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Facile synthesis of epoxystyrene and its copolymerisations with styrene by living free radical and atom transfer radical strategies

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Abstract

Epoxystyrene (ethenylphenyloxirane) has been synthesised in a single-stage process by mono-epoxidation of divinylbenzene using magnesium monoperoxyphthalic acid. Copolymers of epoxystyrene and styrene were then synthesised by living free radical polymerisation and atom transfer radical polymerisation methods. In both cases the oxirane group of epoxystyrene was found to be stable under the conditions of polymerisation, though at the temperatures required for LFRP, copolymers with bimodal molecular weight distributions resulted. In contrast, as long as the temperature used for ATRP was kept below 100°C, copolymers with narrow, monomodal distributions could be obtained.

Keywords: Epoxystyrene; Styrene; Living radical copolymerisation

1. Introduction

Epoxy oligomers and polymers have been of interest for many years because of the ease with which crosslinking can be achieved through the cationic ring-opening of the oxirane group [1]. Typical applications of this facility are to be found in adhesives, surface coatings, imaging technology, etc. In the last context, they were first investigated for use as negative-working resists in electron beam lithography over 20 years ago [2], and recently Hatzakis and co-workers [3] have reported the lithographic performance of epoxynovalacs in formulations with a photo-acid generator (PAG). The modelling of the lithographic performance of this resist system is of current interest to us [4–6], and it against this background that the present investigations were conducted. The Hatzakis systems have a number of desirable properties for lithographic processing and can attain feature sizes of 0.1 μm. However, optimisation of their lithographic performance through systematic structural variation cannot be achieved as there is no easy way of altering the composition or molecular weight of an epoxynovalac in a controlled fashion. Thus, as an analogue of this structure we have developed a series of poly(epoxystyrene-*stat*-styrene) copolymers and have recently reported their lithographic performance as e-beam resists in formulations with a PAG [5,6]. The results were promising in the sense that structural variation that can be used for process optimisation is easy, but the procedures used in the synthesis of the epoxystyrene [7], depicted in Scheme 1, proved to be cumbersome and inefficient. In addition, the conventional free radical polymerisation method that was used only allowed for the synthesis of copolymers with normal distributions, and disallowed the possibility for variation of molecular weight distribution, which is an important device in resist optimisation. Accordingly, new synthetic procedures have been sought and it is the results of these investigations that are reported here.

2. Experimental

2.1. Materials

Two commercial sources of divinylbenzene were used for the syntheses of epoxystyrene. In the first instance a mixture of the *o*-, *m*- and *p*-isomers (78%) with ethylvinylbenzene (20%) and diethylbenzene/naphthalene (1%) was obtained from the Aldrich Chemical Co. Ltd. Latterly, however, a 99% pure mixture of the *m*- and *p*-isomers was obtained from the Nippon Steel Co. Ltd. Bipyridine, dibenzoyl peroxide (BPO), copper(I) bromide, methyl (4-bromomethyl)-benzoate and styrene were also supplied by Aldrich. The

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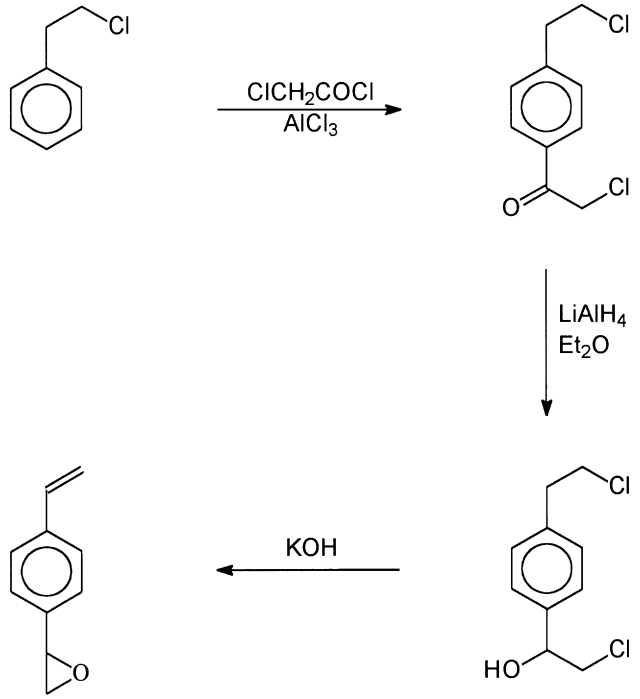


Scheme 1.

