

Phase-transfer-catalysed chlorination of poly(4-methylstyrene) by hypochlorite

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The effects of variation of the conditions of phase-transfer-catalysed chlorination of poly(4-methylstyrene) using sodium hypochlorite in chloroform/dichloromethane mixtures are investigated. When the reaction is carried out at an aqueous phase pH of 8.5 and using a chloroform-rich organic phase, chlorination is predominantly at the 4-methyl substituent and di-/trichlorination and concomitant modification of the molecular-weight distribution of the polymer are minimal. Kinetic mechanisms compatible with the experimental observations are proposed.

(Keywords: poly(4-methylstyrene); chlorination; polychloromethylstyrene; phase-transfer-catalysis)

INTRODUCTION

Materials that are essentially chlorinated polymethylstyrenes (CPMS) have attracted interest in recent years for their application as negative-working electron beam resists in microlithography. As a group, they are polymers with moderate to high electron beam sensitivities, with the potential for the achievement of submicrometre resolution. To achieve both optimum and reproducible lithographic performance from such materials, however, requires an ability to control readily the structure of the polymers: the molecular weight, the molecular weight distribution and the positional specificity of the chloro and methyl substituents. With this end in mind a number of preparative methods and their limitations have been investigated by various groups:

(i) The Lewis-acid-catalysed chloromethylation of polystyrene^{1,2}, which employs the carcinogenic intermediate chloromethyl methyl ether.

(ii) The copolymerization of a methylstyrene with vinylbenzyl chloride³⁻⁵ (a 60:40 mixture of the *m*- and *p*-isomers), which though offering a degree of substituent positional specificity, confines the molecular weights of the polymers, and their distributions, to those attainable using free-radical initiation.

(iii) The homogeneous solution-phase free-radical-initiated partial chlorination of poly(4-methylstyrene), which though offering the potential for the ready preparation of monodisperse polymers through the preliminary anionic polymerization of the parent monomer, results in main-chain chlorination and di- and tri- as well as monochlorination of the methyl groups^{6,7}. Furthermore, the method of chlorination appears to determine whether the reaction is accompanied by either chain cleavage or crosslinking of the polymer.

Based on earlier work by Hamilton *et al.*⁸ on the chlorination of toluene, Mohanraj and Ford⁹ have recently reported the selective chlorination of the methyl group of poly(4-methylstyrene) in chlorinated aliphatic

hydrocarbons at ambient temperatures using aqueous sodium hypochlorite and a phase-transfer catalyst (PTC) such as benzyltriethylammonium chloride. The method is additionally attractive for being clean and safe. With one exception, however, the series of polymers that they studied were already lightly crosslinked so there was no attempt made to determine any secondary effect that the reaction might have on the molecular weight or polydispersity of the precursor polymer. This paper addresses that question.

EXPERIMENTAL

Materials

4-Methylstyrene (Aldrich) was 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) and AR toluene were further dried by refluxing over sodium metal. The sodium hypochlorite solution used was aqueous commercial bleach (11% determined by iodometric titration).

Benzyltriethylammonium chloride (Aldrich), azobisisobutyronitrile (AIBN, Fluka AG), sulphuryl chloride (Aldrich) and all other materials were used without further purification.

Apparatus and procedures

Anionic polymerizations were carried out in THF solution at methanol/dry-ice temperature under an argon atmosphere in flasks sealed with serum caps, the monomers and the solvent having previously been separately deaerated by flushing with argon. Two-stage initiations were accomplished by injecting measured amounts of butyllithium solution from a dry, argon-flushed syringe. Product polymers were isolated by dropwise precipitation in an excess of methanol and subsequently purified by standard procedures.

A typical PTC chlorination was carried out as follows.

