Copoly(*m,p*-chloromethylstyrene-50% styrene): Copolymer molecular weights, fractionation and derivatization

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Copolymerization of an equimolar mixture of *m,p*-chloromethylstyrene ($\underline{M}_1$) and styrene ($\underline{M}_2$) was carried out in chlorobenzene in the presence of AIBN at 80°C. Molecular weight analysis (by g.p.c.) of the resulting polymer samples was performed at various conversions. $\bar{M}_w$, $\bar{M}_n$, and $(\bar{M}_w/\bar{M}_n)$ values of 21 300, 13 800 and 1.54 were obtained at 8.9% conversion. At higher conversions, the value of $\bar{M}_w$ remained effectively constant while $\bar{M}_n$ decreased to 9200 at *ca.* 80% conversion, and then increased to 12 000 at about 100% conversion (16 h), and to 13 700 if the polymer solutions were maintained at 80°C for an additional 44 h. These results suggest that, although the termination step initially involves the combination of polymer radicals, at high conversions a large number of very low molecular weight, and unsaturated, polymer molecules are formed possibly by disproportionation involving polymer radicals and primary radicals. The unsaturated polymer molecules are subsequently polymerized by growing polymer radicals towards the end of the polymerization. It was noticed that further reaction occurred after complete depletion of monomer, involving radical attack on the unsaturated polymer molecules. Other reactions including chain transfer to polymer will also be important at high polymer concentrations. A copolymer of $\underline{M}_1$ and $\underline{M}_2$ was separated into four fractions on a preparative scale, and molecular weight analysis of the resulting polymer samples provided more evidence of the above interpretation. G.p.c. analysis of several derivatives of a copolymer of $\underline{M}_1$ and $\underline{M}_2$ showed that most molecular weights were much lower than that of the starting polymer. These results in some cases may reflect the chemical or dimensional changes introduced into the polymer molecules during derivatization.

(Keywords: copoly(*m,p*-chloromethylstyrene); styrene; copolymers; fractionation; derivatization; copolymerization; copoly(chloromethylstyrene–styrene))

INTRODUCTION

In a recent paper[1] we described the synthesis of an equimolar copolymer of *m,p*-chloromethylstyrene ($\underline{M}_1$) and styrene ($\underline{M}_2$), and its derivatization to obtain potentially electroreactive polymers suitable for the preparation of modified electrodes[2]. The synthetic study was particularly aimed at producing relatively low molecular weight polymers obtained at virtually complete conversion, (*ca.* 100%). From the published[3,4] values of the reactivity ratios of $\underline{M}_1$ and $\underline{M}_2$, it was expected that the copolymer composition would change slightly during the course of the polymerization. It is also generally known that the molecular weight distribution in free radical polymerizations may become increasingly complicated at high conversions, depending on the exact details of the polymerization mechanism[5–8]. We were, therefore, interested in establishing a quantitative picture of the variation of polymer composition, and polymer molecular weights, during the course of the equimolar copolymerization of $\underline{M}_1$ and $\underline{M}_2$ to 100% conversion. Furthermore, it was previously noted[1] that the preparation of a given polymer derivative may be accompanied by changes in the molecular weight of the polymer, as a result of side reactions (e.g., crosslinking) during the chemical modification, and/or polymer fractionation during the precipitation of the derivatized polymer. This report describes the results of our studies on (i) microanalysis and gel permeation chromatography (g.p.c.) of polymer samples obtained by copolymerization of an equimolar mixture of $\underline{M}_1$ and $\underline{M}_2$ at various conversions, (ii) microanalysis and g.p.c. of four polymer samples obtained by preparative fractionation of an approximately equimolar copolymer of $\underline{M}_1$ and $\underline{M}_2$ prepared at 100% conversion, and (iii) an attempted g.p.c. analysis of a number of derivatives of the last named copolymer of $\underline{M}_1$ and $\underline{M}_2$.