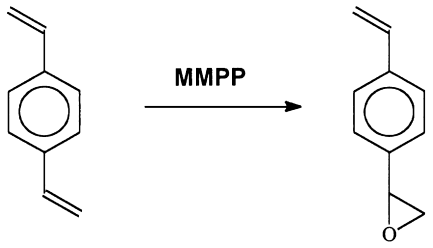
stabiliser, 4-*t*-butylcatechol, was removed from styrene by passing through an Aldrich inhibitor removal column. The BPO was purified by precipitation from chloroform solution into methanol and then re-crystallised from methanol at 0°C. All other materials and solvents used for polymer isolation and purification procedures, which were of SLR grade, were used without further purification.

2.2. Apparatus

Nuclear magnetic resonance (n.m.r.) spectra were obtained using a JEOL JNM-GX270 spectrometer (270 and 67.7 MHz for ^{1}H and ^{13}C, respectively) using tetramethylsilane as an internal standard. Copolymer compositions were established from integration of ^{1}H spectra obtained at room temperature from deuterochloroform solutions of the copolymers. Molecular weights of the polymers were measured as linear polystyrene equivalents in THF solution using size-exclusion chromatographic (SEC) equipment supplied by Polymer Laboratories Ltd. and equipped with a mixed-bed 5 μm PLgel column. The calibration was over the molecular weight range 162–1.03×10^{6}.

2.3. Synthesis of epoxystyrene

Epoxystyrene was prepared by mono-epoxidation of divinylbenzene using magnesium monoperoxyphthalic acid (MMPP) as the epoxidising agent as shown in Scheme 2. To a stirred solution of divinylbenzene (50 mmol, 7.1 ml) in acetone (250 ml) was added MMPP (35 mmol, 21.63 g) in water (250 ml). After stirring at room temperature for 18 h,



Scheme 2.

the solution was extracted with *n*-hexane three times. The organic extract was dried over magnesium sulphate and the solvents were evaporated. The residue was purified by flash chromatography on a silica gel column (230–400 mesh, 45 g) eluted with *n*-hexane (250 ml) and then with a 20% mixture of diethyl ether in *n*-hexane (250 ml). Following evaporation of the solvents, 2.92 g of epoxystyrene were obtained, corresponding to a 40% yield[1]. ^{1}H n.m.r. ($CDCl_3$): $\delta = 2.82$ (q; 1H), 3.09 (q; 1H), 3.81 (q; 1H), 5.23 (dd; 1H) 5.74 (dd; 1H), 6.68 (q; 1H), 7.23 (m; 4H). Prior to use, the product was distilled under reduced pressure (80°C, 0.1 mmHg)[2].

The epoxystyrenes prepared from the impure divinylbenzene obtained from Aldrich were contaminated with about 20% ethylphenyloxirane which was found both to elute from the chromatography column and to distil together with epoxystyrene. Accordingly, the epoxystyrene used in the early atom transfer radical polymerisation (ATRP) studies contained this impurity. It was not believed that it could become involved in the copolymerisations, but nonetheless its presence in the reaction systems is recorded in the footnotes to the tables.

