

Structural Transformations During Chloromethylation of Flexible Polystyrene Networks

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Synopsis

Strong morphologic variations were noted in the chloromethylation of styrene copolymers incorporating TAT or DVB as crosslinking agents. In the first case control over the chloromethylation conditions (solvent, temperature, time) can be applied in order to mold the final porous structure of the chloromethylated polymer. In the case of XE-305 containing higher concentration of crosslinking agent, the chloromethylation conditions have a less, but still significant, effect on the structure and functional group distribution of the product. Under conditions of low ratios of chloromethylating agent (CME) or catalyst (SnCl_4), the chlorine incorporation figures are medium, but chlorine distribution through the cross section of the bead is more or less homogeneous. Increase in the above ratios results in increased chlorine concentrations, but also in higher degree of secondary crosslinking and uneven chlorine distribution profiles. Preselection of the experimental conditions enables calculated introduction of functional groups. In the case of TAT-styrene copolymers, controlled experimental conditions are used to form a porous structure with low and high chlorine distribution. Such a porous polymer can then be functionalized by other reactions. Under certain chloromethylation conditions, the chloromethylated TAT-styrene copolymer is aminated to produce anion exchange resins, without further morphological changes.

INTRODUCTION

Chloromethylated styrene-DVB copolymers are important intermediates on route to anion exchange resins¹ and as such are used in water purification systems. As polymeric reagents they are engaged in the automatic polypeptide synthesis by the Merrifield method² as well as a starting material for a host of other polymeric reagents.³

Taking an interest in the role of the polymeric matrix during various reactions of polymeric reagents,⁴ Warshawsky and Kalir⁵ have recently reported on the irreversible structural reorganization of flexible styrene-divinylbenzene (DVB) networks during the Friedel-Crafts alkylation with 5-chloromethyl-8-hydroxyquinoline in the impregnated (dry) state.

In the present study, we report on aspects of structural transformations observed by stereoscanning electron microscopy (SEM) in two kinds of polystyrene matrices: first, very striking transformations in 1% hexahydro-1,3,5-triacryloyl-S-triazine (TAT) styrene copolymer⁶ during chloromethylation by the method of Schwachula and Hauptmann⁷; second, the crosslinking and morphologic changes in DVB-styrene copolymer (XE-305) during chloromethylation with chlorodimethyl ether. The experimental results point to the significance of the chloromethylation reaction conditions in producing ion exchange resins

of good ion diffusion properties.^{1,8} More important, the chloromethylation conditions can be controlled to produce anion exchange resins of prescribed porosity.

EXPERIMENTAL

Chloromethylation of XE-305

Amberlite XE-305, 5 g, was preswollen in 35 ml CHCl_3 (ethanol-free) for 30 min. Chloromethyl ether (CME) was then added, followed by SnCl_4 . The reaction mixture acquired a slight pinkish coloration. After standing, without stirring, at $21.5 \pm 1^\circ\text{C}$ for 2 hr (or otherwise as indicated in the table), the reaction product was filtered and washed with CHCl_3 , dioxan, dioxan:water (1:1), dioxan, and finally methanol. It was then dried at 50°C at 2–5 torr until constant weight was recorded. The product was weighed (W_p) and analyzed for chlorine (a).

In a blank experiment (all components, except CME), 5.00 g polymer yielded after drying 4.673 g (W_b) of 0% chlorine. Pellets containing 4% polymer in KBr were prepared and infrared spectra taken on a Perkin-Elmer 467 grating infrared spectrophotometer (see Table II and Figs. 13 and 14).

Chloromethylation of TAT-Styrene Copolymer

Styrene monomer was washed first with dilute sodium hydroxide solution and then with water and dried over sodium sulfate prior to use. The initial polymer network was synthesized by the known method of suspension polymerization of styrene and other vinyl monomers in the presence of benzoyl peroxide. The concentration of TAT was 1% by weight, based on monomer mixture. An equimolar mixture of chlorosulfonic acid and methylal was used as the chloromethylating agent. The copolymer was preequilibrated in the reaction solvent at 25°C and then reacted with a mixture of methylal and chlorosulfonic acid (the

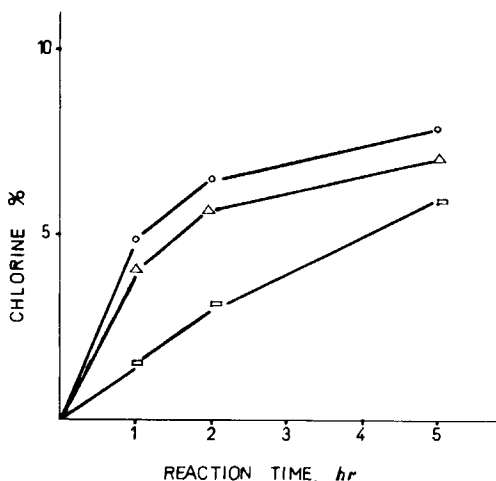


Fig. 1. Chlorine incorporation in 1% TAT-styrene copolymer vs. time of reaction, in nitrobenzene (O-O), carbon tetrachloride (Δ - Δ), and 1,1,2-trichloroethane (\square - \square).

TABLE I
Chloromethylation of 1% TAT-Styrene Copolymer with Chlorosulfonic Acid/Methylal^{10,11}

| Copolymer No. ^a | Swelling factor, % (v/v) toluene | Chloromethylation conditions | | | | | Product swelling factor, % (v/v), toluene | Internal reference numbers |
|----------------------------|----------------------------------|------------------------------|------------------------|--------------------|-----------|----------|---|-------------------------------------|
| | | Solvent | C/M ratio ^b | M-to-polymer ratio | Temp., °C | Time, hr | | |
| 1 | 680 | 1,1,2-trichloroethane | 1 | 6 | 0 | ? | 5.5 | 273 ^R , 261 ^R |
| 2 | 680 | CCl ₄ | 1 | 6 | 0 | ? | 7.6 | 274 ^R , 269 ^R |
| 3 | 680 | cyclohexane ^c | 1 | 6 | 0 | ? | 0.8 | 280 ^R , 295 ^R |
| 4 | 520 | cyclohexane | 1 | 8 | 25 | 1 | 5.5 | 110 ^S |
| 5 | 520 | cyclohexane | 1 | 8 | 25 | 40 | 16.9 | 60 |
| 6 | 520 | cyclohexane | 1 | 6 | 40 | 5 | 12.1 | 296 ^R |
| 7 | 500 | 1,1,2-trichloroethane | 1 | 6 | 0 | 0.5 | | 229 ^R |
| 8 | 500 | 1,1,2-trichloroethane | 1.5 | 6 | 40 | 1 | 16.0 | 200 |
| 9 | 500 | 1,2-dichloroethane | 1.5 | 6 | 40 | 6 | 20.2 | 50 |
| 10 | 520 | 1,1,2-trichloroethane | 1.5 | 6 | 40 | 5 | 20.8 | 50 |
| 11 | 520 | 1,1,2-trichloroethane | 1.5 | 6 | 40 | 5 | 21.4 | 50 |
| | | | | | | 5 | 21.2 | 50 |

^a Copolymers 1-10 contain 1% TAT; No. 11 contains 2% TAT.

^b C = Chlorosulfonic acid; M = methylal.

^c Equilibration time for swelling in this solvent is three days.

