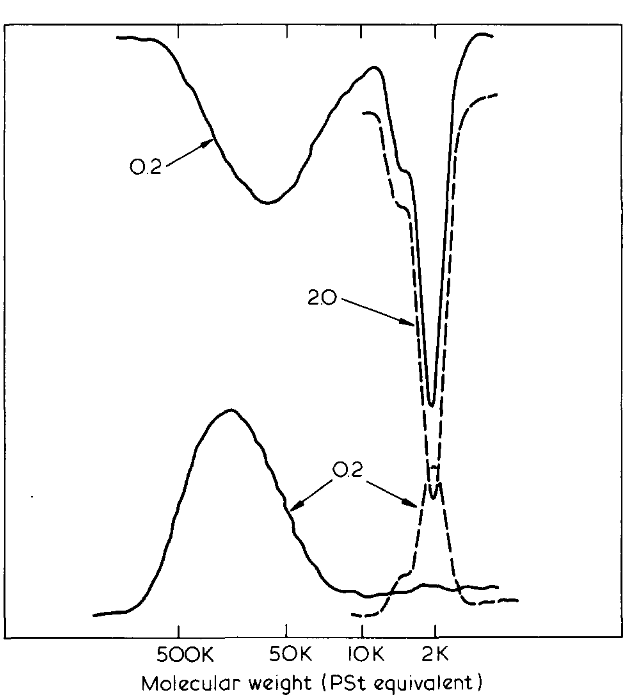

Figure 2 Gel permeation chromatographs using refractive index (lower traces) and ultraviolet (upper traces) detectors for (— — — —) Br–PSt and (———) reaction products from polymerization of MMA using Br–PSt as initiator. Detector attenuator settings are indicated in the diagram

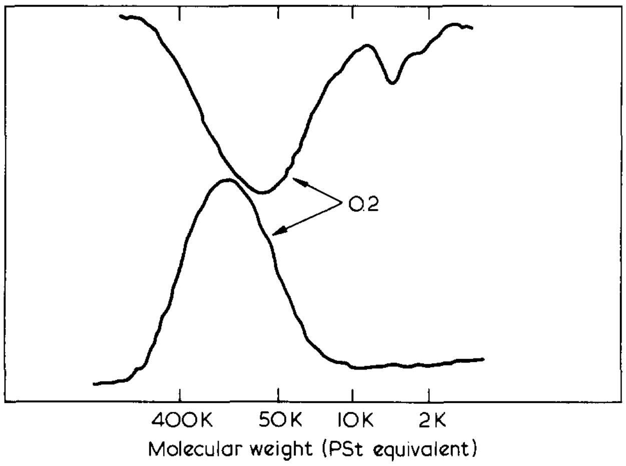

Figure 3 Gel permeation chromatographs of reaction products as in *Figure 2* but after reprecipitation into petroleum spirit. Detector attenuator settings are indicated in the diagram

formation of PSt–PMMA block copolymer according to the proposed mechanism. The major ultraviolet absorption at high molecular weight arises almost exclusively from the low molecular weight Br–PSt used as initiator. The elution volumes at which this PSt appears cover the same range as those for elution of the PMMA, consistent with the PSt being present as end-blocks of PSt–PMMA block copolymer. In addition, the two chromatograms are not identical in shape. The peak of the u.v. trace appears at greater elution volume than the peak of the i.r. trace. This result is entirely consistent with block copolymer formation because every PMMA chain will be attached to a PSt block of molecular weight 2000. Therefore, low molecular weight copolymer molecules will contain larger proportions of PSt than the high molecular weight molecules and, hence, will give relatively large u.v. responses, as observed.

Conclusion

The combination of kinetic and molecular weight data presented above establishes that Br–PSt can be used as a source of free radicals capable of initiating the polymerization of MMA leading to the formation of PSt/PMMA block copolymers. Therefore we conclude that we have established an additional route for block copolymer formation by effecting a transformation from anionic propagation (used in the synthesis of PSt) to free-radical propagation through the intermediate formation of Br–PSt.

We are now attempting to determine the potential efficiency of the transformation and to extend the synthesis to other monomer combinations.

Acknowledgement

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Quantitative characterization of orientation in PET fibres by Raman spectroscopy

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Attempts to obtain quantitative measures of orientation on fibres of diameter ~ 10 µm by the method used earlier on films were unsuccessful. This is believed to be due to polarization scrambling caused by reflection and refraction at the surface of the fibre. It is shown that by immersing the fibres in a liquid of refractive index equal to the mean of those of the fibre the method can be used successfully.

Keywords Orientation; fibre; Raman; polymer; spectra; poly(ethylene terephthalate)

Introduction

Raman spectroscopy has been used to characterize quantitatively the degree of molecular orientation in oriented samples of a number of different polymers[1–5] including poly(ethylene terephthalate) (PET). In the studies on uniacially oriented PET, quantitative agreement was found between values of $\langle \cos^2\theta \rangle$, or $\langle P_2(\cos\theta) \rangle$, determined from refractive index measurements and from Raman measurements, where θ is the angle between the chain axis and the draw direction, $P_2(\cos\theta) = \frac{1}{2}(3\cos^2\theta) - 1)$ and the angle brackets denote the average value. The results of more recent Raman studies of orientation on a biaxially oriented sheet[6] were also consistent with measurements of refractive index.

In all these studies the samples were at least 30 µm thick, and of much greater size in the two directions perpendicular to the thickness, and the propagation directions of both the incident and the analysed Raman scattered light were to a good approximation normal to the edge or to one of the surfaces of the sample. When an attempt was made to apply the method to single-filament yarns of PET of approximate diameter 10 µm, it was found that the values of $\langle P_2(\cos\theta) \rangle$ obtained were very different from those deduced from the birefringence of the fibres. No quantitative explanation has been found so far for the discrepancy, but it is believed that it arises because the incident and Raman scattered light are multiply reflected at the surface of the sample and also refracted on entering or leaving the sample so that their polarization directions become ill-defined when in the plane normal to the fibre axis. The present communication shows that if the fibre is immersed in a liquid with a refractive index close to that of the polymer the discrepancy disappears and meaningful values of both $\langle P_2(\cos\theta) \rangle$ and $\langle P_4(\cos\theta) \rangle$ can be found, where $P_4(\cos\theta) = \frac{1}{8}(3 - 30\cos^2\theta + 35\cos^4\theta)$. In the remainder of this communication we shall abbreviate $\langle P_l(\cos\theta) \rangle$ by P_l.

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