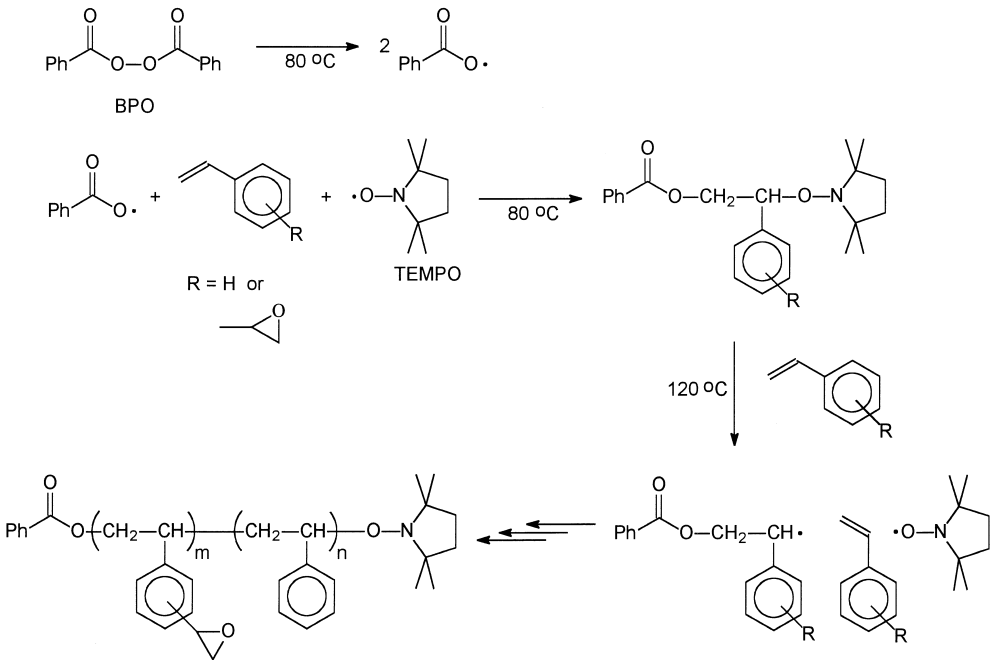
2.4. Living polymerisations

The methods of living radical polymerisation, whether living free radical polymerisation (LFRP) or ATRP (depicted in Scheme 3 and Scheme 4, respectively for the copolymerisations relevant to this study), involve three essential species, the monomer(s), a radical initiator, and a stable counter radical. Although the particular initiating systems are different they operate to a common concept based on the reversible activation of dormant species that are formed by the combination of reactive radicals and stable counter radicals. At 100% conversion of monomer to polymer in such syntheses, the theoretical number average molecular weight, $M_{n,th}$, of the product can be calculated from Eq. (1) in which monomer, and the initiating species[3] are represented by M and I, respectively, and M_M represents

[1] If the duration of reaction or reagent proportions are altered in an attempt to increase the yield, it is in fact reduced as substantial amounts of diepoxybenzene are produced.

[2] It should be noted that if the temperature is allowed to rise to 110°C or greater then epoxystyrene will readily polymerise.

[3] In the case of LFRP, stoichiometric account is taken of the two radicals that arise from the decomposition of dibenzoyl peroxide.



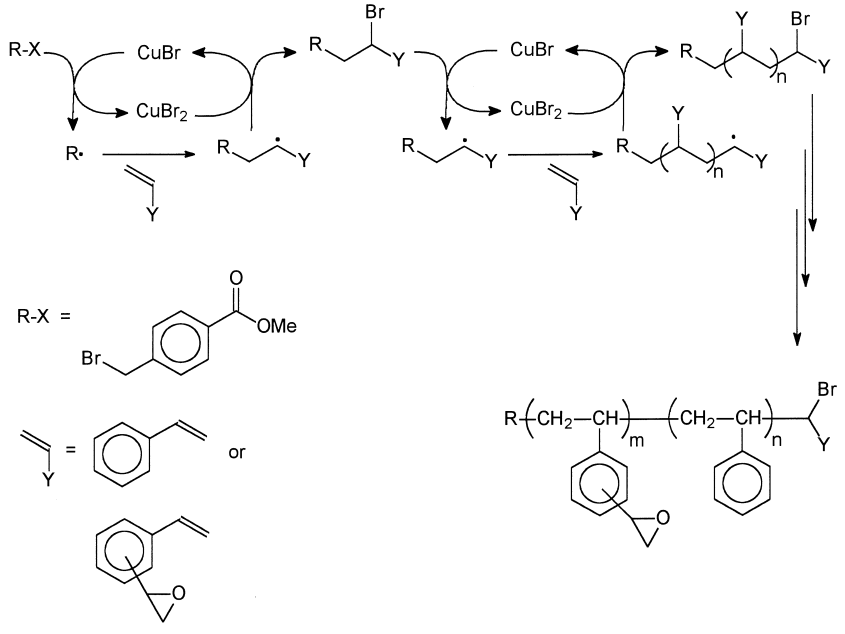
Scheme 3.

the molecular mass of the monomer.

$$M_{n,th} = M_M[M]/[I] \quad (1)$$

The amounts of initiator used in the present work were calculated from the desired value of M_n using Eq. (1) where M_M was taken to be the average molecular mass of the two monomers weighted to accord with the desired copolymer composition.

In a number of cases the copolymerisations were stopped at less than 100% conversion in order to check whether or not the two monomers were consumed uniformly and statistically throughout reaction in accordance with the requirement that the molecular weight of the polymer formed in a living polymerisation varies linearly with conversion. Thus, for a reaction in which there was only x% conversion, the calculated number average molecular



Scheme 4.

weight, $M_{n,calc}$, was expressed in accordance with Eq. (2).

$$M_{n,\,calc} = xM_M[M]/100[I] \quad (2)$$

2.4.1. Living free radical copolymerisation

LFRC was carried out in accordance with the methodology of Georges et al. [8] shown in Scheme 3. The required amounts of BPO were calculated from Eq. (1), and the molar ratio of BPO:TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy radical) was 1:2.4. Two modifications of the method were employed.

