

Vinyl polymerization: 414. Polymerization of vinyl monomer initiated by poly(*N,N,N*-trimethyl-*N*-2-methacryloxyethyl)ammonium chloride

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(Received 25 December 1982; revised 25 April 1983)

The polymerization of vinyl monomer initiated by an aqueous solution of poly(*N,N,N*-trimethyl-*N*-2-methacryloxyethyl)ammonium chloride (poly(Q-DMAEM-Cl)) has been carried out at 85°C. The effects of the amounts of vinyl monomer, poly(Q-DMAEM-Cl) and water on the conversion of vinyl monomer have been studied. The overall activation energy in the polymerization of MMA is estimated as 41.9 kJ mol⁻¹. The polymerization proceeds through a radical mechanism. The location in which the polymerization occurs is discussed. The selectivity for vinyl monomer is explained by 'the concept of hard and soft hydrophobic areas and monomers'.

Keywords Poly(*N,N,N*-trimethyl-*N*-2-methacryloxyethyl)ammonium chloride; methyl methacrylate; hydrophobic areas; radical polymerization; overall activation energy; selectivity for vinyl monomer

INTRODUCTION

It has been established that anion-type macromolecular electrolytes such as sodium poly(2-methyl-2-propene-1-sulphonate)¹, sodium poly(2-propene-1-sulphonate)², sodium polystyrenesulphonate (PSS-Na)³, sodium polyethylenephosphate⁴, sodium poly-*p*-vinylphenolate⁵, poly(styrene-co-sodium acrylate)⁶, poly(methyl methacrylate-co-sodium methacrylate)⁶, and poly(styrene-slaternative-disodium maleate)⁷ can polymerize vinyl monomers, especially methyl methacrylate (MMA), in water without an ordinary initiator through a radical mechanism.

Furthermore, in the preceding paper, it has been reported that poly(vinylbenzyltrimethyl) ammonium chloride as a typical macromolecular electrolyte of cation-type can also polymerize vinyl monomers in water without the usual initiator⁸.

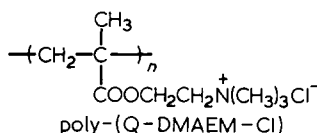
This paper is concerned with the polymerization of vinyl monomer by poly(*N,N,N*-trimethyl-*N*-2-methacryloxyethyl) ammonium chloride (poly(Q-DMAEM-Cl)) as a cation-type macromolecular electrolyte. By 'the concept of hard and soft hydrophobic areas (HA) and monomers'^{6,7}, the selectivity for vinyl monomer is discussed.

EXPERIMENTAL

Poly(Q-DMAEM-Cl)

Poly(Q-DMAEM-Cl) was obtained from the polymerization of corresponding vinyl monomer supplied by Mitsubishi Rayon Co. Ltd. in water using potassium

persulphate as an initiator. It was dialysed thoroughly against water and then lyophilized.



$$\begin{aligned} [\eta]_{0.5\text{N-NaCl aq.}}^{25^\circ\text{C}} &= 3.82(\text{poly(Q-DMAEM-Cl)-1}) \\ &= 0.87(\text{poly(Q-DMAEM-Cl)-2}) \end{aligned}$$

The occurrence of a peroxide group or metallic ion in the poly(Q-DMAEM-Cl) could not be observed by the KI method or fluorescence X-ray analysis. Moreover, it was confirmed by an e.s.r. spectrum that the radical was not included in the poly(Q-DMAEM-Cl). Although poly(Q-DMAEM-Cl)-2 was used in the polymerization to obtain the time-conversion curve, poly(Q-DMAEM-Cl)-1 was used in all other polymerizations.

Other reagents

Methyl methacrylate (MMA), styrene (St), acrylonitrile (AN), and other monomers were purified by the usual methods. Water was ion-exchanged and distilled. The other materials were of special commercial grade and used without further purification.