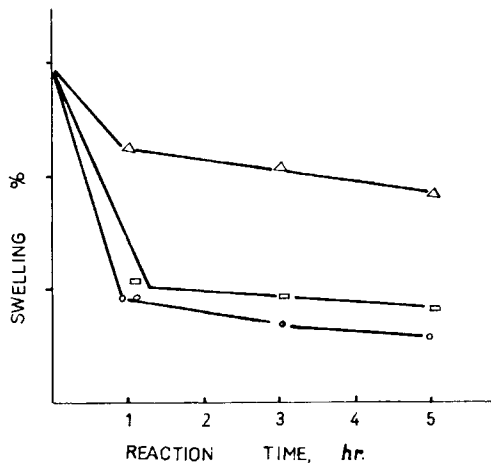


Fig. 2. Variations of percent swelling of chloromethylated 1% TAT-styrene copolymer during reaction progress. Solvents as in Fig. 1.

mixture having been prepared the previous day) at different temperatures for fixed times. Polymer samples were taken at various intervals, and the final products were poured into a large excess of methanol, recovered by filtration, washed with methanol and acetone, extracted with a mixture of benzene and methanol, and then finally dried at 60°C *in vacuo*. The swelling in toluene was determined by observation of volumetric expansion at equilibrium. For SEM, the samples were brittle-fractured and then examined by routine procedures.

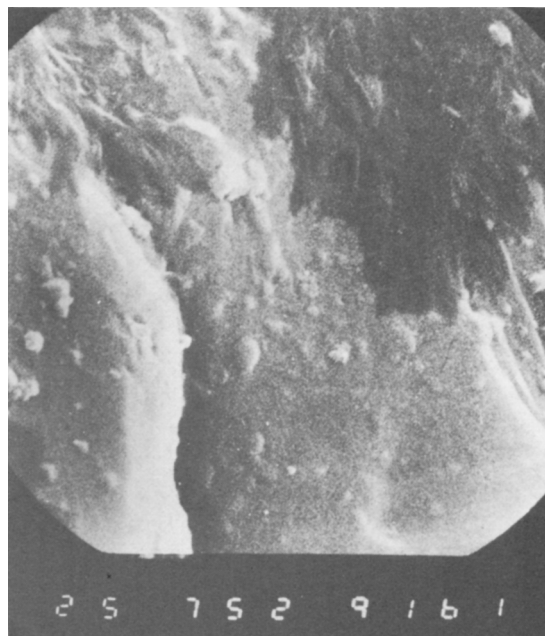
RESULTS AND DISCUSSION

TAT-Styrene System

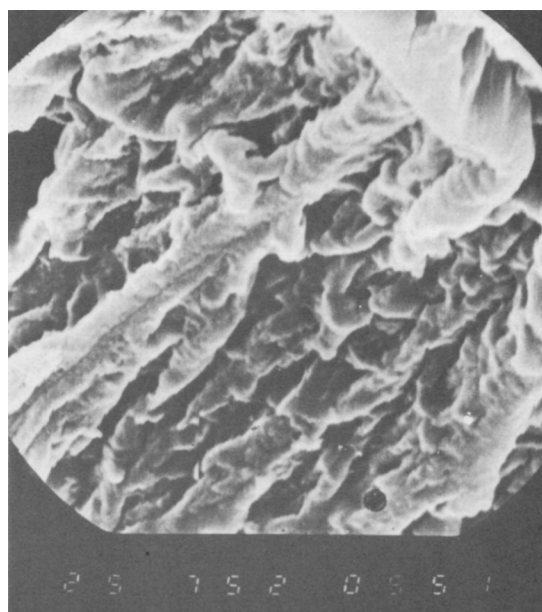
Chloromethylation Reaction

The copolymerization of styrene with TAT and the chloromethylation of this polymer have been reported recently by Belfer and Glozman.⁹ The chloromethylation method of Schwachula and Hauptmann⁷ using methylalchlorosulfonic acid (M/CS) mixture, which avoids direct use of chloromethyl ether, was chosen. It was established⁷ that uncrosslinked and slightly crosslinked DVB-styrene copolymers are chloromethylated at relatively elevated temperature (40–60°C), with low conversion yields, perhaps since only a slight excess of chloromethylating M/CS mixture was applied. (High conversion yields (22% Cl) were reported when a large mole excess of M/CS in the presence of sulfuryl chloride was employed.¹⁰) Changing the M-to-CS ratio had no significant implication. Bearing this in mind, we have used in the early stages of the present study a 1:1 M/CS mixture. Later, however, it was found that variation in the M/CS ratio has an interesting and significant effect on the morphology of the polymer, as will be discussed.

In Table I the chloromethylation conditions of 1% TAT-styrene copolymer (Nos. 1–10) and 2% TAT-styrene copolymer (no. 11) are summarized. The variations in reaction temperature, reaction duration, and solvent have a very drastic influence on the morphology of the resulting products, as will be illustrated in the SEM micrographs.

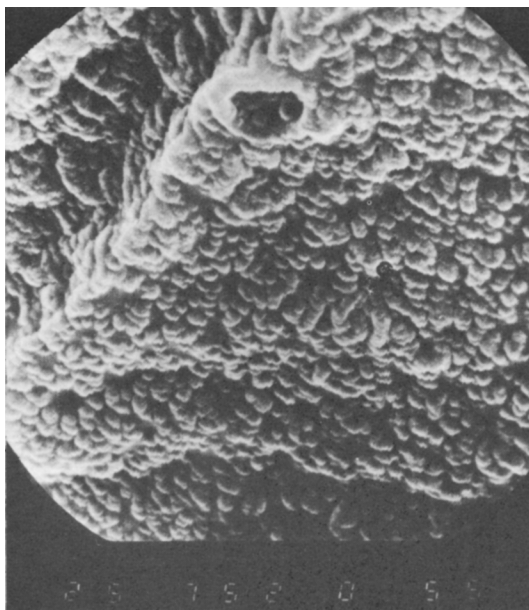


(a)



(b)

Fig. 3. Morphologic patterns at initial stages of chloromethylation of 1% TAT-styrene copolymers with M/CS at 0°C (30 min reaction) in (a) CCl_4 ; (b) 1,1,2-trichloroethane; (c) nitrobenzene.



(c)

Fig. 3. (Continued from previous page.)

In order to understand the role of the crosslinking reaction in directing the morphologic patterns of the polymer products, we first studied the reaction at low temperature (0°C), where the crosslinking is the main reaction path. The degree of conversion, expressed as percent chlorine in the product, is shown in Figure 1 for three solvents, nitrobenzene, carbon tetrachloride, and 1,1,2-trichloroethane (TCE); while Figure 2 shows the degree of swelling in toluene for the corresponding chloromethylated products. While the degree of chlorine introduction is similar in all three solvent systems, the swelling values are much higher for chloromethylated products prepared in CCl_4 . In other words, inter-chain interactions are smallest in nonpolar solvents (CCl_4) and largest in polar solvents (nitrobenzene). (The twisting of DVB-styrene copolymer reported by Warshawsky and Kalir⁵ was observed in nitrobenzene.)

Examining the morphologic patterns of chloromethylated polymers produced at 0°C in various solvents, we note strong differences already at the early stages of reaction (Fig. 3). As the reaction time varies, so does the morphology of the polymer. In low-polarity solvents, such as CCl_4 , the initial homogeneous gel pattern changes after 6 hr at 0°C into a large porous structure (Fig. 4).

In all solvents, the morphologic patterns are related to the reaction temperature. Completely different morphologies are observed when the reaction temperature is varied. For example, chloromethylated polymers of low chlorine content prepared in 1,1,2-trichloroethane [1.7% Cl, Fig. 5(a); 5.5% Cl, Fig. 5(b)] have internal cabbagelike structure stemming from large solvent-filled pockets formed during reaction.