2.4.1.1. Method A. A round-bottomed flask (10 ml) fitted with a PTFE tap was flame dried under vacuum and then flushed three times with argon. After cooling to room temperature, a PTFE stirrer bar, styrene (0.87 g, 8.37 mmol), epoxystyrene (0.13 g, 0.89 mmol), BPO (0.0202 g) and TEMPO (0.0313 g) were placed in the flask which was then sealed by closing the tap under argon. The copolymerisation was carried out by raising the temperature to 80°C for 3 h whilst stirring, and subsequently to 124°C for 24 h. The reaction was then quenched by cooling with liquid nitrogen. The copolymer product was found to be completely soluble in 10 ml of tetrahydrofuran (THF) from which it was precipitated in 200 ml of 2-propanol and filtered. This procedure was repeated six times before the product was dried under vacuum.

2.4.1.2. Method B. A flask containing BPO (0.0202 g), styrene (0.87 g) and TEMPO (0.0313 g) was prepared in accordance with method A, and then stirred at 80°C. After

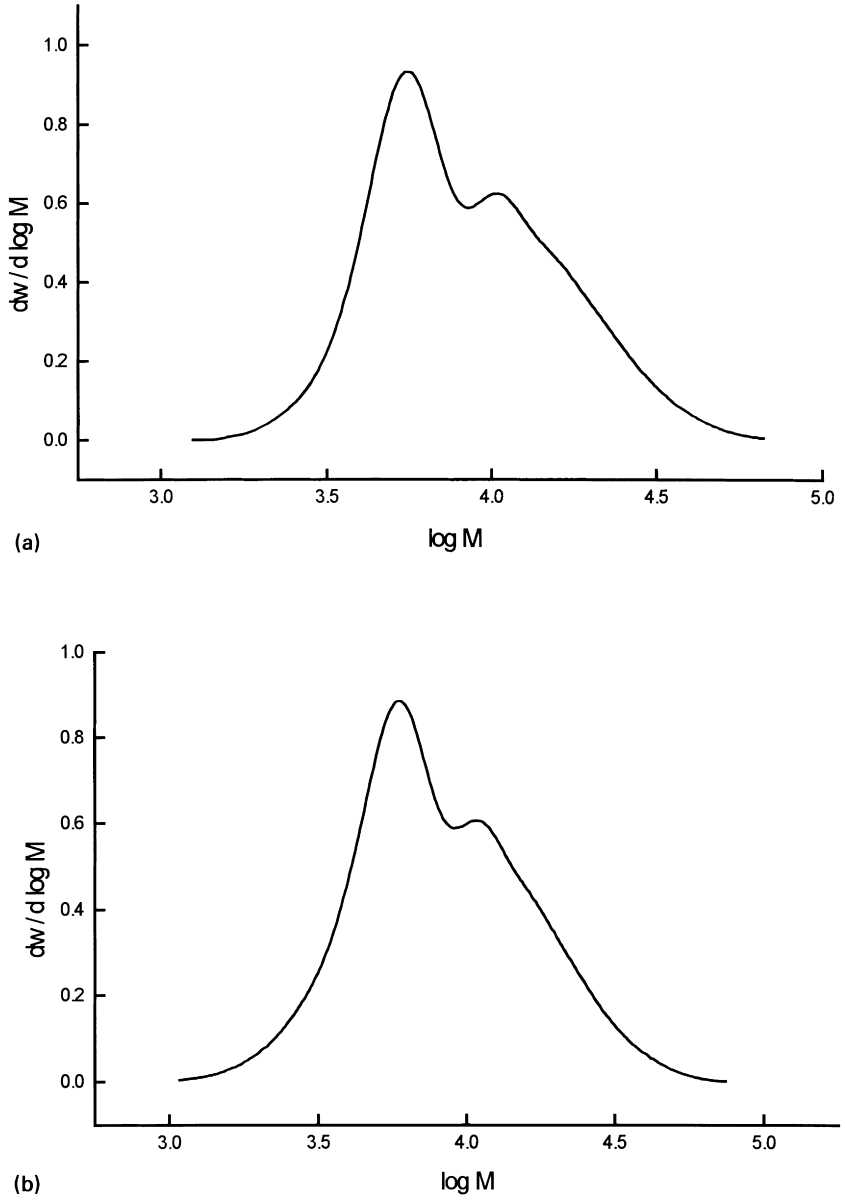


Fig. 1. Size-exclusion chromatograms of poly(epoxystyrene-*stat*-styrene) synthesised by LFRP (a) by method A, (b) method B.

Table 1
Structural parameters of poly(epoxystyrene-*stat*-styrene) by LFRP[a]

Method	ES (%)[b]	$M^{c}_{n,th}$	$M^{d}_{n,cal}$	Yield (%)	M_n	M_w	Pd[e]
A	10	10 000	3700	37	7000	10 500	1.51
B	10	10 000	5200	52	6700	10 400	1.56

[a][BPO]:[TEMPO] = 1:2.4 molar ratio
[b]Epoxystyrene content in copolymer. The polymerisations were carried with epoxystyrene/styrene (10%, mol/mol)
[c]Calculated from Eq. (1)
[d]Calculated from Eq. (2)
[e]Polymodal SEC curve

3 h, epoxystyrene (0.13 g) was introduced under argon, and the mixture was then stirred at 124°C for 36 h. The product was again found to be completely soluble in only 10 ml of THF and was purified by the same method as that described above.

