A comparison of the phase-transfer-catalysed chlorinations of various polymethylstyrenes by hypochlorite

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The phase-transfer-catalysed chlorinations of poly(2-methylstyrene), poly(3-methylstyrene), poly(2,4-dimethylstyrene) and poly(2,5-dimethylstyrene) using sodium hypochlorite in chloroform/dichloromethane mixtures are compared with that for poly(4-methylstyrene). Over the range of conditions employed, the chlorination of poly(2-methylstyrene) is barely detectable and the polymers with methyl substituents in the *meta* position show a lesser tendency to undergo chlorination than those with methyl substituents in the *para* position. In all cases concomitant modification of the molecular weight distributions of the polymers are minimal when the reactions are carried out at an aqueous phase pH of 8.5 and with a chloroform-rich organic phase. With a dichloromethane-rich organic phase, polymer chain scission is marked. The experimental observations are discussed both in terms of a compatible mechanism and of inductive effects involving the phenyl ring substituents.

(Keywords: polymethylstyrene; chlorination; phase-transfer catalysis)

INTRODUCTION

The use of aqueous sodium hypochlorite and a phase-transfer catalyst (p.t.c.) such as benzyltriethylammonium chloride to effect the selective monochlorination of the substituent methyl group of poly(4-methylstyrene) in chlorinated aliphatic hydrocarbons at ambient temperature has recently been reported in detail[1]. In contrast, the homogeneous solution-phase free-radical-initiated partial chlorination of the polymer results in main-chain chlorination and di- and tri- as well as monochlorination of the methyl groups[2,3]. Furthermore, since the linear copolymerization of a methylstyrene with chloromethylstyrene can only be achieved using free-radical initiation, it follows that the application of the p.t.c. method to a narrow distribution polymethylstyrene prepared by anionic polymerization presents probably the most convenient way of synthesizing a poly(chloromethylstyrene-co-methylstyrene) of low polydispersity. This class of materials finds application as high sensitivity, high contrast negative-working electron beam resists in microlithography. In particular, optimal lithographic parameters can be attained with such materials if they are at least 20% substituted with methyl groups at ring *ortho* positions[4,5]. For that reason it is important to compare the p.t.c. chlorinations of various isomeric polymethylstyrenes. In this paper we extend our study to include poly(2-methylstyrene) (poly2MS), poly(3-methylstyrene) (poly3MS), poly(2,4-dimethylstyrene) (poly2,4DMS) and poly(2,5-dimethylstyrene) (poly2,5DMS).

EXPERIMENTAL

Materials

All monomers (Lancaster Synthesis) were dried over anhydrous sodium sulphate and otherwise further purified by distillation under reduced pressure from cuprous chloride, immediately prior to use. n-Butyllithium (Aldrich) was supplied as a 2.0 M solution in hexanes. AR tetrahydrofuran (THF) was further dried by refluxing over sodium metal. The sodium hypochlorite solution used was aqueous commercial bleach (11% determined by iodometric titration). Benzyltriethylammonium chloride (Aldrich) and all other materials were used without further purification.

Apparatus and procedures

All polymerizations were anionic polymerizations initiated by n-butyllithium and were carried out in THF solution at methanol/dry-ice temperature under an argon atmosphere. The details of the preparations and those for the p.t.c. chlorinations have been reported previously, as have the instrumental techniques that were employed[1]. Molecular weights obtained using size-exclusion chromatography are quoted as linear polystyrene equivalents.