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First, 0.35 g of the polymer was dissolved in 15 ml of a chloroform/dichloromethane mixture and added to 80 ml of sodium hypochlorite solution, the pH of which had been adjusted to a value within the range 8.0 to 8.5 with concentrated hydrochloric acid. Benzyltriethylammonium chloride (300 mg) was added and the mixture was stirred vigorously for up to 1 h under an argon atmosphere. The organic layer was separated and twice washed with distilled water before adding dropwise to methanol to recover the chlorinated polymer. The polymer was further purified by repeated precipitation before drying under vacuum. Typically, 80% of the original mass of the polymer would be recovered. For the purposes of comparison, the homogeneous chlorination of poly(4-methylstyrene) was carried out in benzene solution using sulphuryl chloride and AIBN under conditions similar to those reported by previous workers^{6,7}.

¹³C and ¹H n.m.r. spectra were obtained on a JEOL JNM-GX270 spectrometer operating at 67.8 MHz, and a JEOL JNM PMX-60 spectrometer operating at 60 MHz, respectively. Chemical shifts were measured relative to tetramethylsilane (TMS). ¹³C peak area measurements were achieved using inverse gated decoupling with a 10 s pulse delay. Infra-red spectra were obtained using a Perkin-Elmer 683 spectrometer.

Molecular weights and polydispersities were determined as polystyrene equivalents using a gel permeation chromatograph supplied by Polymer Laboratories on a 5 μm PL gel column bank of 10⁴ and 500 Å.

RESULTS AND DISCUSSION

The conditions of PTC chlorination of poly(4-methylstyrene) (poly4MS) were varied so as to yield product polymers with up to 40% of the monomer units chlorinated.

Figure 1 shows the ¹H n.m.r. spectrum of such a polymer. During reaction, the intensity of the peak assigned to -CH₂Cl groups (δ = 4.4 ppm) grew at the expense of that assigned to methyl groups (δ = 1.6 ppm). A weak and broad peak a little upfield from 4.4 ppm, which was reported by Tarascon *et al.*⁷ to be associated with chlorination of the main chain, was not detected. Figure 2a depicts a typical ¹³C n.m.r. spectrum of a PTC chlorinated poly(4-methylstyrene) from which the same conclusion can be reached by comparison with a corresponding spectrum (Figure 2b) for SO₂Cl₂/AIBN chlorinated polymer. While both spectra display strong resonances at 46.1 ppm, attributable to -CH₂Cl groups,

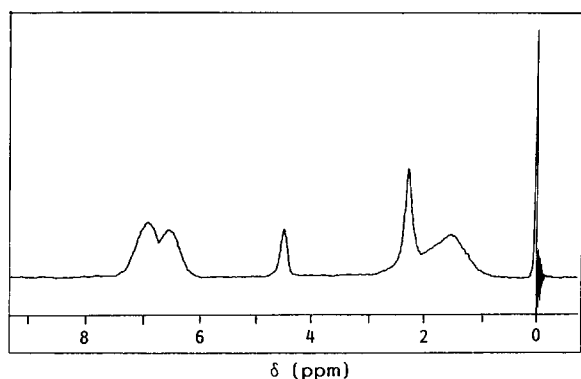


Figure 1 The proton n.m.r. spectrum of poly4MS PTC chlorinated in dichloromethane for 30 min: [NaOCl], 11% w/v; pH 8.4

even allowing for the greater extent of chlorination, the latter spectrum displays a relatively much weaker peak at 40.4 ppm assigned to the main-chain methine carbon atoms, and the broad band at about 45 ppm associated with main-chain methylene groups is barely evident. However, peaks at 51–56 and 68–76 ppm previously attributed^{7,9} to backbone -CHCl-, -C(Ar)Cl- and -CCl₂- groups are evident. The sharp resonance at 72 ppm attributable to carbon atoms of -CHCl₂ groups is barely discernible for the PTC chlorinated product but becomes evident if the reaction is carried out at a slightly lower pH (Figure 2c). These results accord with the conclusion of Mohanraj and Ford⁹ that PTC chlorination is significantly more selective of the site of substitution than homogeneous chlorination by SO₂Cl₂/AIBN.

Figures 3–11 all represent variations in the degree of chlorination and/or the molecular-weight parameters of poly(4-methylstyrene) as a range of conditions of the PTC reaction are varied. In each case, the invariant conditions of reaction are specified in the legends.