Increasing the reaction temperature results in parallel increase in both chloromethylation and crosslinking reaction. In cyclohexane at 25°C , a porous

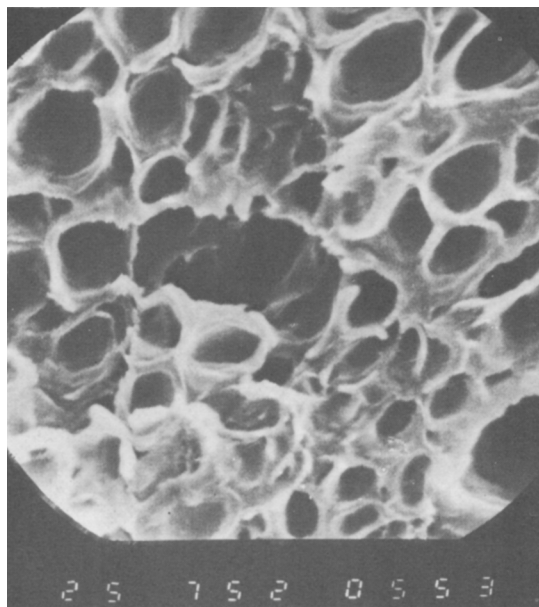


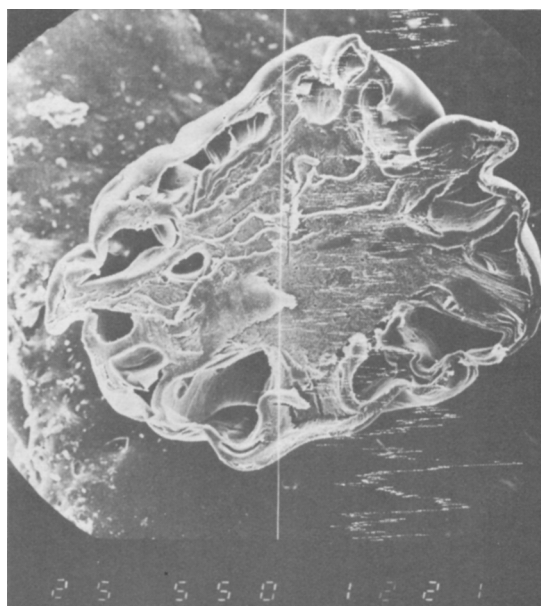
Fig. 4. Macrocellular internal structure of beads obtained in CCl_4 at 0°C for 6 hr; 5.7% Cl; 7500 \times magnification.

structure is observed from 1 hr of reaction [Fig. 6(a)], but when the temperature is raised to 40 – 50°C , most pores have closed but large vacuoles are present [Fig. 6(b)].

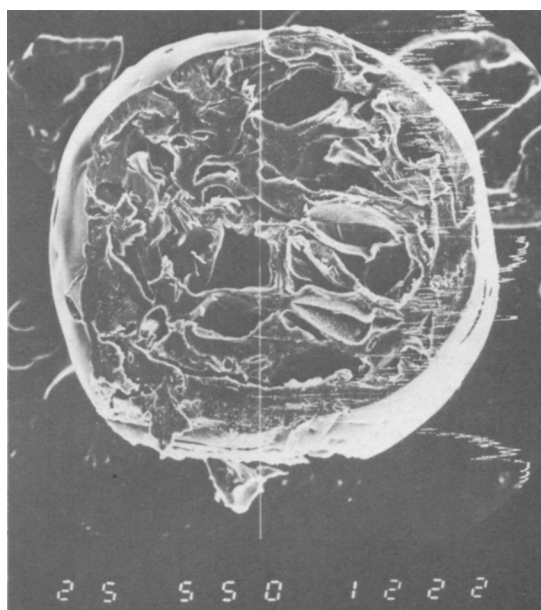
Intermediate conditions, such as temperature gradients, result in very interesting structures. Thus, in case of copolymer 7, Table I, the reaction temperature was controlled at 0°C for 30 min and then raised to 30°C for 1 hr. The results shown in Figure 7 (7500 \times) point to an interchanging congregation of huge and small pores.

As mentioned earlier, it was found that increasing the ratio of chlorosulfonic acid in the M/CS mixture brings about fundamental differences in polymer morphology. In Figure 8(a), the 240 \times magnification of the external structure of beads prepared by adding the polymers into excess of acid and chloromethylating agent (copolymer 2, Table I) is shown, i.e., the drastic structural deformation taking place within the whole volume of the bead, responsible for the formation of numerous strains, and ruptures on the surface of the bead which may sometimes lead to the complete destruction of the bead. Clusters of some crystalline material are visible on the surface of 7200 \times magnified beads [Fig. 8(b)] and also inside the bead [Fig. 8(c)]. Interestingly, the agglomerate structure represented in Figure 8(c) resembles very much the agglomerate structure of macroporous copolymer of 40% DVB content.

One of the possible explanations of the porous structure formation is phase separation during the crosslinking process, as a result of its irregular inhomogeneous character. The spontaneous crosslinking of flexible styrene copolymers during Friedel–Crafts chloromethylation can be regarded in terms of cationic postpolymerization. The initial step of cationic polymerization is the formation of carbonium ions as a result of the attack of the protonated chloromethyl ether

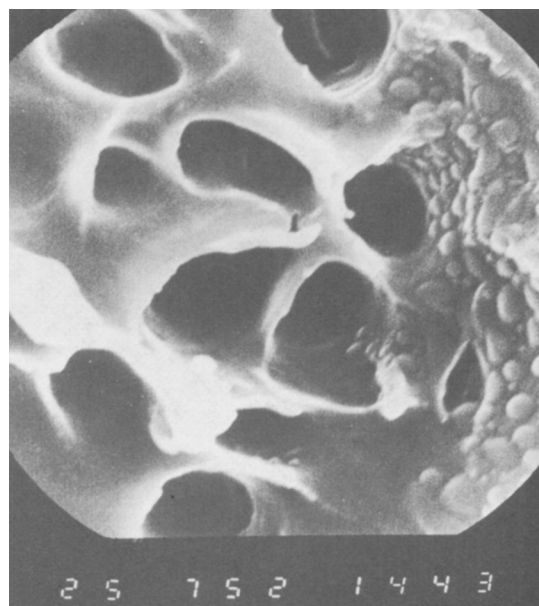


(a)

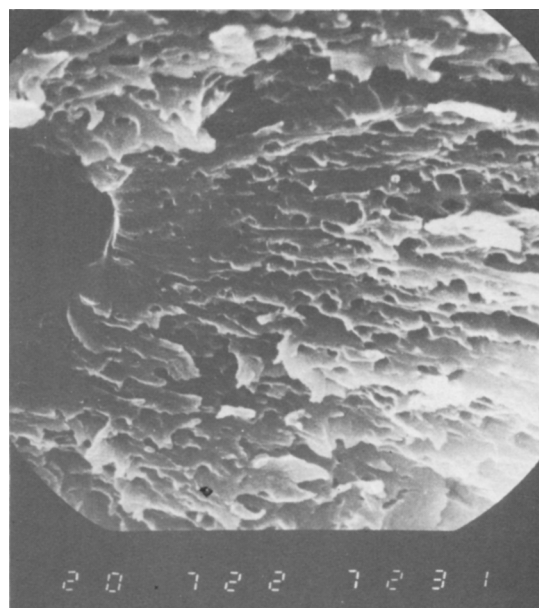


(b)

Fig. 5. Morphologic variations during the chloromethylation of 1% TAT-styrene copolymer in 1,1,2-trichloroethane at 0°C: (a) 0.5 hr; 1.7% Cl, 100× magnification; (b) 5 hr, 5.5% Cl, 100× magnification.