Procedure

Vinyl monomer and an aqueous solution of poly(Q-DMAEM) were placed in a tube. The tube was sealed *in vacuo* after thawing with nitrogen and heated at 85°C with

or without shaking. The reacted solution was poured into 300 cm³ of methanol to precipitate the polymerized product and then six drops of conc. H₂SO₄ was added to perfect the precipitate of poly(Q-DMAEM-Cl). After drying the product at 80°C *in vacuo*, the conversion was calculated by the following equation:

$$\text{Conversion (\%)} = \frac{\text{wt. of product (g)} - \text{wt. of poly(Q-DMAEM-Cl) used (g)}}{\text{wt. of monomer used (g)}} \times 100 \quad (1)$$

The efficiency of grafting (E.G.) of MMA onto poly(Q-DMAEM-Cl) was obtained by extracting homopoly (MMA) with benzene for 50 h using a Soxhlet extractor. E.G. was calculated by following equation:

$$\text{E.G.} = \frac{\text{wt. of total poly(MMA) (g)} - \text{wt. of homopoly(MMA) (g)}}{\text{wt. of total poly(MMA) (g)}} \times 100 \quad (2)$$

The number-average degree of polymerization (\bar{P}_n) of poly(MMA) was calculated by Welch's equation⁹ from the intrinsic viscosity measured in benzene at 30°C.

RESULTS AND DISCUSSION

Polymerization of vinyl monomers

The results of the polymerizations of five types of vinyl monomer by poly(Q-DMAEM-Cl) are summarized in Table 1. It was evident that poly(Q-DMAEM-Cl) had the initiating ability for the vinyl polymerizations. Here the conversions in the absence of poly(Q-DMAEM-Cl) mean those of the thermal polymerizations. Accordingly, the conversion was concluded to increase in the order: AN > VAc > MMA > *i*-BMA > St. This selectivity of vinyl monomer is discussed later.

Proof of radical mechanism

To conform that the polymerization proceeds through a radical mechanism, the copolymerization of MMA(M₁) with St(M₂) was carried out and the results shown in Figure 1 were obtained. From the curve, r_1 and r_2 were calculated as 0.53 and 0.56, respectively.

Into a mixture of 3 cm³ of MMA, 0.04 g of poly(Q-DMAEM-Cl)-1, and 10 cm³ of H₂O, 0.1 g of radical scavenger [hydroquinone (HQ), 2,2-diphenyl-1-picrylhydrazyl (DPPH), or 1,3,5-triphenylverdazyl (TPV)] was added and then the system was shaken at 85°C for 3 h. The results in Table 2 show that these radical scavengers inhibit the polymerization. Thus, it was concluded that the polymerization proceeds through a radical mechanism.

Estimation of overall activation energy

Time-conversion curves were obtained by carrying out

Table 1 Selectivity of vinyl monomer^a

Monomer	Conversion (%)	
	No poly(Q-DMAEM-Cl)	poly(Q-DMAEM-Cl) ^b
MMA	0.63	8.63
St	1.96	6.63
AN	0	12.77
<i>i</i> -BMA	0.69	5.93
VAc	0	8.71