Figure 3 demonstrates that the extent of chlorination tends to a limiting value as the concentration of the phase-transfer catalyst is increased. It also shows that, although this limiting conversion is attained at a lower concentration if the organic phase is a mixture of chloroform and dichloromethane and the reaction time is prolonged, the reaction is ultimately the more rapid if 100% dichloromethane is the organic phase (see also Figure 4), even when a lower concentration of sodium hypochlorite is employed. Consistent with the observations of Hamilton *et al.*⁸, it is thus evident that the catalyst plays an important role in promoting the extraction of the chlorinating species from the aqueous phase to the organic phase.

From Figure 5 it is evident that, although the extent of chlorination increases markedly with the concentration of sodium hypochlorite in the aqueous phase, at concentrations beyond 7%, the molecular-weight distribution of the polymer is significantly broadened. Figure 6 shows that this effect arises from an increase in *M_w* rather than a decrease in *M_n* and can thus be attributed to crosslinking.

Hamilton *et al.*⁸ having recommended a value within the range 7.5 to 9, Mohanraj and Ford⁹ worked at an aqueous phase pH of about 8.5. In the present work, this value was found to be optimum within a working range of pH, for as depicted in Figure 7, although the extent of chlorination increases significantly with decreasing pH, the molecular-weight distributions of the product polymers are correspondingly broader. Figure 8 shows that, while *M_w* alone is increased slightly as the pH is reduced to about 8.25, both *M_w* and *M_n* are reduced if the aqueous medium is made more acidic. Accompanying this last effect is the appearance of the ¹³C n.m.r. peak at 72 ppm attributed to the -CHCl₂ group. Hamilton *et al.*⁸ have asserted the ClO· radical and Cl₂O to be the active reagents in the hypochlorite-PTC system and have explained their more ready formation at the lower values of pH. The instantaneous steady-state concentration of these species within the organic phase will be higher and it would follow that the extent of chlorination would be the greater. The molecular-weight variations imply that, concomitantly, polymer chain scission reactions then overwhelm the crosslinking reactions. Similar effects arise from variation of the composition of the organic phase and are represented in Figures 9 and 10.