(a)



(b)

Fig. 6. Morphologic variations in the chloromethylation of 1% TAT-styrene copolymer in cyclohexane: (a) 1 hr at 25°C, 5.6% Cl in product; (b) 5 hr at 40°C, 18.1% Cl in product.

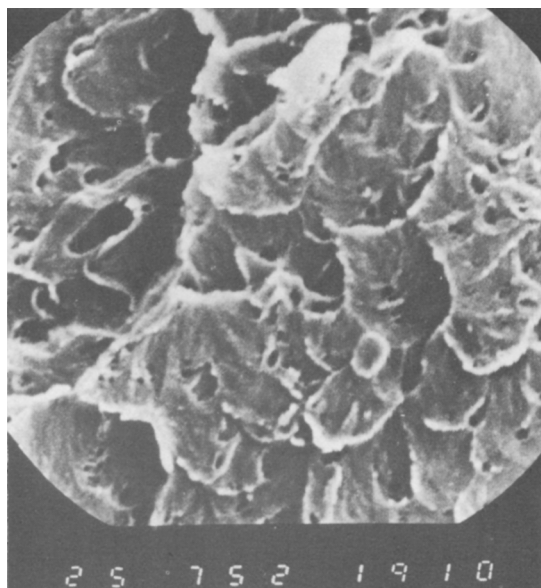


Fig. 7. Morphologic pattern under varying reaction conditions: 0.5 hr at 0°C, then 1 hr at 30°C; 1,1,2-trichloroethane, 16% Cl; 7500 \times magnification.

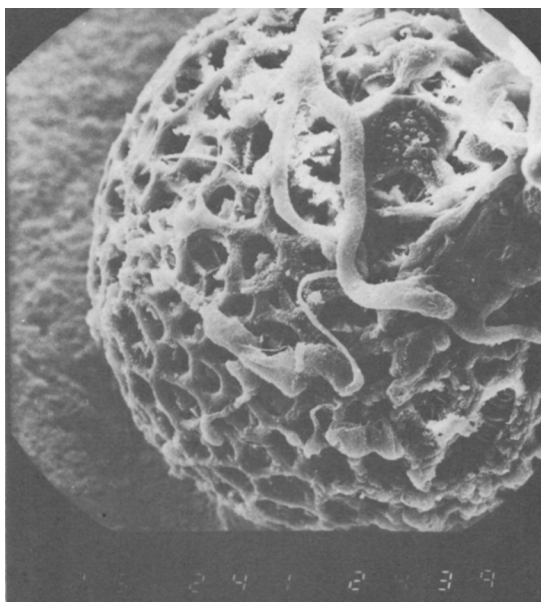
on the polymer. The rapid and irregular growth of crosslinks can lead to local phase separation, which in turn lead to the cracking of the continuous surface and formation of numerous cracks, cavities, and voids. A clear illustration of such development of process porous formation can be seen in Figures 9(a) and 9(b). The cross section of one bead (100 \times) shows one supercavity and a relatively homogeneous internal surface. The 15,000 \times magnification allows to observe a distribution of round tunnels of estimated \AA diameter [Fig. 9(c)]. The chlorine distribution throughout a cross section of the bead is even and high (20% Cl) and shows that under suitable chloromethylation conditions a stable porous structure is formed.

A polymer of high chlorine concentration (20%) and the same porous internal structure is obtained when the chloromethylation is conducted with a CS/M mixture of 1.5:1 ratio in 1,1,2-trichloroethane at 40°C (no. 10, Table I) as shown in Figure 10(a) (7200 \times) and Figure 10(b) (15,000 \times).

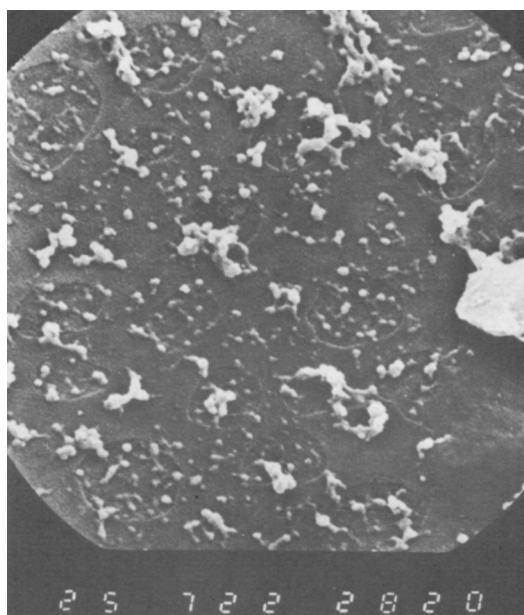
Amination of Chloromethyl-1% TAT-Styrene Copolymer

The amination of chloromethyl-1% TAT-styrene copolymers proceeds under standard conditions. The structure of the aminated resins, invariable of the aminating agent, resembles closely the structure of the starting chloromethyl polymer. The product of the reaction of the chloromethyl-1% TAT-styrene copolymer 10, Table I (shown in Fig. 10), with ethylenediamine is shown in Figure 11 [Fig. 11(a) 7500 \times magnification; Fig. 11(b) 20,000 \times magnification].

Similarly, the product of the reaction of the chloromethyl-1% TAT-styrene copolymer 4 and hexamethylenetetramine (which yields after hydrolysis a primary amine) resembles the starting material.

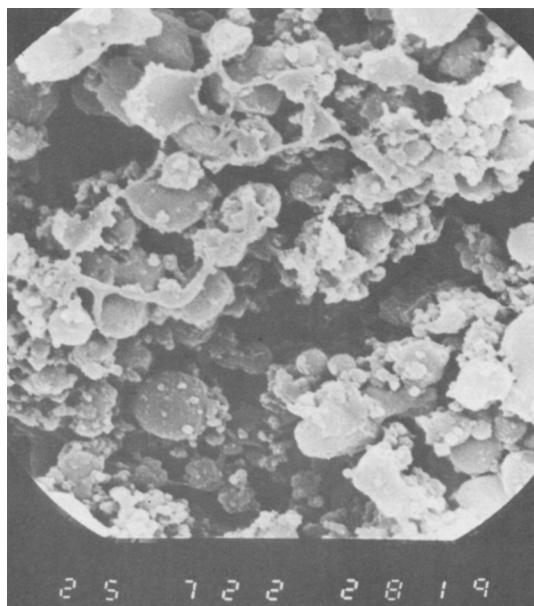


(a)



(b)

Fig. 8. Structural deformation in 1% TAT-styrene beads during chloromethylation with CS/M at excess CS (15.1); in 1,1,2-trichloroethane for 6 hr, 20.2% Cl: (a) surface area of a bead, 240 \times magnification; (b) patches of crystalline material on surface, 7200 \times magnification; (c) internal structure, 7200 \times magnification.



(c)

Fig. 8. (Continued from previous page.)

