

# Polymerization of Ethyl Methacrylate, Methyl Methacrylate, and Vinyl Acetate Using Sulfonated Polystyrene as the Initiator

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## Synopsis

Polymerization of ethyl methacrylate (EMA) and methyl methacrylate (MMA) was achieved in glass dilatometers, at 86°C, using polystyrene sulfonate ( $\text{Na}^+$  and  $\text{H}^+$  forms) as initiators. The conversion of EMA to PEMA and MMA to PMMA increased with the time of polymerization, quantity of initiator, and size of dilatometer but decreased with volume of water. The polymer yield was higher for the  $\text{Na}^+$  than for the  $\text{H}^+$  form of the resin initiator. The average degree of polymerization increased with increase in the volume of water, but decreased with the quantity of initiator. Vinyl acetate could not be polymerized using either the  $\text{Na}^+$  or  $\text{H}^+$  forms of the polystyrene sulfonate as the initiator under the conditions of EMA or MMA polymerization.

## INTRODUCTION

Recently, an account was given of the polymerization of methyl methacrylate (MMA) using the sodium form of sulfonated polystyrene as initiator.<sup>1</sup> Much of the work reported so far indicates the dependence of polymerization of the vinyl monomers on temperature, time of polymerization, and quantity of monomer or monomer/initiator ratio. In particular, the recent work of Ouchi et al.<sup>1</sup> has shown the dependence of the polymerization of MMA in a dilatometer on time, temperature, monomer/initiator ratio, and quantity of water used for the polymerization. Ouchi and co-workers limited their work to small amounts of MMA and  $\text{H}_2\text{O}$  and did not allow the polymerization to proceed beyond 4 h. They also reported the dependence of the average degree of polymerization of PMMA ( $\bar{P}_n$ ) on the quantity of  $\text{H}_2\text{O}$  and initiator present, and concluded that the initiation step proceeded by free radical mechanism which involved a direct interaction of monomer molecules with the ionized sites of the polystyrene sulfonate initiator.

This report deals with the polymerization of ethyl methacrylate (EMA), methyl methacrylate (MMA), and vinyl acetate (VAc) in a dilatometer, using sulfonated polystyrene ( $\text{Na}^+$  or  $\text{H}^+$  form) as the initiator. It discusses the forms of the dependence of the polymerization of these monomers, in dilatometers, on time, quantity of initiator, and volume of water at 86°C, and also the dependence of the average degree of polymerization ( $\bar{P}_n$ ) or viscosity-average molecular weight ( $\bar{M}_v$ ) of the polymers on the quantity of water and initiator used during the polymerization. In addition, it considers the effect of size of the dilatometer and mesh size of the polystyrene sulfonate resins on the conversion of the monomers to the respective polymers. A comparison is also drawn in the polymerization of EMA, MMA, and VAc.

## EXPERIMENTAL

### Materials

The resins used were Amberlite IR-120 (14–52 mesh), Zeokarb 225 SRC 10 (52–100 mesh), and Amberlite CG-120 (400 mesh). They were obtained in analytical grades in the hydrogen form from the British Drug Houses Ltd (BDH). The resins were converted to their sodium form by the method of Ouchi et al.<sup>1</sup> The hydrogen form of each resin was washed thoroughly with deionized water and dried under vacuum. Ethyl methacrylate, methyl methacrylate, and vinyl acetate were all BDH chemicals. They were purified by removing the inhibitor with dilute aqueous NaOH, followed by drying with a drying agent, and finally by vacuum distillation just prior to use.

### Procedure

The monomer, resins, and distilled–deionized water were measured carefully into the dilatometer in the appropriate amounts. The dilatometer was thawed with nitrogen and sealed under vacuum. The tube was placed in a water bath shaker thermostated at  $86 \pm 0.5^\circ\text{C}$ , and polymerization was allowed to proceed for definite lengths of time, with constant speed of agitation, after which the tube was removed and placed in ice-cold water. The contents of each tube were poured into a large quantity of pure methanol to precipitate the polymer and the resin initiator. The polymer and resins were recovered by filtration and dried under vacuum. The pure polymer was recovered from its mixture with the resins by suspension in chloroform (to dissolve the polymer, leaving the resins), separation of the chloroform solution with a separatory funnel, precipitation by pouring the concentrated chloroform solution of the polymer into a large quantity of pure methanol, filtration under suction, and finally drying under vacuum.