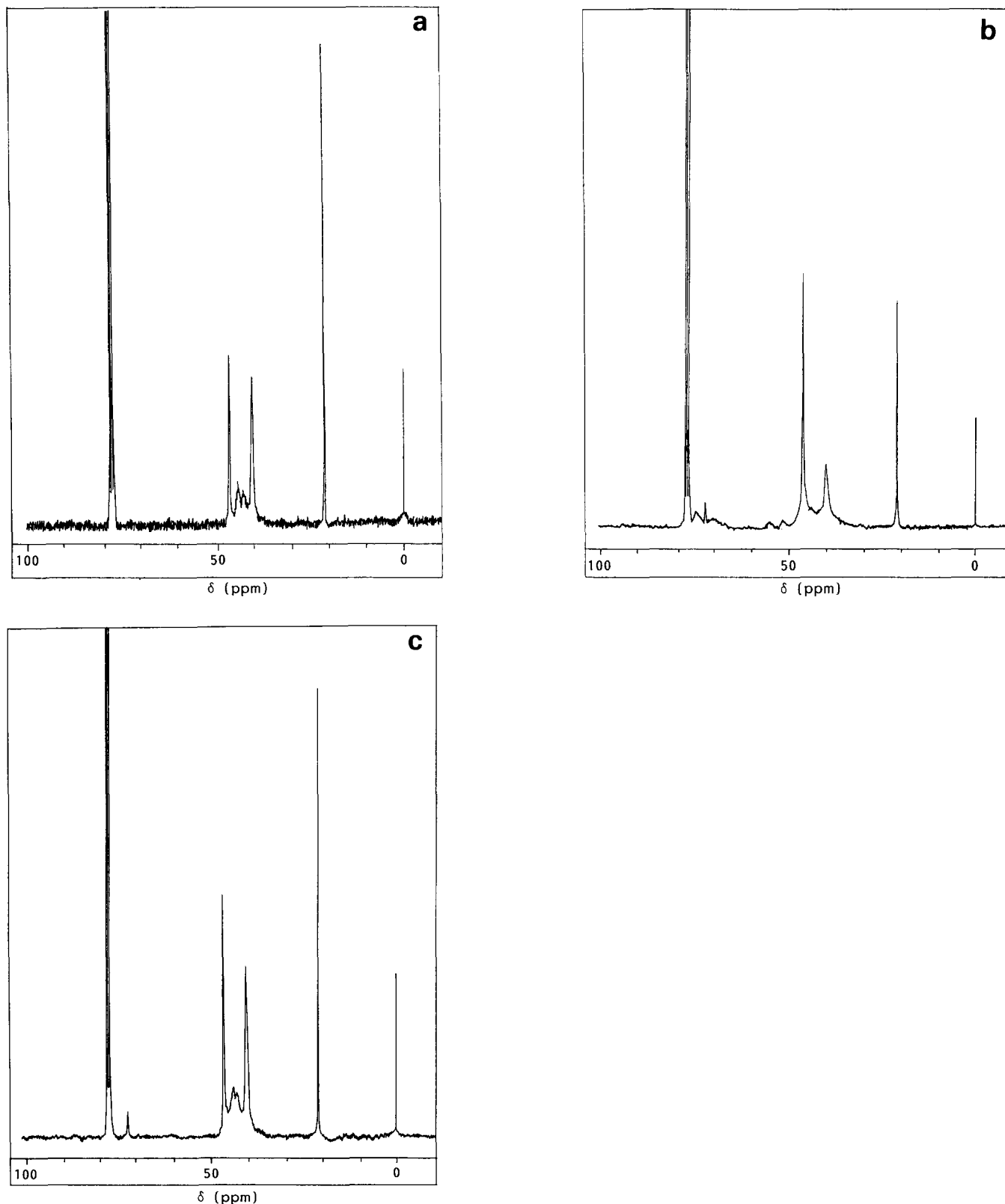


Figure 2 ^{13}C n.m.r. spectra of poly4MS. (a) PTC chlorinated in dichloromethane for 15 min: $[\text{NaOCl}]$, 6% w/v; pH 8.4. (b) Chlorinated using $\text{SO}_2\text{Cl}_2/\text{AIBN}$ in benzene. (c) PTC chlorinated in 1:1 dichloromethane/chloroform for 30 min: $[\text{NaOCl}]$, 11% w/v; pH 8.05

A greater extent of chlorination can be achieved using dichloromethane-rich mixtures rather than chloroform-rich mixtures, but at $\text{CH}_2\text{Cl}_2:\text{CHCl}_3$ ratios greater than 1:1 chain scission is again seen to dominate crosslinking, leading to a broader distribution about lower average molecular weights.

For those systems in which chain scission effects are

evident, discoloration was pronounced. The product polymers were yellow. No features to which this could be linked were apparent in the n.m.r. spectra but in the i.r. spectra (*Table 1*), in addition to the expected assignments associated with monochlorination of the substituent methyl groups, broad bands appeared at 3420 and 1740 cm^{-1} , and shoulders at 840 and 750 cm^{-1}

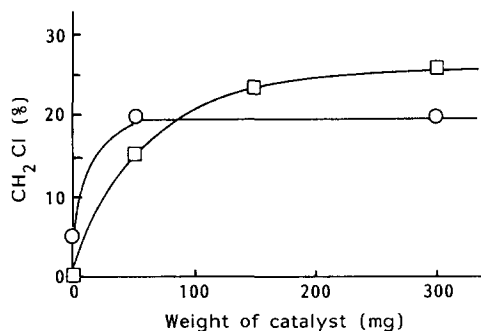


Figure 3 Variation of the extent of PTC chlorination of poly4MS with catalyst concentration: (□) [NaOCl], 6% w/v; pH 8.4; in dichloromethane for 15 min; (○) [NaOCl], 11% w/v; pH 8.4; in 1:1 dichloromethane/chloroform for 60 min