2.4.2. Atom transfer radical copolymerisation

ATRC was performed in accordance with the method of Wang and Matyjaszewski [9] depicted in Scheme 4 as follows: a round-bottomed flask (10 ml) fitted with a PTFE tap was flame dried under vacuum and then flushed three times with argon. After cooling to room temperature, appropriate amounts of methyl 4-(bromomethyl)benzoate (initiator), copper(I) bromide (catalyst), 2,2′-bipyridine (bpy, ligand), styrene and epoxystyrene were placed in the flask. The amounts of initiator were calculated from Eq. (1). The amounts of the other components used are indicated in Table 2. The heterogeneous mixture was degassed in three freeze–pump–thaw cycles, and the tap was then closed under vacuum. The flask was immersed in an oil bath at the desired temperature for a predetermined time. The products were again found to be completely soluble in small amounts of THF so the copolymers were once more purified using the method described above.

3. Results and discussion

The synthesis of epoxystyrene from divinylbenzene shown in Scheme 2, uses MMPP, a relatively new and safe oxidising agent [10]. Although the yield of about 40% is not particularly high, the methodology has several advantages over that of Truxa and Suchopárek [7]. The procedure is straightforward, it involves only one step instead of three, and the yield is substantially higher. Furthermore, the method of flash chromatography use for the work-up of the product allows for recovery of unreacted divinylbenzene which can be recycled to achieve a higher overall conversion.

Although the poly(epoxystyrene-*stat*-styrene) obtained by method A of the LFRC methodology described above had a polydispersity index of only 1.51, the size exclusion chromatogram depicted in Fig. 1a is polymodal. For a homopolymerisation of styrene, the formation of the initial adduct of initiator fragment, monomer and counter radical accounts for virtually all reaction that occurs whilst the system is held at only 80°C, i.e. significant polymerisation only occurs after the temperature is raised to 124°C or thereabouts [11]. However, in the copolymerisation it is possible

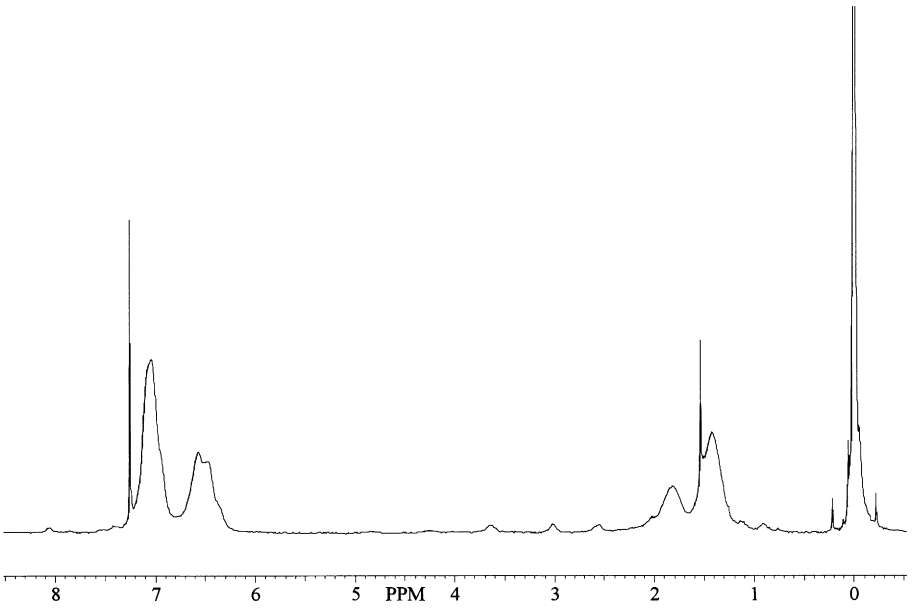


Fig. 2. Typical ^{1}H n.m.r. spectrum of poly(epoxystyrene-*stat*-styrene) synthesised by LFRP.