RESULTS AND DISCUSSION

The optimum conditions for achieving the selective chlorination of poly4MS by the p.t.c. method were reported in an earlier paper[1]. Typically, resonances in

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Table 1 Aliphatic ^{13}C chemical shifts for chlorinated polymethylstyrenes

	δ (ppm)					
Polymer	*o*-Me	*m*-Me	*p*-Me	>CH–	–CH$_2$–	–CH$_2$Cl
Poly2MS	18.1 and 19.3	–	–	34.9	43.6	<50
Poly3MS	–	21.4	–	40.0	44.9	46.2
Poly4MS	–	–	21.0	40.4	44.9	46.1
Poly2,4DMS	18.5 and 19.3	–	20.9	34.0	44.8	46.3
Poly2,5DMS	17.6 and 18.6	21.0	–	34.7	43.4	46.3

the ^{13}C n.m.r. spectrum of a poly4MS, chlorinated to a chloromethyl group content of 26% in dichloromethane using 6% w/v NaOCl at a pH of 8.4 for 15 min, were assigned as follows: $\delta = 21$ ppm, 4-methyl carbon atoms; $\delta = 40.4$ ppm, main-chain methine carbon atoms; $\delta \approx 45$ ppm main-chain methylene carbon atoms; $\delta = 46.1$ ppm, 4-chloromethyl carbon atoms. These chemical shifts are reproduced in *Table 1* together with the corresponding data for the other isomeric polymethylstyrenes chlorinated under the same conditions. Resonances associated with *ortho*-methyl substituents in those polymers that contain them display fine structure. Resonances at 51–56 and 68–76 ppm previously attributed[3,6] to backbone –CHCl–, –C(Ar)Cl– and –CCl$_2$– groups were not observed in the spectra of any of the chlorinated polymers. It is evident that whereas *meta*- and *para*-methyl substituents are readily chlorinated, *ortho*-methyl substituents are difficult to chlorinate. In particular, the chlorination of poly2MS was barely detectable using ^{13}C n.m.r. and although it is likely that the proximity of the polymer main chain and *ortho*-methyl substituents is responsible for each hindering the other's chlorination, it appears that p.t.c. chlorination is significantly more selective of the site of substitution than had previously been realized.

With the exception of poly2MS (for the reasons indicated above), *Figures 1–4* represent variations in the degree of chlorination and molecular weight parameters of the various polymers (of initial polydispersity 1.5 to 1.7) as the composition of the organic phase is varied whilst holding the pH and the concentration of NaOCl in the aqueous phase constant at 8.4 and 11% w/v respectively. For an understanding of the effects of varying pH, the NaOCl concentration, the concentration of benzyltriethylammonium chloride or the duration of reaction, the reader is referred to an earlier paper[1].

Figure 1 shows that a greater extent of chlorination can be achieved using dichloromethane-rich mixtures rather than chloroform-rich mixtures but that at all compositions of the organic phase, *para*-methyl substituents are more susceptible to chlorination than corresponding *meta*-methyl substituents, the presence or absence of an *ortho*-methyl substituent being apparently inconsequential. On the other hand, *Figure 2* shows the polydispersities of poly3MS, poly2,4DMS and poly2,5DMS to be more markedly broadened during the chlorination than that of poly4MS, particularly in dichloromethane-rich mixtures. *Figures 3* and *4* represent the variations in M_w and M_n taken separately over the range of compositions of the organic phase. In chloroform-rich mixtures, it is evident that the broadening of the molecular weight distributions arises from increases in M_w rather than from decreases in M_n and is attributable to crosslinking. With the exception of the poly3MS system, this effect dominates up to a CH$_2$Cl$_2$: CHCl$_3$ ratio of about 3:1, beyond which both M_w and