Benzene and ethyl acetate were used as solvents for PMMA and PEMA, respectively, in the viscosity study. From the limiting viscosity values obtained for PMMA at  $30^\circ\text{C}$  and PEMA at  $35^\circ\text{C}$ , the average degree of polymerization ( $\bar{P}_n$ ) was calculated for PMMA from Welch's equation,<sup>2</sup> while the viscosity-average molecular weight ( $\bar{M}_v$ ) for PEMA was calculated from the Mark–Houwink–Sakurada equation. In calculating  $\bar{M}_v$  for PEMA, the values of  $8.6 \times 10^{-3} \text{ cm}^3/\text{g}$  and 0.71 were used for  $K$  and  $\alpha$ , respectively, in the Mark–Houwink–Sakurada equation.<sup>3</sup>

## RESULTS AND DISCUSSION

### Poly(ethyl Methacrylate) (PEMA), Kinetic Study

Polymerization of ethyl methacrylate (EMA) was achieved in dilatometers of different sizes, using both the sodium and hydrogen forms of the sulfonated polystyrene as initiator. Figure 1 represents the kinetic study of the polymerization of EMA. The polymer yield was negligibly small during the first few hours of the polymerization but increased rapidly with time of polymerization. After about 4 h, the polymer yield increased, approximately linearly, with time of polymerization, in agreement with the work of Ouchi et al.<sup>1</sup> This behavior was also observed for the polymerization using different volumes of water.

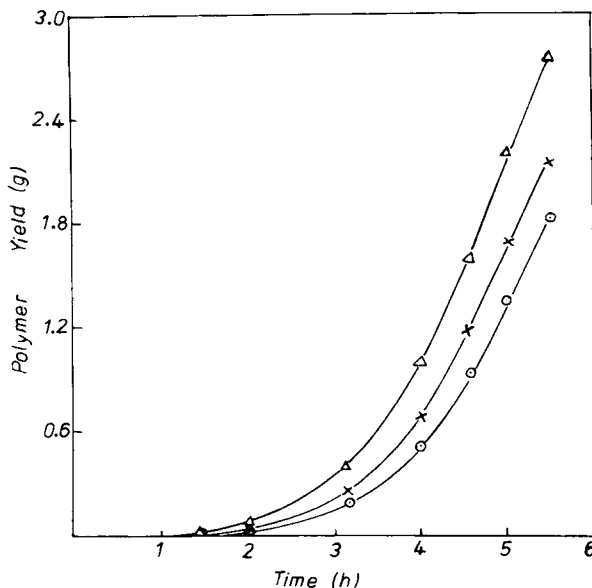


Fig. 1. Polymerization of EMA in a dilatometer of 1.6 cm i.d.: 86°C; 0.2 g IR-120 (Na<sup>+</sup>): EMA, 10 cc; H<sub>2</sub>O: (Δ) 2 cc; (×) 5 cc; (O) 10 cc.

In addition, the polymer yield decreased with increase in volume of water. This result may be accounted for by assuming that the propagation step of the polymerization reaction involved a chain reaction, with rapid addition of monomers to a small number of active sites. Monomer concentration decreased slowly during the reaction, with polymers of high molecular weight produced at low conversion.<sup>4,5</sup> The initial approximately zero rate might be due to the initial complete separation of the monomer from the resin initiator and is dependent on the volume of water present in the dilatometer, decreasing as the volume of water increased. The sharp increase in polymer yield that followed was expected kinetically.