Table 2
Structural parameters of poly(epoxystyrene-*stat*-styrene) by ATRP

[I]:[CuBr]:[bpy][a]	Temp. (°C)	ES (%)[b]	Time (h)	$M_{n,th}^{d}$	$M_{n,cal}^{e}$	Yield (%)	M_n	M_w	Pd
1:1:2	124	8[c]	6	10 000	10 000	100	11 800	22 400	1.90[f]
1:1:3	80	28[c]	5	10 000	2000	20	8400	12 100	1.45
1:1:3	80	23[c]	7	10 000	10 000	100	10 400	15 000	1.45
1:1:3	90	10[c]	2.5	5000	1750	35	3600	4400	1.23
1:2:4	90	8[c]	2.5	5000	1750	35	4100	5100	1.25
1:1:3	100	10	2.5	5000	3250	65	4000	4800	1.21
1:1:3	100	10	2.5	9000	4050	45	4700	5700	1.20
1:1:3	100	10	2.5	11 000	4510	41	5000	5900	1.18
1:1:3	100	10	5	7000	5390	77	5700	7300	1.28
1:1:3	100	10	6	9000	6450	72	6900	8500	1.24

[a]Molar ratio
[b]Epoxystyrene content in copolymer. The polymerisations were carried with epoxystyrene/styrene (10%, mol/mol) except entries 2 and 3 which were carried with epoxystyrene/styrene (20%, v/v)
[c]Contains 20% ethylphenyloxirane as a impurity (see Section 2)
[d]Calculated from Eq. (1)
[e]Calculated from Eq. (2)
[f]Polymodal SEC curve

that at 80°C the bond between an epoxystyryl radical and the TEMPO counter radical might be more labile than the corresponding styryl–TEMPO bond and allow significant homopolymerisation to occur. This would account for the increased polydispersity but not for the bimodality of the molecular weight distribution, since in a nine-fold excess of styrene propagation would lead to all chain ends rapidly reverting to the styryl–TEMPO structure. Nevertheless, this possibility was investigated through the synthetic procedure of method B in which the epoxystyrene was only added immediately before raising the temperature to 124°C. The copolymer that resulted had about the same polydispersity, 1.56, but as shown in Fig. 1b, the size-exclusion chromatogram was still bimodal. Accordingly, it was concluded that this effect must be attributed to epoxystyrene being very effective at initiating autopolymerisation at temperatures greater than 110°C. This conclusion is born out by the discrepancy of the theoretical and experimental molecular weight parameters listed in Table 1, and the ease with which the monomer undergoes polymerisation if the temperature is allowed to rise significantly above 80°C in the reduced pressure distillation used during its purification.

The compositions of the poly(epoxystyrene-*stat*-styrene) copolymers formed by LFRC as determined by ^{1}H n.m.r. are also shown in Table 1. A typical spectrum is shown in Fig. 2 in which the resonances associated with the two methylene protons and the methine proton of the oxirane group of the dominant epoxystyrene isomer (thought to be *para*) are seen at 2.55, 3.0 and 3.65 ppm, respectively. Minor resonances can just be discerned at higher field, and these are thought to arise from the *meta*-isomer. The resonance seen at about 8 ppm in the aromatic region of the spectrum is attributed to the hydrogen atom at the 2-position of the *meta*-isomer.

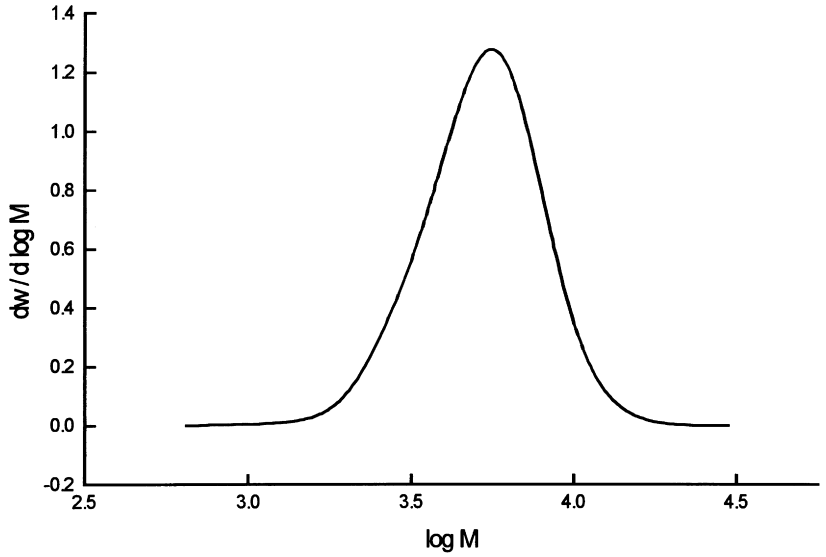


Fig. 3. Typical size-exclusion chromatogram of poly(epoxystyrene-*stat*-styrene) synthesised by ATRP at 100°C.