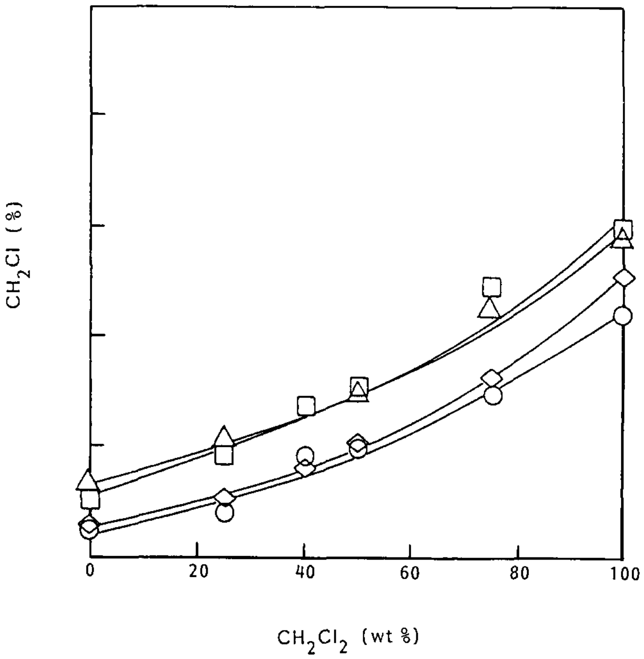

Figure 1 Variation of the extent of p.t.c. chlorination of polymethylstyrenes with solvent composition: (○) poly3MS; (□) poly4MS; (◇) poly2,5DMS; (△) poly2,4DMS

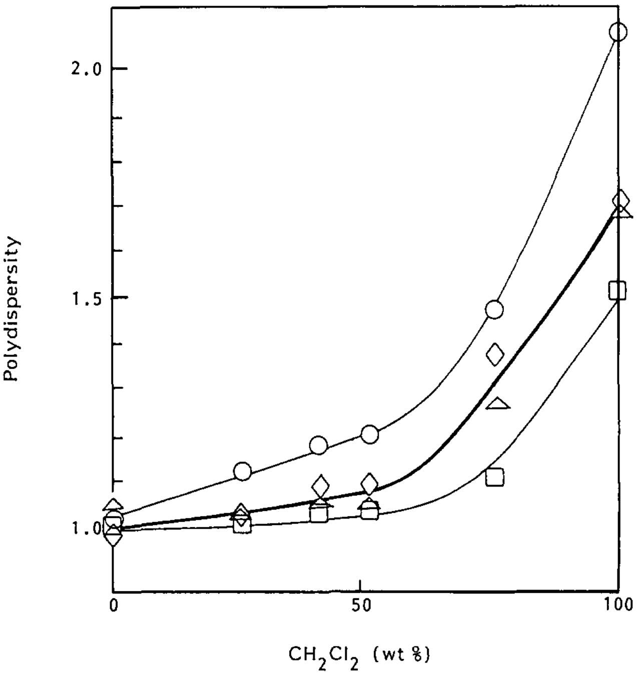

Figure 2 Variation of polydispersites (normalized to the initial values) of polymethylstyrenes with solvent composition: (○) poly3MS; (□) poly4MS; (◇) poly2,5DMS; (△) poly2,4DMS. The heavy line represents essentially coincident plots for the DMS systems

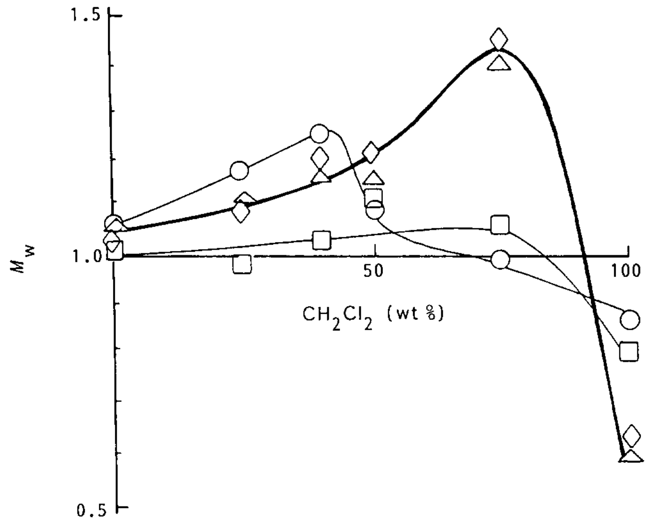

Figure 3 Variation of the weight average molecular weights (normalized to the initial values) of polymethylstyrenes with solvent composition: (○) poly3MS; (□) poly4MS; (◇) poly2,5DMS; (△) poly2,4DMS. The heavy line represents essentially coincident plots for the DMS systems