### Effect of Water

Figures 1, 2, and 3 show that conversion to PEMA was highly influenced by the quantity of water that was present in the dilatometer. Figures 1 and 2, in particular, represent the results observed using the smallest-size dilatometer, 1.6 cm internal diameter. Over the range of volume of water studied, the percentage conversion of EMA to PEMA decreased as volume of water used in the polymerization increased. The decrease in the polymer yield with volume of water was more drastic below about 5 cc of H<sub>2</sub>O. This is seen as a deviation from the linear relationship between polymer yield and 1/volume of H<sub>2</sub>O (Fig. 2). This is true for 0.2 and 0.4 g of the resins used.

These results further confirm the observation previously made in the kinetic study and emphasize that the separation of the monomer from the initiator actually caused an initial delay in the polymerization. And until there was sufficient interaction of the monomer molecules with the initiator, a reaction that is influenced by the separation between the former and the latter, polymerization was impossible or reduced significantly. The results shown in Figure 3 for the

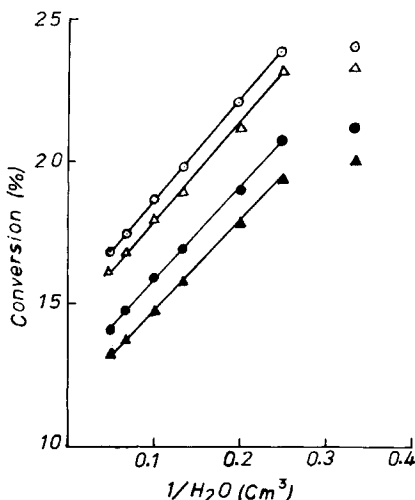


Fig. 2. Conversion vs. reciprocal  $H_2O$  volume for polymerization of 10 cc EMA: (▲) 0.2 g; (●) 0.4 g and 10 cc MMA; (△) 0.2 g, (○) 0.4 g IR-120 ( $Na^+$ ); under  $86^\circ C$ , 5 h, and with dilatometer 1.6 cm i.d.

dilatometer of 3.6 cm internal diameter are different, however. The polymer conversion increased with volume of water, and although the plot of conversion vs.  $1/\text{volume of } H_2O$  is linear, it has a negative slope. This is in agreement with the work of Ouchi et al.<sup>1</sup> but is in conflict with the results observed for the other two dilatometers in this work. This might be explained as due to the nearness of the monomer to the initiator, which allowed immediate and effective interactions between the monomer and the monomer and the initiator. The polymer yield increased to its highest value at about 10 cc  $H_2O$  and appeared to be insensitive to further increases in the volume of water. It is expected that this might be followed by a decrease in polymer yield when very large volumes of water are used as observed for the other two dilatometers.

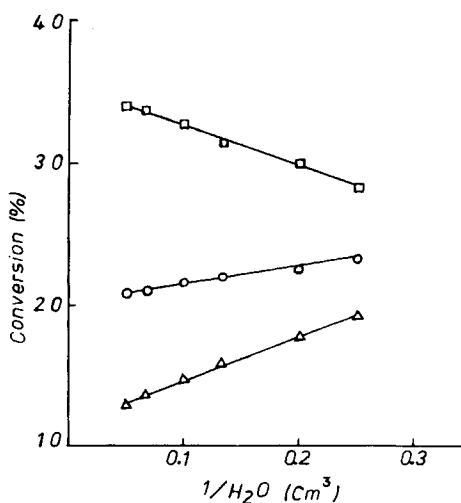


Fig. 3. Conversion vs. reciprocal  $H_2O$  volume for polymerization of 10 cc EMA: 0.2 g IR-120 ( $Na^+$ );  $86^\circ C$ ; 5 h, and dilatometers of (△) 1.6 cm i.d.; (○) 2.6 cm i.d.; (□) 3.6 cm i.d.