EXPERIMENTAL

Materials

m,p-Chloromethylstyrene (Fluka), styrene, solvents, initiator (azo-bis-isobutyronitrile, AIBN), as well as the copoly(*m,p*-chloromethylstyrene-styrene) (**2a**), and the polymer derivatives **2b**–**2f**, were those described previously[1].

Polymer characterization

Elemental analyses were carried out at the Microanalytical Laboratory in this Department. Gel permeation chromatography (g.p.c.) of the polymers was performed at the Polymer Supply and Characterization Centre, Rubber and Plastic Research Association, England. Tetrahydrofuran solvent stabilized with 2,6-di-t-

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butyl-*p*-cresol, polystyrene standards, and a flow rate of 1.0 ml/min were employed for the analyses at 30°C. The molecular weights are not corrected for peak broadening effects and the variation of refractive index with molecular weight.

Controlled equimolar copolymerization of m,p-*chloromethylstyrene and styrene*

A solution of *m,p*-chloromethylstyrene (3.05 g, 20 mmol), styrene (2.08 g, 20 mmol), and AIBN (77 mg, 0.45 mmol, ~0.3 g/100 ml total volume) in chlorobenzene (20.5 ml) was flushed with nitrogen for about 10 min. The solution was then tightly stoppered, and maintained at 80° ± 1°C in a water bath. Aliquots were withdrawn from the polymerization mixture (under nitrogen) at certain intervals (see *Table 1*), and added dropwise into excess methanol, while stirring. The precipitated polymer was filtered, washed with methanol twice, and dried to constant weight *in vacuo*, at room temperature.

Polymer fractionation

The polymer isolated from the copolymerization of an approximately equimolar mixture of *m,p*-chloromethylstyrene and styrene in chlorobenzene (2 ml/g monomer) in the presence of AIBN (2 g/100 ml total volume), at 75°C for 20 h, was fractionated into four fractions as follows. (N.B. In each factionation step the immediate boundary phases were discarded to avoid contamination of the separated fractions.)

Fraction A. The polymer (2 g) was dissolved in dichloromethane (DCM, 30 ml), and was then diluted by dropwise addition of methanol (15 ml), while stirring vigorously. This was then transferred into a dropping funnel, shaken for about 5 min, and allowed to stand for 15 min, to obtain two immiscible polymer solutions. The lower more viscous phase was then separated, and added dropwise into methanol (400 ml). The precipitated polymer was washed with methanol, and dried at 40°C, to obtain the higher molecular weight polymer, fraction A (240 mg).

Fraction B. The less viscous solution obtained above was further diluted by dropwise addition of methanol (15 ml) in a similar fashion, followed by shaking for 5 min, and allowed to stand for 15 min. The more viscous phase was again precipitated into methanol (600 ml) to give, after drying, fraction B (980 mg).

Fraction C. The less viscous phase obtained above was added dropwise into methanol (400 ml), and the precipitated polymer was collected as fraction C (210 mg).

Fraction D. The mother liquor remaining after the filtration of fraction C above, was evaporated to dryness (~180 mg residue). This was dissolved in diethylether (4 ml), and precipitated into petroleum ether (30°–40°C, 100 ml), maintained at 0°C for 1 h, and the polymer was filtered and dried to produce the low molecular weight fraction C (~35 mg).

RESULTS AND DISCUSSION

Equimolar copolymerization of m,p-*chloromethylstyrene* ($\underline{M}_1$) *and styrene* ($\underline{M}_2$)

The copolymerization of $\underline{M}_1$ and $\underline{M}_2$ was carried out in chlorobenzene ($[\underline{M}_1] = [\underline{M}_2] \simeq 0.78$ $\underline{M}$), and in the presence of AIBN ($[\text{AIBN}] = 1.8 \times 10^{-2}$ M) at 80° ± 1°C. The polymer samples obtained at various time intervals were characterized by microanalysis, and gel permeation chromatography (g.p.c.). These results are summarized in *Table 1*. The course of the monomer to polymer conversion, and the variation of the polymer dispersity index ($\bar{M}_w/\bar{M}_n$) during the polymerization are also shown graphically in *Figure 1*. The yield of the polymerization after both 16 h and 60 h was 93%. This was assumed to correspond to complete (~100%) conversion within experimental error, and the remaining 7% representing the loss of polymer during the precipitation/recovery procedure described previously.