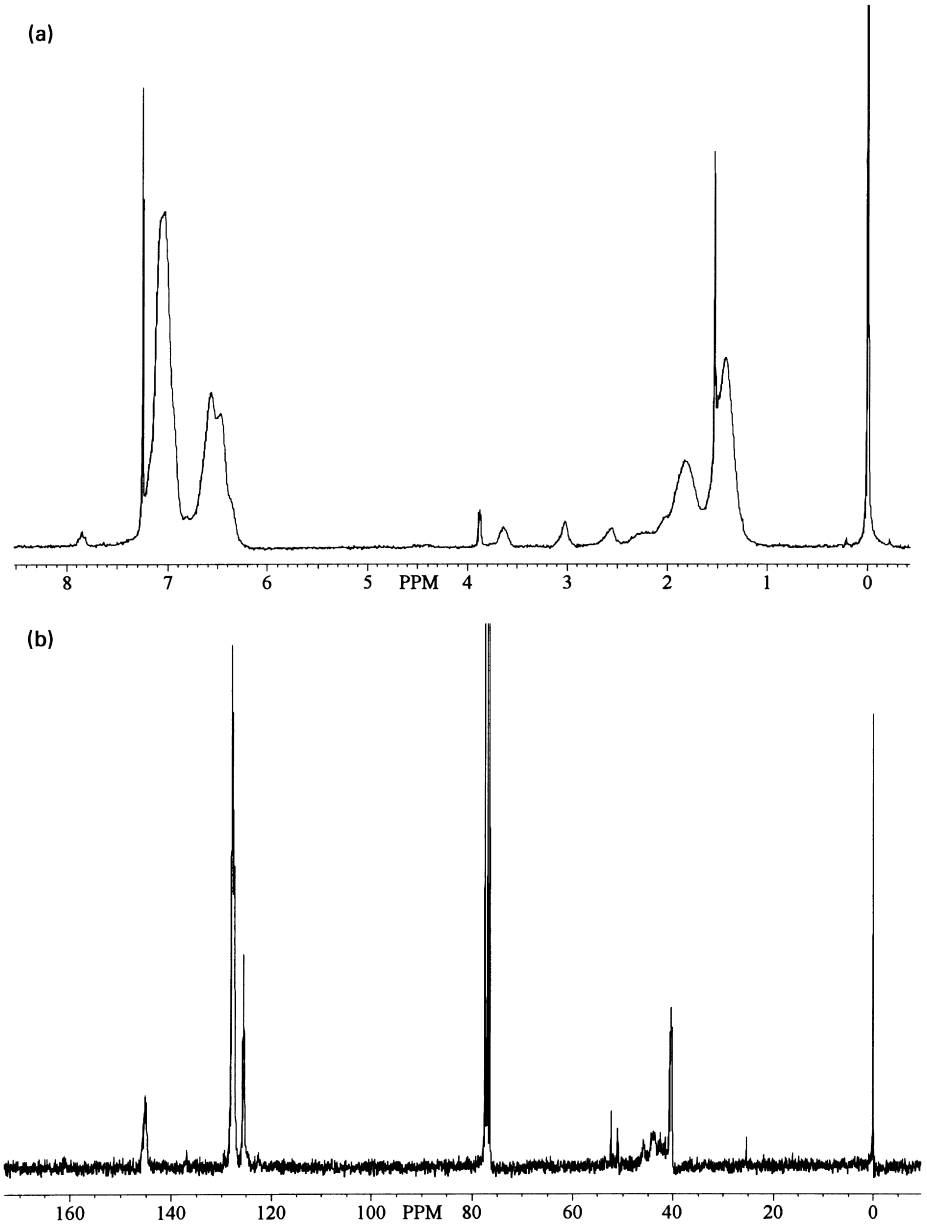


Fig. 4. Typical (a) ^{1}H and (b) ^{13}C n.m.r. spectra of poly(epoxystyrene-*stat*-styrene) synthesised by ATRP.

At conversions approaching 50% it is evident that there has been no obvious preferential incorporation of either styrene or epoxystyrene into the copolymer. From the n.m.r. evidence, taken in conjunction with the observation that no intractable material was formed during the course of the LFRCs, it is concluded that the epoxystyrene was incorporated entirely through its vinyl group and not through the oxirane group.

Since the initiating centres are different from those of the LFRC systems, the ATRC systems do not require such elevated temperatures to achieve a reasonable rate of reaction [12]. Accordingly, a series of ATRC reactions were carried out at various temperatures using a range of different [I]:[CuBr]:[bpy] ratios. The results are summarised in Table 2. The product copolymers are mostly of lower polydispersity than those formed using LFRC, and significantly lower than those (~1.8) of the copolymers obtained using conventional free radical copolymerisation [6]. The most notable exception is the polydispersity of 1.9 for the copolymer formed at 124°C, which can be explained in exactly the same way as the broad distributions of the products of the corresponding LFRC reactions. All the other ATRC reactions were conducted at temperatures sufficiently below the 110°C threshold for efficient autopolymerisation of epoxystyrene, and in all instances, as typified in Fig. 3, the size exclusion chromatograms of the product polymers were monomodal.