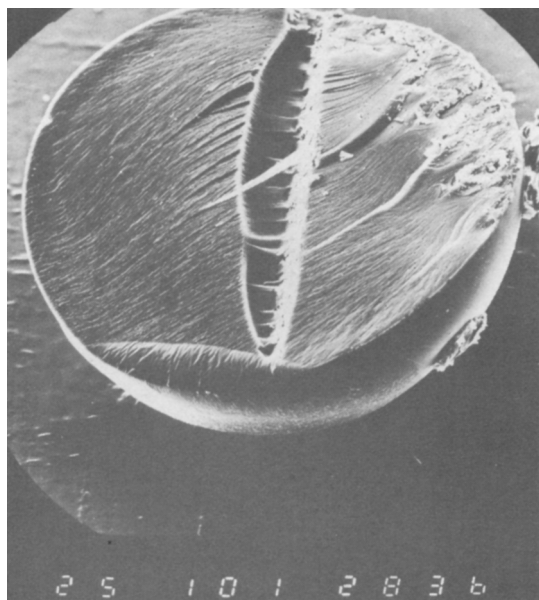
DVB-Styrene Copolymer System

Chloromethylation of 4% DVB-Styrene Copolymer (Amberlite XE-305)

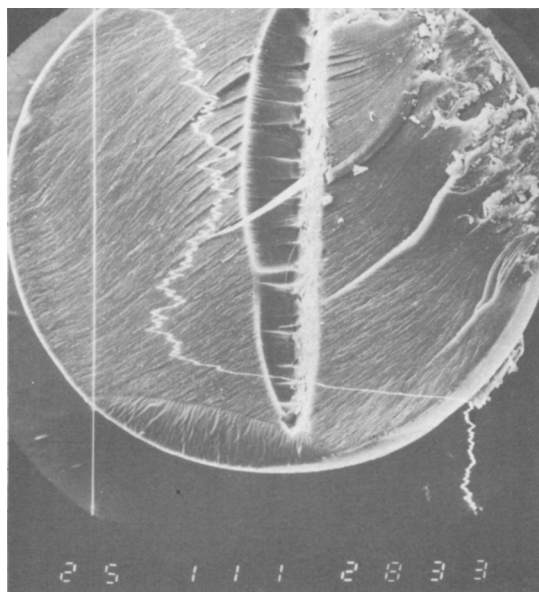
Amberlite XE-305 belongs to a class of so-called macroporous (or macroreticular) polymers. In a number of publications, Warshwasky et al.¹¹ have utilized the high flexibility of this polymer (which is due to the low amount of crosslinking agent) in order to produce twisted polymer structures⁵ or oppositely to build a very porous structure (e.g., polymeric pseudocrown ethers).¹²

In the present study, the chloromethylation was performed in dry chloroform at $21.5 \pm 1^\circ\text{C}$, varying the concentration of chloromethylating agent and catalyst (SnCl_4). First, the chloromethylation at constant chloromethyl ether (CME): polymer ratio (3:1 molar ratio) and varying catalyst concentration (see Fig. 12) has established that the reaction is completed within 2 hr. In a second set of experiments, both catalyst and CME concentrations were varied. The results, presented in Figure 13, show that changing the catalyst concentration is more significant at low CME concentrations. But even at the highest CME concentration, it is yet important to control the catalyst concentration. In fact, making use of the results plotted in Figure 13, it is possible to control the degree of chloromethylation of XE-305, as shown in the experimental part.

To allow for accurate analysis of the reaction products, the polymer samples were washed thoroughly with large volumes of solvents and dried carefully at 50°C at 1 torr to constant weight. Blank samples of the polymer underwent the same reaction sequence and washing, except that one component in the reaction mixture was deliberately removed. The weight of such blank polymer, W_b , served for weight gain calculations. The concentration of $-\text{CH}_2-$ groups was

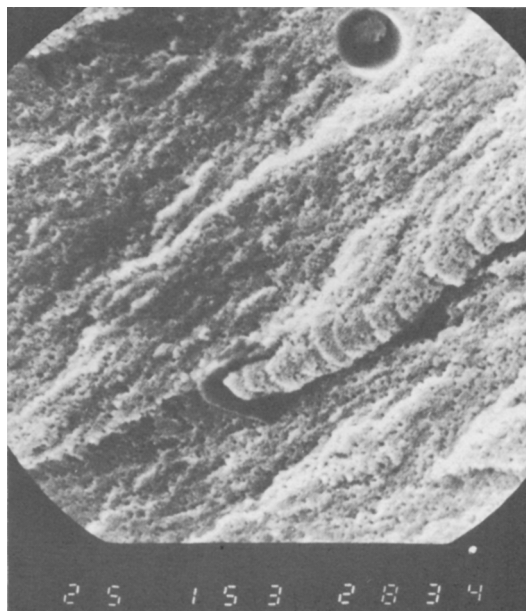


(a)



(b)

Fig. 9. Internal bead structure obtained during chloromethylation in 1,2-dichloroethane at 40°C for 6 hr: (a) fractured bead, 100× magnification; (b) perforated internal structure, 15,000× magnification; (c) chlorine distribution profile, 110× magnification.



(c)

Fig. 9. (Continued from previous page.)

calculated from the following formula:

$$[\text{CH}_2] \text{ groups (in mmole/g)} = \frac{W_p - W_b - \frac{W_p \times a}{100} \times \frac{49.5}{35.5}}{14 \times W_p}$$

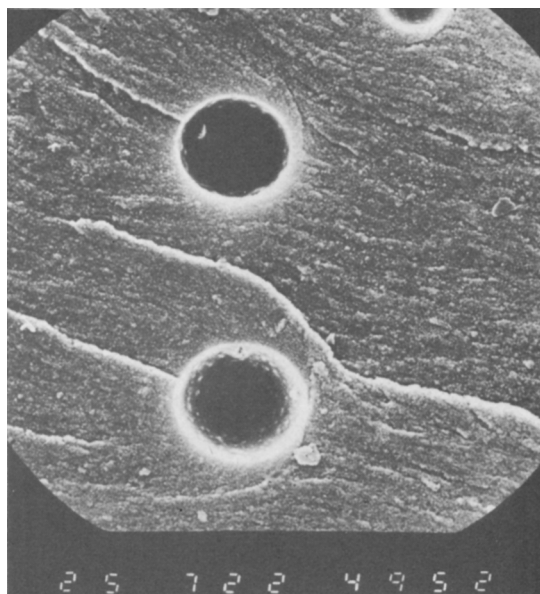
where W_b = weight of blank, W_p = weight of reaction product, a = % chlorine in product, and 14, 35.5, and 49.5 are the formula weights of $-\text{CH}_2-$, Cl, and CH_2Cl , respectively.

An attempt was made to develop also a spectroscopic method for the measurement of the amount of $-\text{CH}_2\text{Cl}-$ and $-\text{CH}_2-$ groups introduced during the chloromethylation. We followed the work of Freeman et al.¹³ and Laskorin et al.,¹⁴ who used the A_2 out-of-plane aromatic proton bending vibration appearing for disubstituted benzene rings at $\sim 841 \text{ cm}^{-1}$ for *p*-DVB copolymer and at 831 cm^{-1} for polybenzylpyridinium resins, respectively.

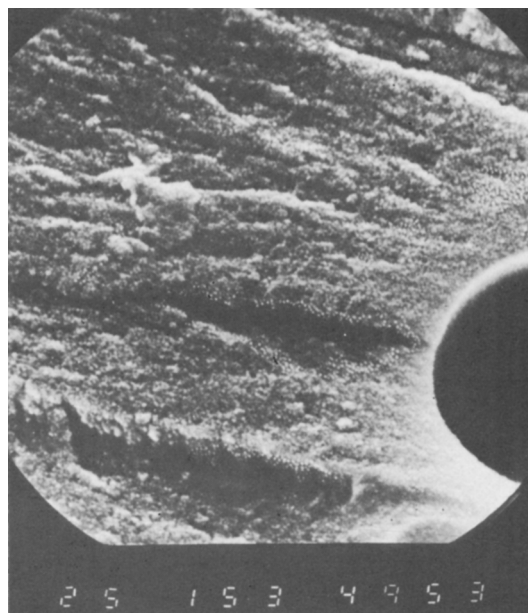
Examining the IR spectra of polymer/KBr pellets, reproduced in Figure 14, we note the gradual increase of the 830 cm^{-1} band [Fig. 14(a)], with gradual decrease of the 750 cm^{-1} band and a buildup of a strong adsorption band at 1270 cm^{-1} attributed to 1,4 in-plane bending. A quantitative method for the evaluation of the ratio of $-\text{CH}_2\text{Cl}-$ to $-\text{CH}_2-$ groups uses the 1270 cm^{-1} band to represent the CH_2Cl groups and the 830 cm^{-1} band to represent the total ($\text{CH}_2\text{Cl} + -\text{CH}_2-$) groups.