The results of chlorine analysis given in *Table 1* show that the polymers formed at low conversions are richer in $\underline{M}_1$, and that the polymer composition approaches that of the initial monomer mixture towards the end of the polymerization. This was expected from the known reactivity ratios of $\underline{M}_1$ and $\underline{M}_2$, i.e. (i)[3], $r_1 = 1.08$, $r_2 = 0.72$, and (ii)[4], $r_1 = 1.4$, $r_2 = 0.7$. However, it is interesting to note that the composition of the polymer obtained at 8.9% conversion corresponds almost exactly to the value predicted (cf. equations (1)–(2)) by the former pair of the above mentioned reactivity ratios.

$$m_1 = \frac{r_1 a + 1}{r_1 a + (r_2/a) + 2} \tag{1}$$

m_1 = mole fraction of $\underline{M}_1$ in the polymer at low conversion; $a = [\underline{M}_1]/[\underline{M}_2] = 1$ for equimolar copolymerization.

Table 1 Equimolar copolymerization[a] of *m,p*-chloromethylstyrene ($\underline{M}_1$) and styrene ($\underline{M}_2$)

	Polymerization		Polymer composition		Molecular weights[d]		
No.	Time (h)	Conversion (%)[b]	% Cl[c]	Mole fraction of $\underline{M}_1$	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$
1	0.33	8.9	14.87	0.55	13782	21285	1.54
2	0.75	23.1	–	–	14387	22163	1.54
3	1.50	42.4	–	–	13698	21464	1.57
4	5.5	63.0	14.33	0.52	12547	20451	1.63
5	8.0	80.6	–	–	9176	21031	2.29
6	16	≃100	–	–	12208	21143	1.73
7	60	≃100	14.10	0.51	13663	20398	1.49

[a] $[\underline{M}_1] = [\underline{M}_2] = 0.78$ $\underline{M}$, $[\text{AIBN}] = 1.8 \times 10^{-2}$ $\underline{M}$ in chlorobenzene at 80° ± 1°C
[b] Corrected for the loss of polymer during the precipitation/recovery procedure
[c] Calculated for the equimolar copolymer 14.02%
[d] By g.p.c.

$$m_1 = \frac{r_1 + 1}{r_1 + r_2 + 2} \qquad (2)$$

More remarkable is, however, the pattern in which the molecular weights ($\bar{M}_w$ and $\bar{M}_n$) vary during the course, and after the formal completion of the polymerization. The polymer dispersity index, ($\bar{M}_w/\bar{M}_n$), 1.54 at 8.9% conversion, suggests that the main termination mechanism is that of combination of polymer radicals, as may be expected[5,6] for a styrene-type polymerization. At moderate conversions, the value of $\bar{M}_n$ decreases gradually with increasing conversion, which can probably be explained by the gradual decrease in the concentration of the monomers M_1 and M_2. But a rather more marked decrease in $\bar{M}_n$ is observed from about 60% to 80% conversion, which was carefully checked experimentally followed by its increase again towards the end of polymerization (16h). There is a further increase in $\bar{M}_n$ when the polymerization mixture is maintained at 80°C after the formal completion of the polymerization. However, $\bar{M}_n$ remains relatively unaffected throughout this period.