The copolymers obtained at 80°C were synthesised from feed stocks containing 20% epoxystyrene. As might be expected for the system taken to 100% conversion, within

the bounds of experimental error, the theoretical value of M_n corresponds to the experimental value, and the predetermined and actual copolymer compositions are also in sufficient agreement. However, for the system at 20% conversion neither of these comparisons hold. The experimental value of M_n is four times greater than the calculated value and the copolymer is significantly richer in epoxystyrene than is the feed stock. In both cases the product polydispersities were high. For the reactions conducted at 90°C, though copolymers of lesser polydispersity were obtained and their compositions accorded with those of the feed stocks (within the bounds of experimental error), the theoretical and experimental M_n values were still awry.

Some of the discrepancies identified above might be attributed to loss of polymer during the isolation and purification procedures, but such results do not hold promise for achieving a controlled copolymerisation that would serve the purposes of resist synthesis. However, when the ATRC reactions were conducted at 100°C using a feed stock containing 10% of the more pure samples of epoxystyrene, and at a constant composition of the initiating system, copolymers with low polydispersities were obtained. Although obtained in various yields that were more or less in accordance with the duration of reaction, their compositions were consistently those of the feed stock, and the theoretical and experimental values of M_n also proved to be satisfactorily in agreement. Typical ^{1}H and ^{13}C n.m.r. spectra of the copolymers produced in this way are shown in Fig. 4. The oxirane group resonances are again evident at 2.55, 3.0 and 3.65 ppm in the ^{1}H spectrum and can be seen at 51 and 51.4 ppm in the ^{13}C spectrum. That there is no evidence of any resonances in the vicinity of 73 and 80 ppm that could be attributed to ether linkages, nor at 113 and 135 ppm attributable to vinyl groups, demonstrates that the copolymerisations have not involved the oxirane group. This is again consistent with the absence of intractable material from the product mixtures.

It has thus been shown that, as a consequence of the high temperatures required, living free radical polymerisation is not suited to the synthesis of copolymers of epoxystyrene and styrene, but that the methodology of atom transfer radical polymerisation can be adapted to suit the purpose. Reactions conducted at 100°C can be used to prepare narrow distribution copolymers of epoxystyrene (10%) and styrene (90%) in high yield (this composition being the one required for resist formulations that are of particular interest in our lithographic studies). It has yet to be demonstrated that this method of controlled polymerisation is entirely general for the synthesis of copolymers of other composition, and for each one it must be established that the monomers are incorporated without preference in order that a statistical copolymer should result. However, from these studies there is every hope that this could prove to be the case. In addition, a ready synthesis of epoxystyrene has been proven, opening the way to the possibility of its wider use in a number of applications.

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References

[1] Paul S. In: Allen G, Bevington JC, editors. Comprehensive polymer science, vol 6. Oxford, UK: Pergamon Press, 1989:149; Fouassier JP, Rabek JF, editors. Radiation curing in polymer science and technology. London: Elsevier Applied Science, 1993, and references therein.
[2] Hirai T, Hatano Y, Nonogaki SJ. Electrochem Soc 1971;118:669; Taniguchi Y, Hatano Y, Shiraishi H, Horigome S, Nonagaki S, Noraoka K. Jpn J Appl Phys 1979;18:1143; Thompson LF, Ballantyne JP, Feit ED. J Vac Sci Technol 1975;12:1280.
[3] Stewart KJ, Hatzakis M, Shaw JM, Seeger DE. J Vac Sci Technol B 1989;7:1734; Hatzakis M, Stewart KJ, Shaw JM, Rishton SA. J Electrochem Soc 1991;138:1076.
[4] Miller Tate PC, Jones RG, Murphy J, Everett J Microelectronic Eng 1995;27:409.
[5] Murphy JJ, Jones RG, Cordina G Microelectronic Eng 1997;35:121.
[6] Jones RG, Cordina GP-G, Murphy JJ J Mater Chem 1997;7:421.
[7] Truxa R, Suchopárek M Makromol Chem 1931;1990:191.
[8] Georges MK, Veregin RPN, Kazmaier PM, Hamer GK Macromolecules 1993;26:2987.
[9] Wang JS, Matyjaszewski K Macromolecules 1995;28:7901.
[10] Heaney H Aldrichim Acta 1993;26:35.
[11] Veregin RPN, Georges MK, Kazmaier PM, Hamer GK Macromolecules 1993;26:5316.
[12] Samamoto M, Kamigaito M Trends Polym Sci 1996;4:371.