Further information on the distribution of CH_2Cl groups and on the general morphology of the chloromethyl polymer was gained from stereoscanning electron microscopy.

A priori it is expected that the chloromethylation of styrene-DVB copolymers

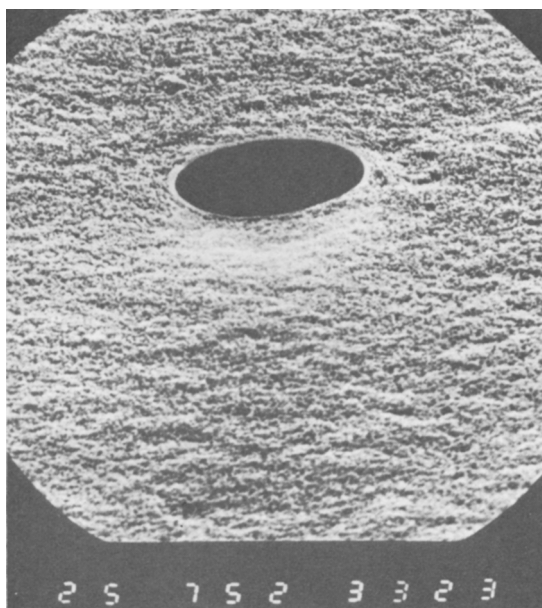


(a)

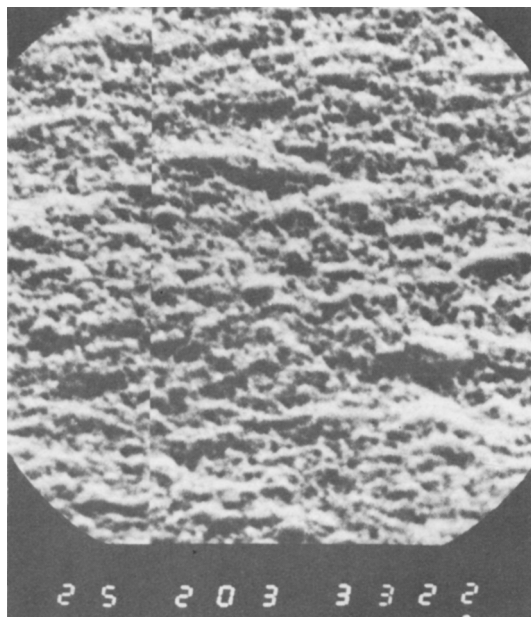


(b)

Fig. 10. Perforated bead structure obtained in 1,1,2-trichloroethane at 40°C, 5 hr reaction: (a) 7200× magnification; (b) 15,000× magnification.



(a)



(b)

Fig. 11. Perforated bead structure of the ethylenediamine exchange resin produced from the chloromethyl polymer shown in Fig. 10, containing 5.9 mmole nitrogen per gram polymer: (a) 7500 \times magnification; (b) 20,000 \times magnification.

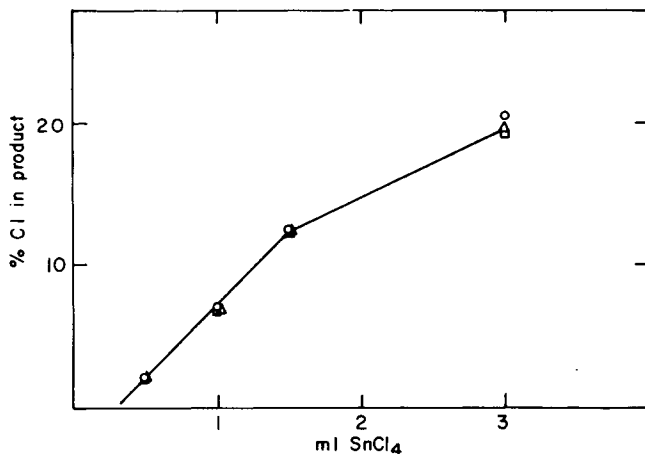


Fig. 12. Chloromethylation of XE-305 at CME-to-polymer molar ratio of 3:1 in CHCl_3 at 21.5°C ; polymer-to- CHCl_3 ratio (w/v) 1:7. (Δ) 2.5 hr, (\square) 8 hr, (\circ) 24 hr.

would follow a homogeneous reaction model, as pointed out by Schmuckler and Goldstein.¹⁵ It was noted, however, that anion exchange resins show a zoning effect¹⁶ which is probably due to uneven nitrogen distribution,^{4,16} which in turn is due to uneven chlorine distribution. It seems that the mechanism of chloromethylation depends on the solvent. In chloromethyl ether as solvent, the reaction proceeds by a homogeneous reaction model mechanism,¹⁵ while in chloroform, a good swelling solvent but less polar and without metal complexing power, a different situation prevails.

In Figure 15(a) we see a distinctly zoned bead (No. 1, Table II) with an even chlorine distribution profile [Fig. 15(b)] [the sharp minimum is due to a crack in the bead, seen clearly in Fig. 15(a)].

A general picture emerges. In all experiments where low SnCl_4 or CME

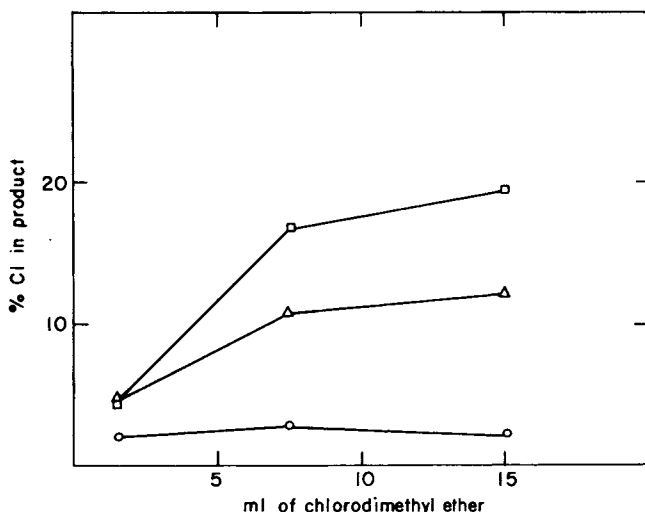


Fig. 13. Chloromethylation of XE-305 at varying CME and SnCl_4 concentrations in CHCl_3 at 21.5°C for 2 hr; polymer-to- CHCl_3 ratio (w/v) 1:7. (\circ — \circ) 0.5 ml SnCl_4 ; (Δ — Δ) 1.5 ml SnCl_4 ; (\square — \square) 3.0 ml SnCl_4 .