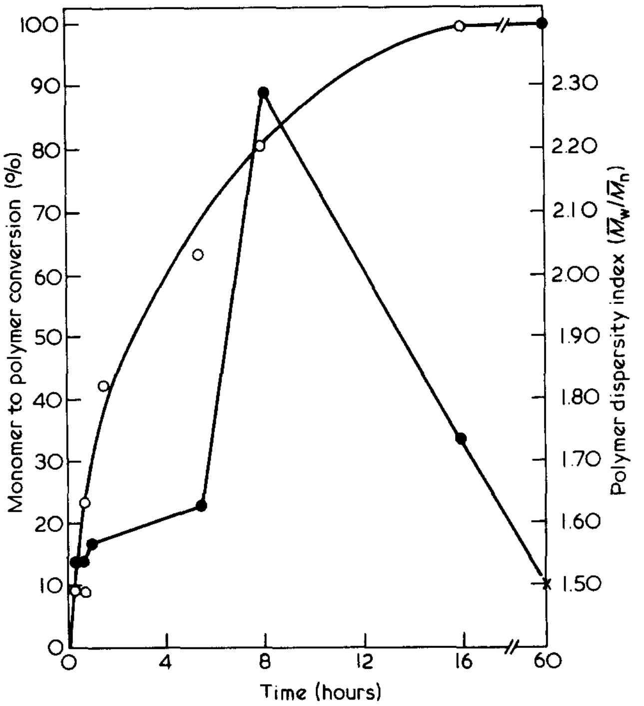


Figure 1 Equimolar copolymerization of *m,p*-chloromethylstyrene (M_1) and styrene (M_2) in chlorobenzene at 80°C) ($[M_1]=[M_2]=0.78\times10^{-2}$, $[AIBN]=1.8\times10^{-2}$), –O– =monomer to polymer conversion, –●–=polymer dispersity index ($\bar{M}_w/\bar{M}_n$) (see *Table 1*)

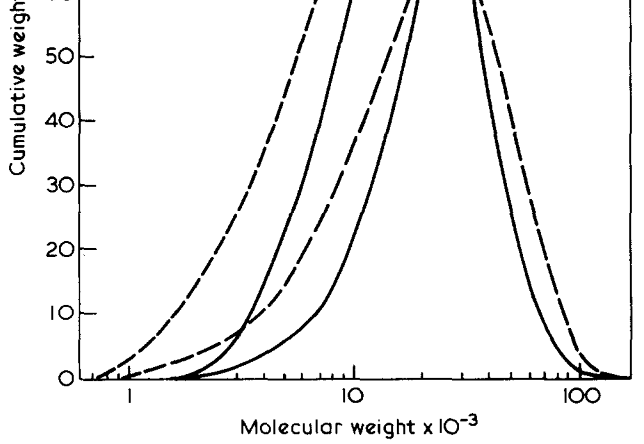
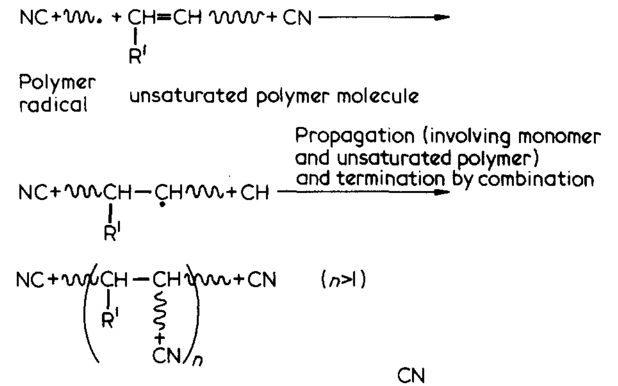


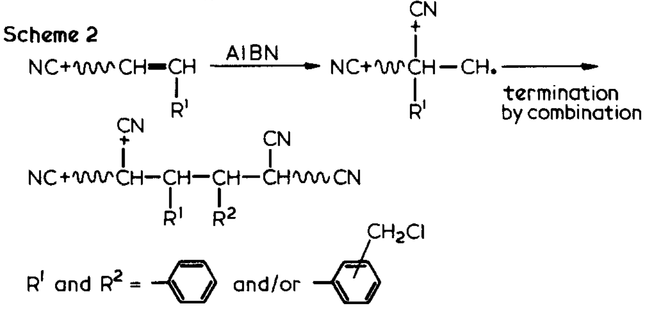
Figure 2 G.p.c. molecular weight distribution of polymer samples 5 (– – –) and 7 (———) as given in *Table 1*