The viscosity-average molecular weight ( $\bar{M}_v$ ) of PEMA increased linearly with the volume of water used in the polymerization experiment, as shown in Figure 4 for 0.2 and 0.4 g Amberlite IR.120 resins, Na<sup>+</sup> form. The increase in  $\bar{M}_v$  with volume of water is faster with 0.4 g than with 0.2 g resin, as observed for the two dilatometers. The chain propagation reaction might be assumed to produce vertically growing polymer chains and is regarded as involving a diffusion mechanism. Consequently, there is a relationship between average degree of polymerization or average molecular weight and the volume of water through which diffusion occurred, assuming that only linear polymer molecules were produced.

### Effect of Size of Dilatometer

As shown in Figure 3, monomer conversion increased with increase in dilatometer size under the same polymerization conditions. Viscosity-average molecular weight ( $\bar{M}_v$ ) of PEMA also decreased with increase in size of the dilatometer, as seen in Figure 4. Figure 5 indicates that polymer yield increased with (1) the size of dilatometer for each weight of resin, as previously reported,<sup>6</sup> and (2) the resins weight, also in support of a previous study.<sup>1</sup> The polymer yield was found to be less strongly dependent on dilatometer size with smaller volumes of water under the same polymerization conditions, as evident by the results obtained with 5 and 10 cc H<sub>2</sub>O.

### Effect of Polystyrene Sulfonate Weight

Figures 2 and 5 indicate how monomer conversion and polymer yield respectively were affected by the quantity of the polystyrene sulfonate resins used in the polymerizations. Both the monomer conversion and polymer yield increased as the resin weight was increased. This was expected. Figure 4 shows that the

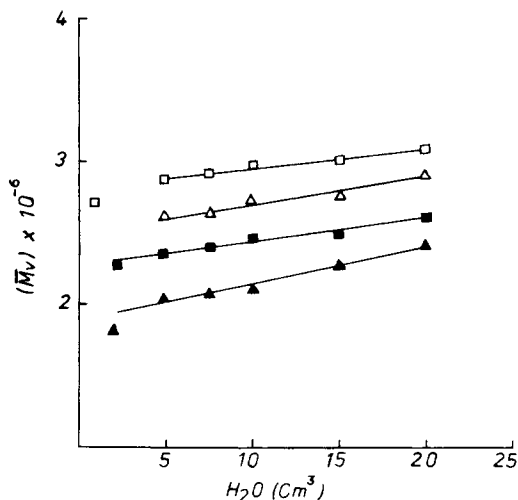


Fig. 4. Dependence of viscosity-average molecular weight ( $\bar{M}_v$ ) of PEMA on H<sub>2</sub>O volume: 86°C; 5 h; 10 cc EMA; (□) 0.2 g; (Δ) 0.4 g IR-120 (Na<sup>+</sup>) for dilatometer of 1.6 cm i.d. and (■) 0.2 g; (▲) 0.4 g IR-120 (Na<sup>+</sup>), for dilatometer of 3.6 cm i.d.

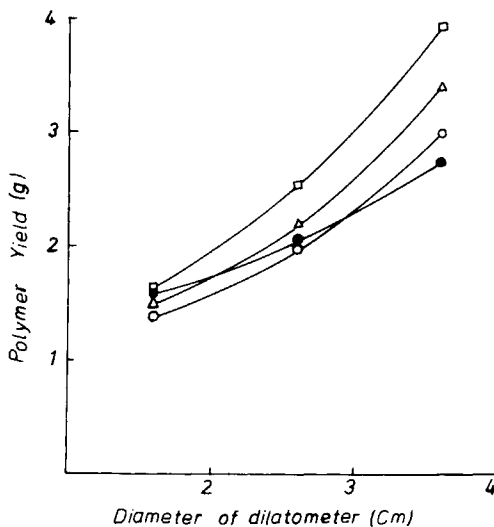


Fig. 5. Variation of yield of PEWA with size of dilatometer. Conditions: 86°C, 5 h, 10 cc EMA: (○) 0.2 g; (△) 0.3 g; (□) 0.4 g IR-120 (Na<sup>+</sup>), using 10 cc H<sub>2</sub>O and (●) 0.2 g IR-120 (Na<sup>+</sup>) using 5 cc H<sub>2</sub>O.

molecular weight of PEWA varied inversely as the weight of the resins used as initiator, in agreement with the recent results of Ouchi et al.<sup>1</sup> The above results were expected on the assumption that all the sites on the resins were active and could initiate the production of a monomer free radical EMA or MMA. Hence, termination of a growing polymer chain would occur more frequently since the number of monomer free radicals was large and directly proportional to the number of sites on the resins.