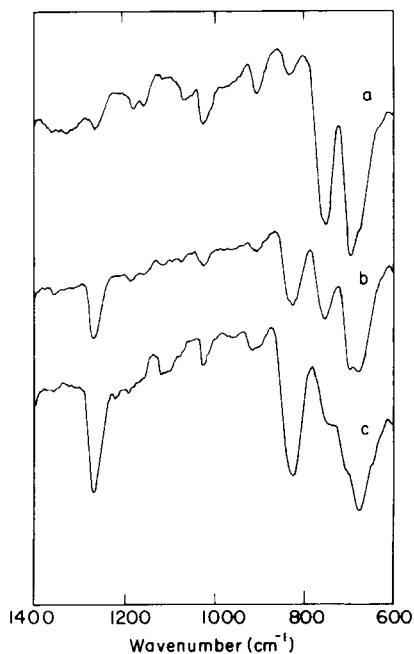


Fig. 14. The IR spectra of chloromethylated polystyrene (XE-305) at varying degrees of substitution: (a) 0.61 mmole/g $-\text{CH}_2\text{Cl}$ groups; zero $-\text{CH}_2-$ groups; (b) 3.5 mmole/g $-\text{CH}_2\text{Cl}$ groups; 1.3 mmole/g $-\text{CH}_2-$ groups; (c) 5.46 mmole/g $-\text{CH}_2\text{Cl}$ groups; 2.95 mmole/g $-\text{CH}_2-$ groups.

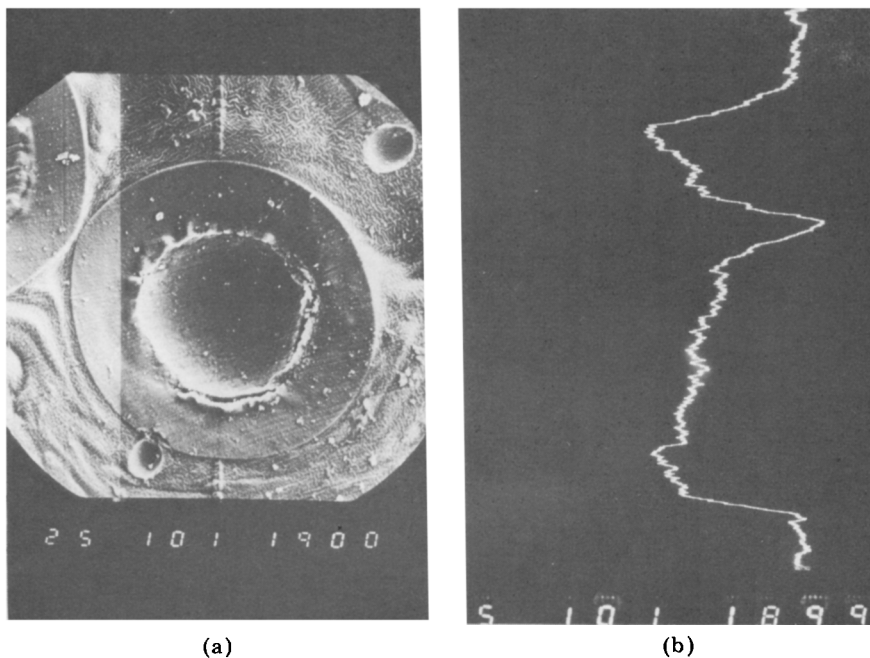
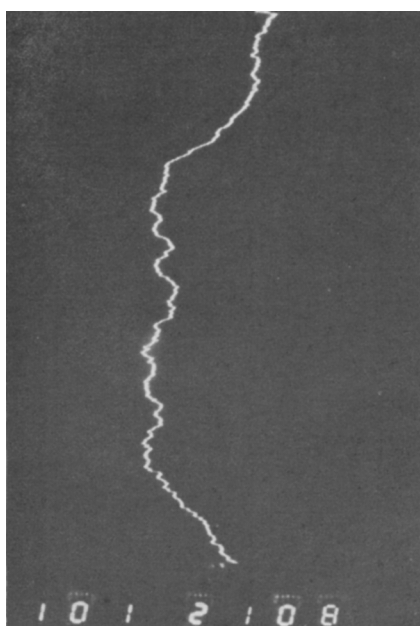
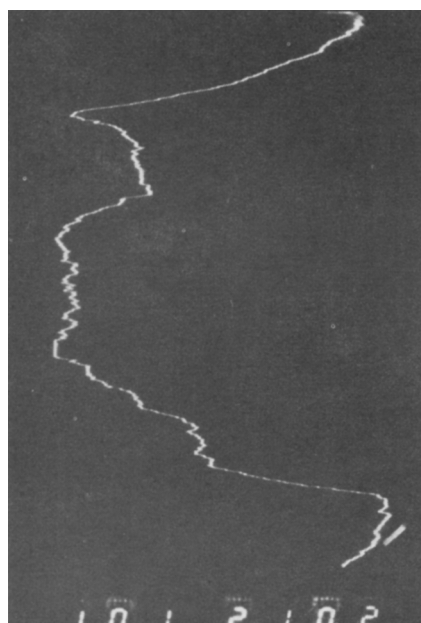


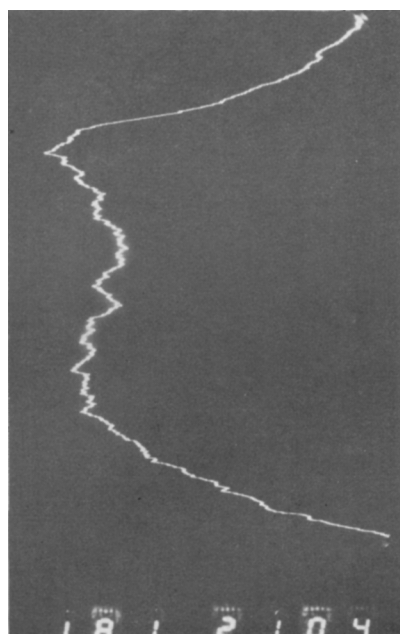
Fig. 15. (a) Zoning effect in chloromethylated XE-305 (0.56 mmole/g Cl), No. 1, Table II, 101 \times magnification; (b) chlorine distribution through a bead cross section. Chlorine percentage falls to zero at the crevice.



(a)

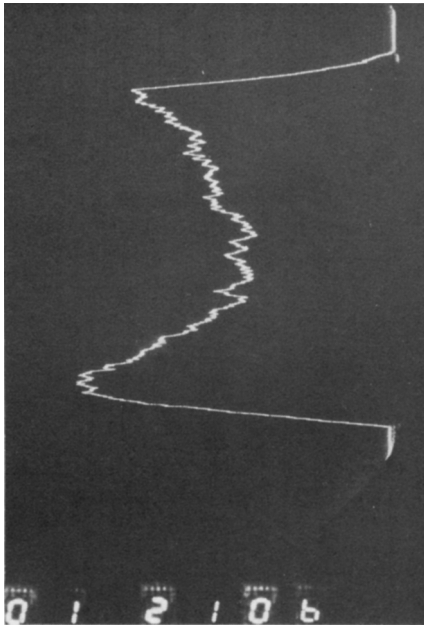


(b)

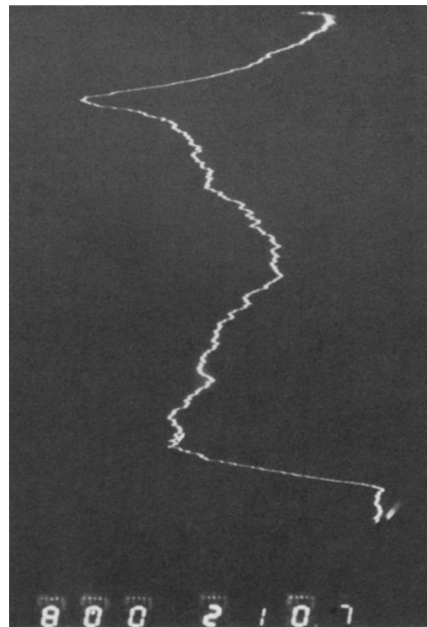


(c)