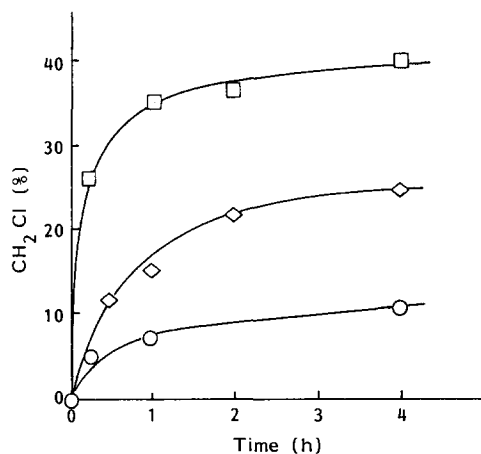


Figure 4 Variation of the extent of PTC chlorination of poly4MS with time at pH 8.4: (□) [NaOCl], 6% w/v; in dichloromethane; (◇) [NaOCl], 11% w/v; in 1:1 dichloromethane/chloroform; (○) [NaOCl], 6% w/v; in 1:2 dichloromethane/chloroform

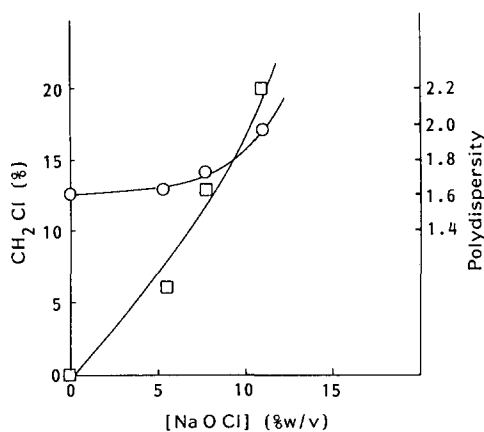


Figure 5 Variations of the extent of PTC chlorination (□) and the molecular-weight distribution (○) of poly4MS with NaOCl concentration: pH 8.4; in 1:1 dichloromethane/chloroform for 60 min

appeared on the peaks assigned to the aromatic out-of-plane bending modes. Tarascon *et al.* attributed the feature at 750 cm^{-1} to dichlorination of main-chain β -carbon atoms and that at 840 cm^{-1} is characteristic of olefins of the type $\text{RCH}=\text{CR}_2$ (ref. 10) and so can be associated with the occurrence of main-chain unsaturation, which if conjugated, would explain the discoloration. The two broad bands can reasonably be assigned to oxidized end-groups ensuing from chain scissions, typically hydroxy and carbonyl groups.

It can be concluded that, accompanying the chlorination, some broadening of the molecular-weight distribution arising from limited crosslinking (no gel formation was observed) is inevitable, even at the optimum pH of 8.5 and using a chloroform-rich mixture for the organic phase, under which conditions multiple chlorination of the methyl substituent is minimal. Figure 11 when compared with the corresponding plot of Figure 4 shows

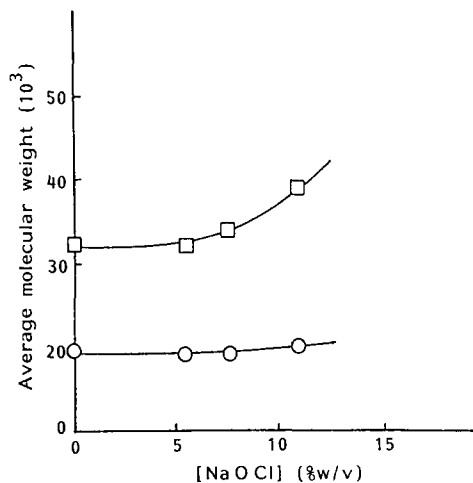


Figure 6 Variations of the number-average (○) and weight-average (□) molecular weights of the polymer with NaOCl concentration during PTC chlorination of poly4MS: conditions as for Figure 5