^a Monomer, 3 cm³; H₂O, 10 cm³; 85°C; 3 h; with shaking

^b poly(Q-DMAEM-Cl)-1, 0.04 g

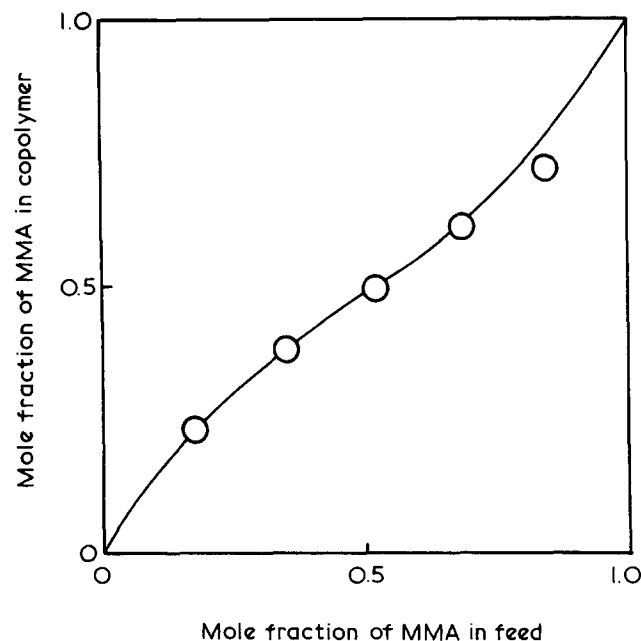


Figure 1 Copolymerization of MMA(M₁) with St(M₂). Monomer, 3 cm³; poly(Q-DMAEM-Cl)-1, 0.04 g; H₂O, 10 cm³; 85°C; 3 h; with shaking

Table 2 Effect of radical scavenger on the polymerization of MMA^a

Radical scavenger (g)	Conversion (%)
HQ 0.1	0
DPPH 0.1	0
TPV 0.1	0
None	8.63

^a MMA, 3 cm³; poly(Q-DMAEM-Cl)-1, 0.04 g; H₂O 10 cm³; 85°C; 3 h; with shaking

polymerizations at 75–90°C with a system of 3 cm³ of MMA and 10 cm³ of H₂O in the presence or absence of 0.04 g of poly-Q-DMAEM-Cl-2. The results obtained are shown in Figure 2. Non induction period was observed and there were the rectilinear relations between the polymerization time and the conversion. Thus, the rate of polymerization (R_p) of MMA was calculated by equation (3):

$$R_p \text{ (g h}^{-1}\text{)} = \frac{\left[\frac{\text{wt. of overall poly(MMA) obtained in the presence of poly(Q-DMAEM-Cl)}}{\text{wt. of poly(Q-DMAEM-Cl)}} \right] - \left[\frac{\text{wt. of poly(MMA) obtained in the absence of poly(Q-DMAEM-Cl)}}{\text{wt. of poly(Q-DMAEM-Cl)}} \right]}{\text{time (h)}} \quad (3)$$

On applying the values of R_p to the Arrhenius equation, a good rectilinear relation shown in Figure 3 was obtained. From the slope of this line, the overall activation energy was calculated to be 41.9 kJ mol⁻¹.

Necessity of water

Keeping the amount of MMA and poly(Q-DMAEM-Cl) constant at 3 cm³ and 0.04 g, respectively, the polymerizations of MMA were carried out with shaking in the presence and absence of 10 cm³ of H₂O. The former and latter conversions were obtained as 8.63 and 0.95%, respectively. The conversion of 0.95% corresponded to that of MMA by thermal polymerization. Thus, the co-existence of water is concluded to be indispensable.