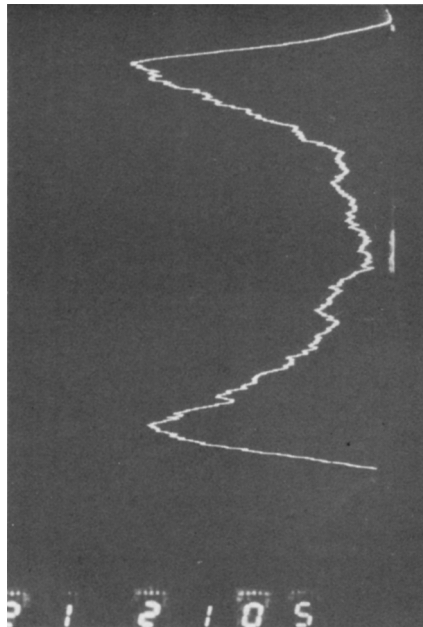
Fig. 16. Chlorine profiles in chloromethylated XE-305 produced at low CME, or SnCl_4 concentrations: (a) No. 5, Table II; (b) No. 8, Table II; (c) No. 11, Table II.



(a)



(b)



(c)

Fig. 17. Decreased chlorine concentrations in chloromethylated XE-305 beads produced at intermediate CME or SnCl_4 concentrations: (a) No. 2, Table II; (b) No. 9, Table II; (c) No. 12, Table II.

TABLE II
Chloromethylation^a of 4% DVB-Styrene Copolymer (XE-305). Reactant Ratios and Product Composition

| Copolymers No. | Reactant ratios | | | Product | |
|-------------------|---|-------------------------------------|---|--|--|
| | Ratio of SnCl ₄ to polymer (v/w) | Ratio of CME to polymer (v/w) | Ratio of CME to SnCl ₄ (v/v) | mmole CH ₂ Cl per g polymer ^b | mmole —CH ₂ — per g polymer ^c |
| 1 | 1:10 | 3:1 | 30:1 | 0.56 | 0 |
| 2 | 1:5 | 3:1 | 15:1 | 1.78 | 1.08 |
| 3 | 1:3 | 3:1 | 10:1 | 3.49 | 1.29 |
| 4 | 1:10 | 1:3 | 3:1 | 0.56 | 0.58 |
| 5 | 1:10 | 1.5:1 | 15:1 | 0.79 | 0.42 |
| 6 | 1:10 | 3:1 | 30:1 | 0.62 | 0 |
| 7 | 1:3 | 1:3 | 1:1 | 1.26 | 1.39 |
| 8 | 1:3 | 1.5:1 | 5:1 | 3.04 | 1.15 |
| 9 | 1:3 | 3:1 | 10:1 | 3.43 | 1.29 |
| 10 | 3:5 | 1:3 | 1:2 | 1.30 | 2.25 |
| 11 | 3:5 | 1.5:1 | 2.5:1 | 4.73 | 2.70 |
| 12 | 3:5 | 3:1 | 5:1 | 5.52 | 1.14 |
| 13 | 3:5 | 3:1 | 5:1 | 5.46 | 2.95 |
| 14 | 3:5 | 3:1 | 5:1 | 5.5 | 3.10 |

^a 5 g XE-305, 35 ml CHCl₃ at 21.5°C, no stirring; CME = chloromethyldimethyl ether.

^b From percent Cl analysis.

^c Calculated.

concentrations were applied, the chlorine profiles are generally quite homogeneous throughout the bead cross section, as shown in Figures 16(a) (No. 5, Table II), 16(b) (No. 8, Table II), and 16(c) (No. 11, Table II).

Increasing the concentrations of either SnCl₄ or CME results in increased reactivity. As a result, higher yields of chlorine incorporation are achieved, but accompanied with higher yields of internal crosslinking. This produces a barrier to reactant diffusion, and as a result the chlorine concentrations are higher at the periphery than at the core of the bead. This is shown in Figures 17(a) (No. 2, Table II), 17(b) (No. 9, Table II), and 17(c) (No. 12, Table II).

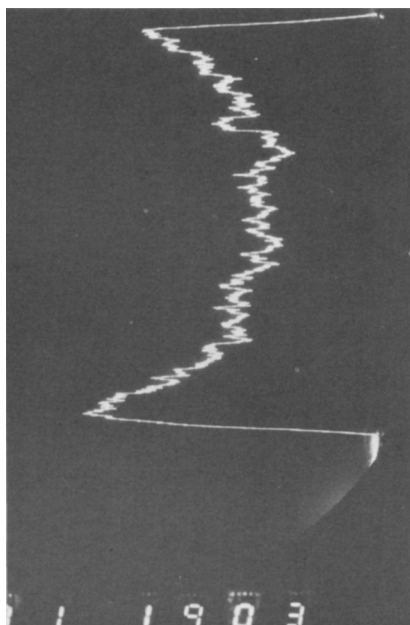
Finally, when highest reactant concentrations are applied (Nos. 13–15), the zoned structure is erupted and core-directed tunnels are observed (Fig. 18(a), for No. 14, Table II). The chlorine distribution becomes more even (Fig. 18(b), No. 17, Table II; and Fig. 18(c) No. 15, Table II).

CONCLUDING REMARKS

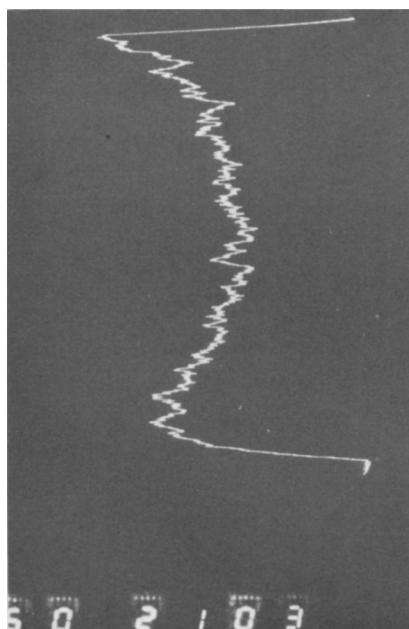
Strong morphologic variations were noted in the chloromethylation of styrene copolymers incorporating TAT or DVB as crosslinking agents. In the first case, control over the chloromethylation conditions (solvent, temperature, time) can be applied in order to mold the final porous structure of the chloromethylated polymer. In the case of XE-305 containing higher concentration of crosslinking agent, the chloromethylation conditions have a smaller, but still significant, effect on the structure and functional group distribution of the product. Under conditions of low ratios of chloromethylating agent (CME) or catalyst (SnCl₄), the



(a)



(b)



(c)

Fig. 18. Bead structure and chlorine profiles for chloromethylated XE-305 beads produced at high CME or SnCl_4 concentrations: (a) bead structure, No. 14, $101\times$ magnification; (b) No. 14, Table II; (c) No. 15, Table II.

chlorine incorporation figures are medium, but chlorine distribution through the cross section of the bead is more or less homogeneous. Increase in the above ratios results in increased chlorine concentrations, but also in higher degree of secondary crosslinking, and uneven chlorine distribution profiles. Preselection of the experimental conditions enables calculated introduction of functional groups.

In the case of TAT-styrene copolymers, controlled experimental conditions are used to form a porous structure with low and high chlorine distribution. Such a porous polymer can then be functionalized by other reactions. Under certain chloromethylation conditions, the chloromethylated TAT-styrene copolymer is aminated to produce anion exchange resins, without further morphologic changes.

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