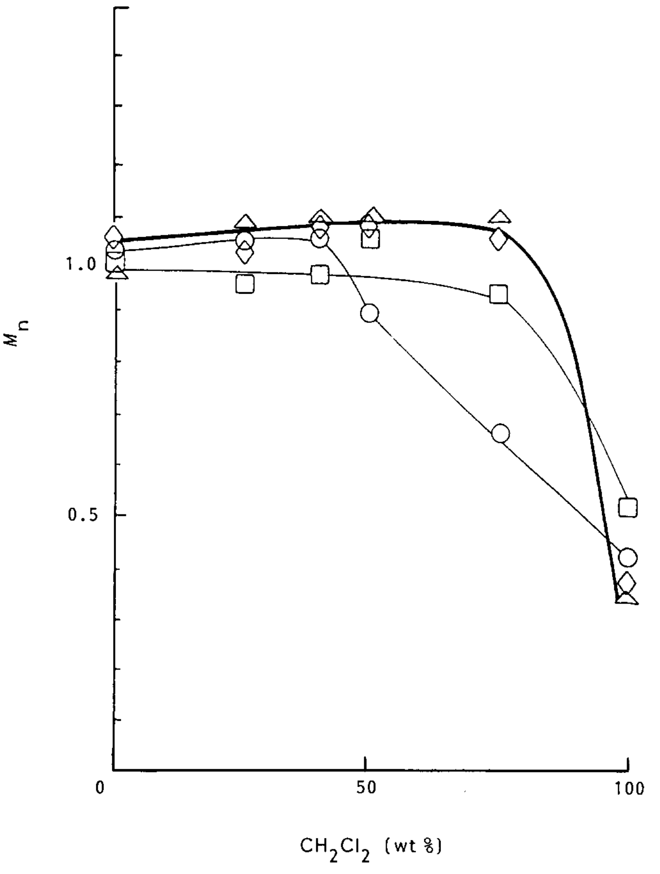

Figure 4 Variation of the number average molecular weights (normalized to the initial values) of polymethylstyrenes with solvent composition: (○) poly3MS; (□) poly4MS; (◇) poly2,5DMS; (△) poly2,4DMS. The heavy line represents essentially coincident plots for the DMS systems

$\bar{M}_n$ fall drastically. Such broader distributions about lower average molecular weights arise from chain scission dominating over crosslinking and the onset of this phenomenon evidently occurs in an organic phase of significantly lower dichloromethane content for the poly3MS system, whilst being the most pronounced for the polyDMS systems. In all the systems in which chain scission effects were evident, so also was discolouration. The product polymers were yellow. This has previously been attributed to the occurrence of main-chain unsaturation conjugated to carbonyl groups arising from the oxidation of the new chain ends that ensue from chain scission.

The overall reaction mechanism, previously represented and discussed[1] solely in relation to the chlorination of poly4MS, is shown in *Scheme 1*. R_M, R_C and R_E represent radicals situated at what was formerly a methyl substituent, on a chain (at either α- or β-carbon atoms) and at a chain end respectively, and P represents polymer molecules (more particularly, it represents sites on polymer molecules that are available for hydrogen atom abstraction). The various possible radical combination, disproportionation and chlorination reactions are represented as involving all the polymer radical species ($R = R_M + R_C + R_E$).

Based on the assumption that different experimental conditions determine different concentrations of Cl_2O in the organic phase, it was shown that in accordance with this mechanism, the rates of chlorination, crosslinking, chain scission and discolouration would all increase with increasing dichloromethane content of this phase. It was further shown that in an organic phase that was high in dichloromethane, chain scission would increasingly dominate over crosslinking.