The observed increases in $\bar{M}_n$ (cf. polymers 5–7 in *Table 1*) appear to represent the effect of the polymerization of the smaller unsaturated polymer molecules to larger ones, which is particularly important when the monomer concentrations are small. This polymerization of smaller molecular weight unsaturated polymer molecules to produce larger ones is also seen from the molecular weight distributions of polymer samples 5 and 7 presented graphically in *Figure 2*. The cumulative distribution of sample 7 shows a considerably lower percentage of lower molecular weight molecules and a higher percentage of higher molecular weight polymer. The involvement of chloromethyl groups in direct intermolecular grafting reactions is unlikely since the chlorine content of the final polymers correspond within experimental error, to the theoretically expected value. It is, on the other hand, known[4] that crosslinked copolymers of M_1 and M_2 may contain up to 0.5 mmol/g double bonds in the polymer chains. The decrease in $\bar{M}_n$ observed between 60% and 80% conversion may be due to the formation of unsaturated polymer molecules possibly by disproportionation of the polymer radicals with primary initiator radicals. Subsequent polymerization of these terminally unsaturated polymer molecules explains the molecular weight increases towards the end of polymerization (*Scheme 1*). After virtual complete polymerization of monomer further increases in molecular weight can occur

Scheme 1:



Scheme 2



as shown, for example, in *Scheme 2*. However, there might also be considerable polymer or initiator radical attack on dead copolymer molecules by chain transfer involving chlorine atoms along the polymer backbone.

A possible interpretation of the observed molecular weight increases shown in *Schemes 1* and *2* involves the formation of polymer molecules having >3 nitrogen atoms per molecule. Parallel observations of the chemical composition and molecular weight distribution of narrowly fractionated copolymer samples of $\underline{M}_1$ and $\underline{M}_2$ support this explanation. However, other mehcanisms, such as chain transfer to benzylic chlorine atoms which leads to grafting may also contribute to the observed molecular weight changes reported in *Table 1*.

Fractionation of copoly(m,p-*chloromethylstryene–styrene*)

The polymer employed for the fractionation study was prepared similarly to those reported in *Table 1*, but under a 2-fold higher monomer, and 6.5-fold higher initiator concentration, and at 75°C for 20 h. The polymer has a lower overall molecular weight, and a heterogeniety index of 1.71. The details of separation of the polymer to four fractions A, B, C and D are given in the Experimental section. Chlorine and nitrogen contents, as well as $\bar{M}_w$, $\bar{M}_n$ and $(\bar{M}_w/\bar{M}_n)$ of all four fractions are shown in *Table 2* together with those of the starting polymer. Chlorine content of the samples shows that the higher molecular weight fraction (A) contains a relatively higher concentration of $\underline{M}_1$ units, and thus higher proportions of the polymer formed in the early stages of the copolymerization (cf. *Table 1* and the appropriate discussion section). The accuracy of nitrogen analysis in fractions A and B is probably not sufficiently high to justify detailed discussion of the nitrogen content of these fractions.

The results for fractions C and D indicate that these copolymers have relatively high nitrogen contents, perhaps due to branching, and low values of molecular weights. However, the copolymer would have been fractionated using dichloromethane–methanol system in terms of molecular weight, composition and internal molecular structure.

Furthermore, g.p.c. analysis of copolymer is difficult due to the lack of the appropriate calibration curves, so that further interpretation requires a much more detailed study.