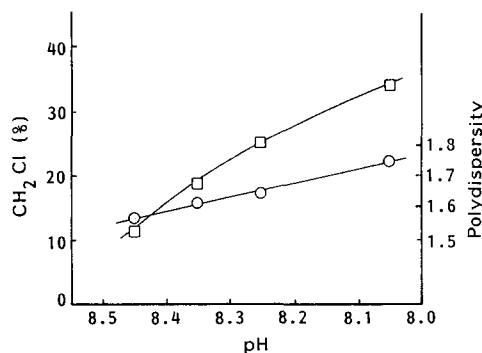


Figure 7 Variations of the extent of PTC chlorination (□) and the molecular-weight distribution (○) of poly4MS with pH: [NaOCl], 11% w/v; in 1:1 dichloromethane/chloroform for 30 min

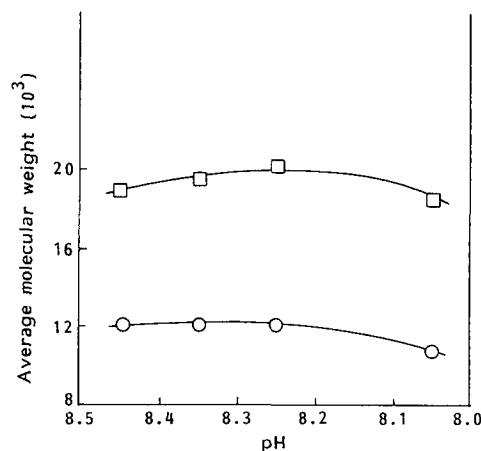


Figure 8 Variations of the number-average (○) and weight-average (□) molecular weights of the polymer with pH during PTC chlorination of poly4MS: conditions as for Figure 7

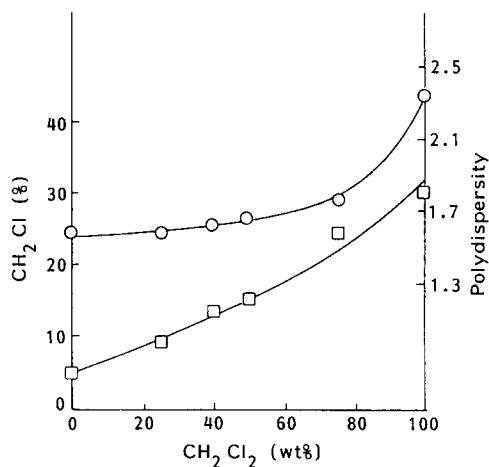


Figure 9 Variations of the extent of PTC chlorination (□) and the molecular-weight distribution (○) of poly4MS with solvent composition: [NaOCl], 11% w/v; pH 8.4; 30 min

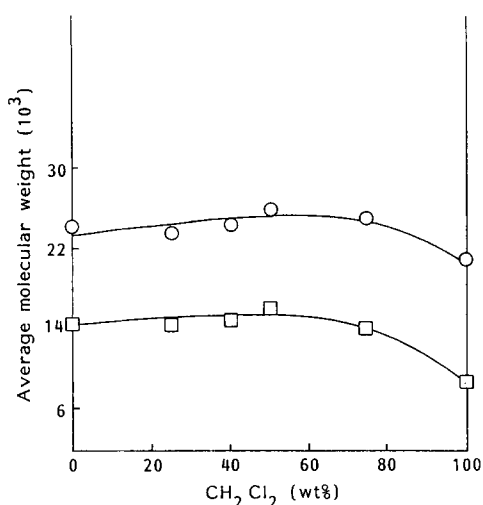


Figure 10 Variations of the number-average (□) and weight-average (○) molecular weights of the polymer with solvent composition during PTC chlorination of poly4MS: conditions as for Figure 9

Table 1 Results of i.r. spectroscopy

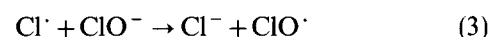
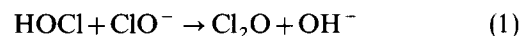
Frequency (cm ⁻¹)	Assignment
680	C-Cl stretching
725	Aromatic C-H out-of-plane bending
750 ^a	-CCl ₂ -
815	Aromatic C-H out-of-plane bending
840 ^a	CHR=CR'R''
1000-1250	Aromatic in-plane bending
1265 ^a	-CH ₂ Cl wagging
1400-1500	Skeletal bands of aromatic ring
1510	Aromatic C-C stretching
1580-1620	Skeletal bands of aromatic ring
1650-1800 ^a	C=O stretching
1800-2000	Aromatic overtone
2800-3000	Alkane stretching
3000-3100	Aromatic stretching
3200-3700 ^a	OH stretching