Since the same trends are evident for the chlorination of all the other polymethylstyrenes as for that of poly4MS, the present results relate more to the extent of reaction in the various systems than to its mechanism. Comparing the poly3MS and poly4MS systems, by virtue of the inductive effect exerted by the remaining ring *para*-alkyl substituent, the benzylic radicals R_M and R_C derived from the latter would be more stable than the corresponding radicals derived from the former. As a consequence, both the unimolecular (reaction 7) and bimolecular (reactions 10 and 11) reactivities of these radicals in the poly3MS system would be higher than in the poly4MS system. This accords with the observed variations of molecular weight with solvent composition; the poly3MS system displaying both a greater tendency to crosslink at all compositions of the organic phase, and the onset of chain scission which ultimately swamps crosslinking appearing at a much lower dichloromethane

$$\mathrm{HOCl + ClO^- \rightarrow Cl_2O + OH^-} \qquad (1)$$

$$\mathrm{Cl_2O \rightarrow Cl^\bullet + ClO^\bullet} \qquad (2)$$

$$\mathrm{Cl^\bullet + ClO^- \rightarrow Cl^- + ClO^\bullet} \qquad (3)$$

$$\mathrm{ClO^\bullet + P \rightarrow R_M + HOCl} \qquad (4)$$

$$\mathrm{ClO^\bullet + P \rightarrow R_C + HOCl} \qquad (5)$$

$$\mathrm{R_C + P \rightarrow R_M + P} \qquad (6)$$

$$\mathrm{R_C \rightarrow R_E + P} \qquad \text{scission} \qquad (7)$$

$$\mathrm{R_E + P \rightarrow R_M + P} \qquad (8)$$

$$\mathrm{R_E + P \rightarrow R_C + P} \qquad (9)$$

$$\mathrm{R + R \rightarrow P} \qquad \text{crosslinking} \qquad (10)$$

$$\mathrm{R + R \rightarrow P + P'} \qquad \text{discolouration} \qquad (11)$$

$$\mathrm{R + Cl_2O \rightarrow PCl + ClO^\bullet} \qquad \text{chlorination} \qquad (12)$$

Scheme 1

content. There would be a lesser steady-state radical concentration in the poly3MS system, so even accepting the possibility that radicals R_M in the two systems are of equal reactivity in the radical–molecule reaction 12, it would be expected that, as observed, a lesser degree of chlorination would result in this system.

The molecular weight variations in the poly2,4DMS and poly2,5DMS systems are remarkably similar and appear to fall somewhere between those of the poly3MS and poly4MS systems. The similarity might well arise from them both being 1,2,4-trialkyl benzenes. It has long been recognized[7] that any steric hindrance to the near planarity of a benzyl radical will result in decreased reactivity in the abstraction process that leads to its formation. The proximity of the polymer chain and the *ortho*-methyl substituent at the 1 and 2 positions in these systems is mutually hindering, so the formation of benzylic radicals at either centre will be significantly inhibited. The other methyl substituent is not hindered, so in all likelihood the radicals in these systems are predominantly of the R_M type and reactions involving radicals R_C will be suppressed. This view is supported by the observation[8] that all coupling reactions of benzyl radicals derived from *o*-cymene (isopropyltoluene) are suppressed in comparison with the corresponding reactions of radicals derived from *p*-cymene. This at least explains why chlorination in the polyDMS systems is site-selective and why molecular weight variations arising from crosslinking persist up to organic phase compositions as high as 75% in dichloromethane. However, it is difficult to rationalize through such considerations why chain scission has ultimately such a pronounced effect on the molecular weights.

A lesser degree of chlorination is observed for the systems that contain a *meta*-methyl substituent than for those that contain a *para*-methyl substituent. Although this was argued above for the poly3MS and poly4MS systems solely in terms of the steady-state concentration of radicals R_M, this is an insufficient rationale for the behaviours of the polyDMS systems, which are identical in all other ways. It would thus seem likely that the transition state in the radical–molecule reaction 12 is of higher energy for the *meta*- than for the *para*-methyl substituted systems and that the rate of chlorination of a *meta*-methyl group is accordingly reduced.

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