Table 2 Fraction of copoly(*m,p*-chloromethylstyrene–styrene)

Polymer fraction	Molecular weights[b] $\bar{M}_w$	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$	Polymer composition %Cl	Mole% of $\underline{M}_1$[c]	%N
Starting polymer	8805	5144	1.71	14.73	54	–
A(16.4)	16402	11996	1.37	14.85	55	0.18 (1.54)[d]
B(66.9)	9895	7148	1.38	14.47	53	0.36 (1.84)
C(14.3)	4174	3850	1.08	13.41	48	0.70 (1.92)
D(2.4)	2610	2340	1.11	13.32	48	1.32 (2.21)

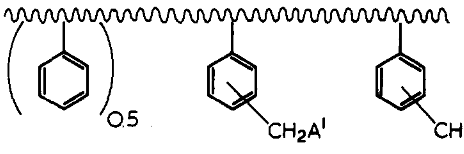
[a] Relative yield of each fraction (in percentage) is given in parentheses, but the values are regarded as approximate since the boundary phases discarded during the fractionation were not necessarily proportional to the value of the respective fractions

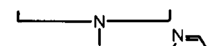
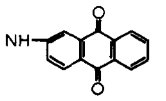
[b] By g.p.c.

[c] $\underline{M}_1$ = *m,p*-chloromethylstyrene

[d] Number of atom gram nitrogen per mole polymer, based on $\bar{M}_n$, is given in parentheses

Table 3 G.p.c. molecular weights of various derivatives of copoly(*m,p*-chloromethylstyrene–50% styrene)

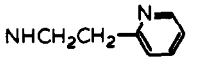


Derivative[a]	A^1[b]	A^2	$\bar{M}_w$[c]	$\bar{M}_n$[c]	$\bar{M}_w/\bar{M}_n$
2a	Cl	Cl	8805	5144	1.71
2b	Cl (0.24)	$P(C_6H_5)_2$	4345	1548	2.81
2c	$P(C_6H_5)_2$	$P(C_6H_5)_2$	2452	1641	1.49
2d[d]			74	65	1.14
2e	$\overset{CH_3}{\overset{\mid}{N}}CH_2CH_2CN$	$\underset{\underset{CH_3}{\mid}}{N}CH_2CH_2CN$	17118	8449	2.03
2f	Cl (0.36)		7495	6241	1.38

[a] Compound numbers are the same as those given in ref. 1, where their synthetic details are to be found

[b] Mole fraction of the chloromethyl groups is given in parentheses

[c] Molecular weights are reduced to represent values equivalent to those of the starting polymer **2a**

[d] About 78% of the 2-(2-aminoethyl)pyridine residues are attached to the polymer chains as shown, about 22% as  $NHCH_2CH_2$– (see ref. 1)

Molecular weight analysis of polymer derivatization

In our previous report[1] on the derivatization of copoly(*m*,*p*-chloromethylstyrene–styrene) (**2a**) we suggested that the derivatized polymer samples **2b**–**2f** may have considerably increased molecular weights due to possible polymer branching/crosslinking during derivatization, and/or fractionation during the precipitation of the derivatized polymer. Several of these derivatives were, therefore, analysed by g.p.c. to verify any molecular weight changes which might have occurred during the derivatization. A number of the results are presented in *Table 3*, and in general appear to show quite the opposite of what was anticipated. All of the molecular weights, except that of **2e**, appear lower than that of the starting polymer **2a**. Ironically, preparation of **2e** was the least complicated, and it was obtained in a relatively high yield.

A full discussion on the g.p.c. behaviour of polymer derivatives **2b**–**2f** would obviously require more elaborate molecular weight analysis by the use of alternative techniques. However, the generally increased retention of the polymers on the column is evidently a measure of the reduced macromolecular dimensions. In particular, in **2d** most of the 2-(2-aminoethyl)pyridine residues are attached to two points on the same polymer chain. This may reduce the overall dimension of the polymer molecule as a result of cyclization. The apparently higher molecular weights of **2e** may, on the other hand, reflect the relatively increased polarity of the polymer molecules, as compared with **2a**.

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