^a New bands evident following PTC chlorination in dichloromethane-rich mixtures

that the broadening effect progresses to a limit over the same time period as the chlorination reaction and that in all likelihood they are parallel reactions. At lower values of pH or when dichloromethane-rich mixtures are

used for the organic phase, polymer scission reactions compete with, and ultimately overwhelm, the crosslinking reaction.

Reactions (1)–(5) depict the PTC chlorination mechanism proposed by Hamilton *et al.*⁸ as it would apply to the chlorination of toluene (Scheme 1). It is noted that the equilibrium reactions (1)–(3) only proceed rapidly in the forward direction when the pH of the aqueous solution is ~8 to 9, conditions under which significant amounts of HOCl are present to allow Cl₂O to form.



Scheme 1

Absent from such a scheme are representations of the transfers of the reactive species from the aqueous phase to the organic phase, which must occur in order that reactions (4) and (5) can ensue. The transfer is of particular importance in the present study for it is likely that this is the controlling variable as the composition of the organic phase is changed. It is stated, however, that the organic phase must have a good supply not only of Cl₂O but also of ClO⁻, in order to regenerate ClO[·] by reaction (3). A PTC would increase the concentration of ClO⁻ in the organic phase. In doing so it would also be expected to increase the concentration of Cl₂O through reaction (1). It is further noted that it is well established¹¹ that quaternary ammonium ions frequently extract an adduct of an acid and its conjugate base into the organic phase. In this case such an adduct would contain HOCl and ClO⁻; these are the reactants of equation (1). The PTC would further facilitate this reaction by stabilizing the OH⁻ ion at the interface. It is thus reasonable to assume that the maintained conditions of the aqueous phase assure essentially steady concentrations of Cl₂O and ClO⁻ in the organic phase throughout the course of reaction. These concentrations will vary in accordance with the aqueous phase conditions and particularly with the composition of the organic

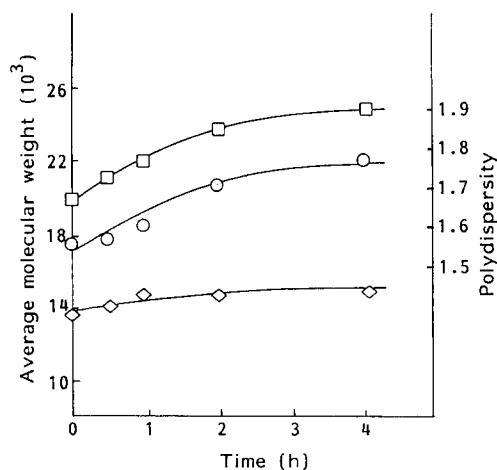
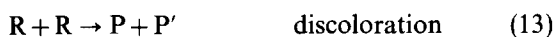


Figure 11 Variation of the number-average (◇) and weight-average (□) molecular weights and the polydispersity (○) with time during PTC chlorination of poly4MS: [NaOCl], 11% w/v; pH 8.4; in 1:2 dichloromethane/chloroform

solvent. The higher dielectric constant of dichloromethane would make it more receptive of the ionic species than chloroform.

Hydrogen-atom abstraction from poly(4-methylstyrene), though analogous to that from toluene as represented in equation (4), occurs at three distinct sites: the substituent methyl group and the main-chain α - and β -carbon atoms. Chlorination would follow from reaction of derived radicals with Cl_2O in accordance with reaction (5). Any of the possible radical-radical combination reactions would lead to crosslinking of the polymer molecules¹², while disproportionation of either of the chain-centred α - and β -radicals with another radical would build the unsaturation required to explain the discoloration. Chain scissions would be first-order reactions of the chain α - and β -radicals.