### Poly(methyl Methacrylate) (PMMA)

The results of the kinetic study of the polymerization of MMA are similar to those of EMA, except that the initial delay in the polymerization was shorter for MMA than for EMA. The graphs for the kinetic study of MMA polymerization are not presented. The conversion of MMA to PMMA at 86°C decreased with increased in volume of water but increased with resin weight (Fig. 2). The average degree of polymerization ( $\bar{P}_n$ ) of PMMA also decreased with increase in resin weight and dilatometer size but increased with volume of water (Figs. 6 and 7). The dependence of the  $\bar{P}_n$  of PMMA on the volume of water used in the polymerization was more pronounced when the polymerization was carried out in the dilatometer 3.6 cm in diameter than in the one 1.6 cm in diameter. The actual value of  $\bar{P}_n$  is much higher for the products obtained using the smallest dilatometer (1.6 cm in diameter). The results for the medium-size dilatometer (2.6 cm in diameter) have been omitted for clarity, but lie between those of the largest and smallest dilatometers. The results obtained for the polymerization of MMA generally agree with those of Ouchi et al.<sup>1</sup>, though the initiators used were not exactly the same.

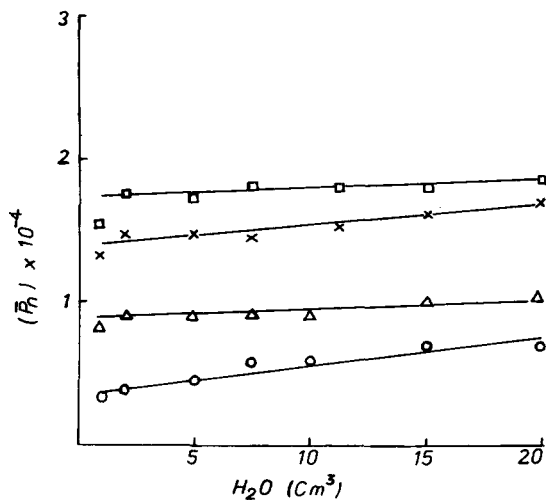


Fig. 6. Dependence of average degree of polymerization of PMMA on H<sub>2</sub>O volume used in the polymerization under 86°C, 5 h, 10 cc MMA. For dilatometer of 1.6 cm i.d., (□) 0.2 g; (×) 0.4 g IR-120 (Na<sup>+</sup>) and for dilatometer of 3.6 cm i.d.; (Δ) 0.2 g; (○) 0.4 g IR-120 (Na<sup>+</sup>).

### Comparison of Results PEMA and PMMA

Except for the conversion and the average degree of polymerization (or viscosity-average molecular weight), the polymerization of EMA and MMA in a dilatometer using cation exchange resins (sulfonated polystyrene, sodium form) as initiator followed essentially the general patterns described in Figures 1-5. For the same conditions of polymerization, the yield of PMMA was higher than that of PEMA (Table 1). This might be due to a difference in the general reactivity ( $Q$ ) of the monomer, being higher for methylmethacrylate.<sup>7</sup>

The molecular weight of PEMA was much higher than that of PMMA produced under the same polymerization conditions. This might be due to differences in the extent of the propagation in the polymerization of the respective monomers. Presumably the termination of a growing PEMA chain was slower than that of a growing PMMA chain, if the two chains were assumed to grow at the same rate. The alternative is that the rate of propagation of a PEMA chain

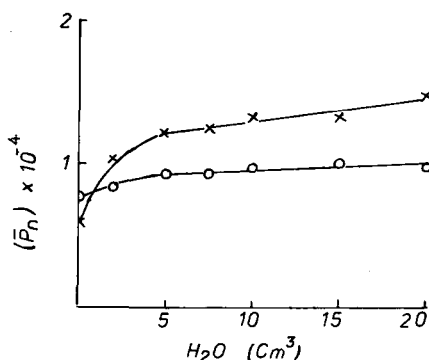


Fig. 7. Dependence of average degree of polymerization of PMMA on H<sub>2</sub>O volume used in the polymerization under 86°C, 5 h, 20 cc MMA, dilatometer of 3.6 cm i.d.; (×) 0.2 g; (○) 0.8 g IR-120 (Na<sup>+</sup>).

TABLE I  
Polymerization of Vinyl Monomers Initiated by Different Types of Sulfonated Polystyrene<sup>a</sup>

| Resin type                            | Mesh size | Conversion, % |       |       |       |       |
|---------------------------------------|-----------|---------------|-------|-------|-------|-------|
|                                       |           | EMA           | MMA   |       | VAc   |       |
|                                       |           | 0.2 g         | 0.4 g | 0.2 g | 0.4 g | 0.4 g |
| Amberlite IR-120 (Na <sup>+</sup> )   | 14-52     | 19.81         | 15.91 | 17.96 | 18.55 | —     |
| Zeo Kerb 225 SRC10 (Na <sup>+</sup> ) | 52-100    | 21.22         | 21.80 | 24.25 | 21.12 | —     |
| Amberlite CG-120 (Na <sup>+</sup> )   | 400       | 25.16         | 25.12 | 28.24 | 29.00 | —     |
| Amberlite IR-120 (H <sup>+</sup> )    | 14.52     | 12.73         | —     | 15.20 | —     | —     |

<sup>a</sup> Conditions: 10 cc monomer; 10 cc H<sub>2</sub>O; 86°C; 5 h.

might be faster than that of a PMMA chain. In either case, termination is assumed to be by the combination of a monomer radical and a polymer radical. Its rate is expected to vary directly with the reactivity of the monomer and hence the concentration of the monomer radicals.

Polymerization of both EMA and MMA was possible using the hydrogen form of the sulfonated polystyrene as initiator. The results in Table I also indicate that the percentage conversion to polymer was greater when the sodium form of the sulfonated polystyrene was used as initiator for polymerizing EMA or MMA. Again the yield of PMMA was greater than that of PEMA for polymerization under the same conditions. Monomer conversion was found to be highly dependent on mesh size of the resins and increased somehow with it. This was expected, as the number of the available —SO<sub>3</sub><sup>-</sup> effective sites on the resins for the initiation step of the polymerization also increased with increase in resin mesh size. Monomer conversion could be seen here as a colligative property of the system and therefore would be dependent on the number of particles, in ideal behavior. Polymerization of VAc was not achieved using sulfonated polystyrene as initiator, as shown in Table I. This might be due to the fact that VAc is highly electron rich and the initiation step was not favorable. Also, at the temperature of polymerization (86°C), VAc might have been mainly in the vapor phase, thus making polymerization impossible.

## CONCLUSIONS

This work has shown that polymerization of EMA and MMA in a dilatometer using polystyrene sulfonate (Na<sup>+</sup> and H<sup>+</sup> forms) is possible. The conversion of the monomer to the polymer is negligibly slow at first but increases very sharply and approximately linearly with time. The conversion is faster for MMA than for EMA and is largely determined by the amount of water used in the polymerization, with all other polymerization conditions kept constant. The monomer conversion is highly dependent on the mesh size of the resin, increasing as the former increases.

The polymer produced has a high molecular weight which depends on (1) the volume of water used for the polymerization, (2) the size of the dilatometer, and (3) the quantity of resins used. Under the same conditions of polymerization, PEMA formed has a higher molecular weight than PMMA. It was not possible to polymerize vinyl acetate in a dilatometer using polystyrene sulfonate (Na<sup>+</sup>) as initiator under the same conditions that EMA and MMA were polymerized. Work is in progress to establish the mechanisms of the polymerization of EMA and MMA reported here.



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