Reactions (1)–(3) and those of Scheme 2, which is an adaptation of that proposed for the thermal crosslinking and scission of styrene/4-methylstyrene copolymers by Schröder¹³, adequately represent the totality of reactions in the organic phase. R_M , R_C and R_E represent radicals situated at a methyl substituent, on a chain (at either α - or β -carbon atoms) and at a chain end respectively. P represents a polymer molecule. The notation thus far accords with that of Schröder. The various possible radical combination, disproportionation and chlorination reactions are represented as involving all the polymer radical species ($R = R_M + R_C + R_E$). This assumes that the distinct radicals have equal reactivities in these reactions but it does not invalidate the conclusion drawn from the subsequent kinetic analysis and is done solely to simplify the mechanism and thus minimize algebraic complexity. Since chlorination under optimum conditions was observed to be site-selective at the substituent methyl group, a reasonable alternative to this assumption is to identify R solely with R_M . It is then necessary to discount reaction (13). The analysis is further simplified, but otherwise similar results ensue.



Scheme 2

The concentration of reactive sites on the polymer molecules is determined by the total number of monomer repeat units, so the notation [P] will be used to represent this concentration; this is effectively constant throughout the reaction, whereas the concentration of polymer molecules varies with the number-average degree of polymerization.

Assuming instantaneous stationary-state conditions for all radicals it is readily shown that:

$$(k_{12} + k_{13})[\text{R}]^2 = 2k_2[\text{Cl}_2\text{O}] \quad (15)$$

and

$$(k_6 + k_7)[\text{ClO}^\cdot][\text{P}] = 2k_2[\text{Cl}_2\text{O}] + k_{14}[2k_2/(k_{12} + k_{13})]^{1/2}[\text{Cl}_2\text{O}]^{3/2} \quad (16)$$

It follows that the rates of chlorination (R_{ch}), crosslinking (R_x), chain scission (R_s) and discoloration (R_d) are given by:

$$R_{ch} = k_{14}K_1^{1/2}[\text{Cl}_2\text{O}]^{3/2} \quad (17)$$

$$R_x = k_{12}K_1[\text{Cl}_2\text{O}] \quad (18)$$

$$R_s = K_2(2k_2[\text{Cl}_2\text{O}] + k_{14}K_1^{1/2}[\text{Cl}_2\text{O}]^{3/2}) \quad (19)$$

$$R_d = k_{13}K_1[\text{Cl}_2\text{O}] \quad (20)$$

where

$$K_1 = 2k_2/(k_{12} + k_{13})$$

and

$$K_2 = \frac{k_7k_9(k_{10} + k_{11})[\text{P}]}{(k_6 + k_7)\{k_8(k_{10} + k_{11})[\text{P}]^2 + k_9(k_{10} + k_{11})[\text{P}] - k_9k_{11}\}}$$

Accepting that different experimental conditions determine different concentrations of Cl_2O in the organic phase, the trends represented by the above equations are consistent with those observed. From the earlier arguments, the concentration of Cl_2O would be expected to increase with the increasing hypochlorite concentration, decreasing pH (within the working range) and increasing dichloromethane content in the organic phase. As the reaction conditions are changed in these ways, in accordance with equations (17), (18) and (20) the rates of chlorination, crosslinking and discoloration increase, with chlorination doing so more pronouncedly. Equation (19) taken in ratio to equation (18) gives the form shown below:

$$R_s/R_x = K + K'[\text{Cl}_2\text{O}]^{1/2} \quad (21)$$

Although equation (21) represents chain scission and crosslinking as being in limiting ratio at zero concentration, consistent with observation, scission increasingly dominates as the Cl_2O concentration increases.

CONCLUSIONS

Overall, it is concluded that PTC chlorination is a more controllable route to partially chlorinated poly(4-methylstyrene) than homogeneous solution-phase chlorination. If the reaction is carried out at lower rates, then the chlorination occurs predominantly at the substituent methyl group and di/trichlorination and concomitant polymer degradation reactions are minimized.

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