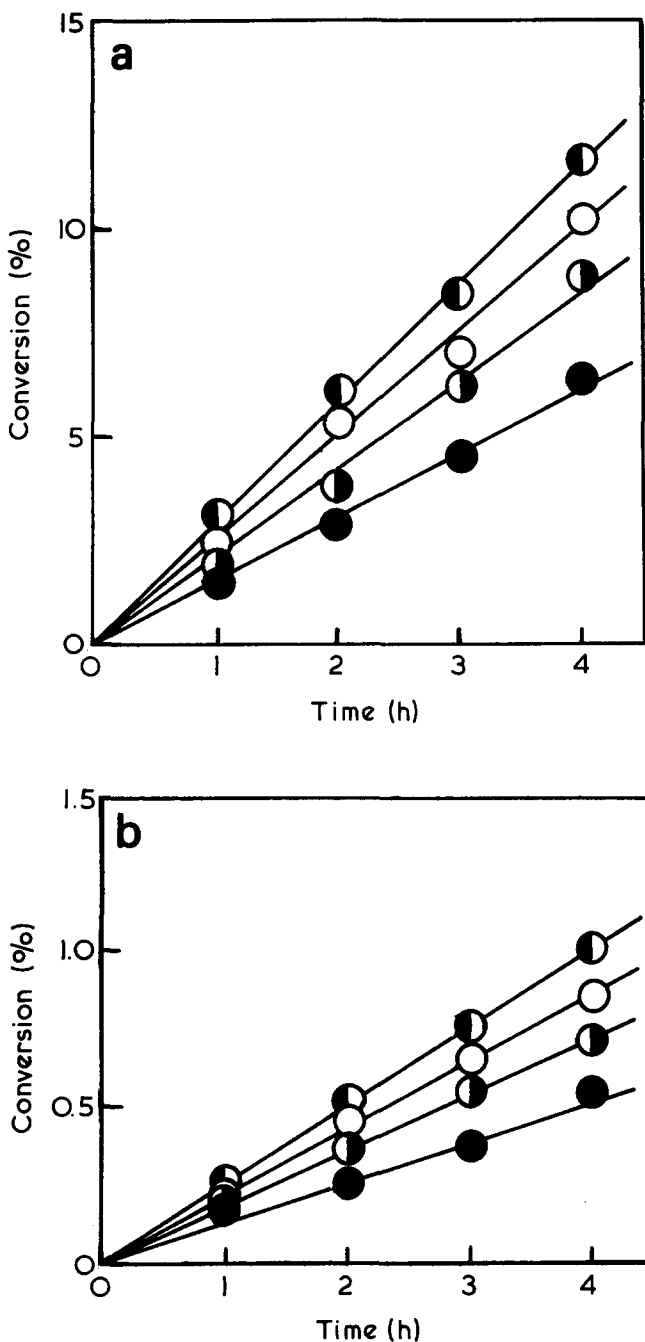


Figure 2 Time-conversion curves. MMA, 3 cm³; H₂O, 10 cm³; with shaking; ●, 75°C; ○, 80°C; ○, 85°C; ○, 90°C. (a) Polymerization in the presence of 0.04 g of poly(Q-DMAEM-Cl)-2; (b) polymerization in the absence of poly(Q-DMAEM-Cl)-2

Phase where the polymerization takes place

To observe the locale where the polymerization proceeds, the polymerization of MMA, St and AN were carried out without shaking. The reaction tubes were allowed to stand at 85°C for 3 h. After the polymerizations, the upper clear layers were pipetted out and poured into methanol. Also the muddy aqueous layers were poured into methanol. The results are shown in Table 3.

The conversions in the monomer layers were due to thermal polymerizations. Accordingly, it was concluded that the polymerization by poly(Q-DMAEM-Cl) was initiated, propagated and terminated in the water layer.

Formation of hydrophobic areas

The direct evidence of the formation of hydrophobic areas (HA) was obtained by scanning electron microscopy. The results are shown in Figure 4.

As mentioned previously, the presence of water was indispensable. The reason for this is that water is necessary for the formation of HA in which the polymerization proceeds. Thus, the process of polymerization is concluded to be as follows: (1) poly(Q-DMAEM-Cl) forms HA in the aqueous phase, (2) Vinyl monomer is incorporated into the HA, (3) in the HA, the polymerization commences.

Effect of the amount of monomer on the polymer yield

The polymerizations (MMA and AN) in the presence of 0.04 g of poly(Q-DMAEM-Cl)-1 and 10 cm³ of H₂O were carried out at 85°C for 3 h with shaking at various amounts of monomers. The results are shown in Figure 5. Beyond some amounts of monomer used, the polymer yields of MMA and AN were constant in spite of the varied amounts of monomers. This is attributed to the polymerization occurring in certain limited areas, i.e., in HA formed by poly(Q-DMAEM-Cl) in the aqueous solution. As the amount of MMA, which is incorporatable into HA, is smaller than that of AN, the polymer yield of MMA becomes constant at smaller amounts of monomer used than that of AN, i.e., these results can be explained by the concept of hard and soft HA and monomers^{6,7}.

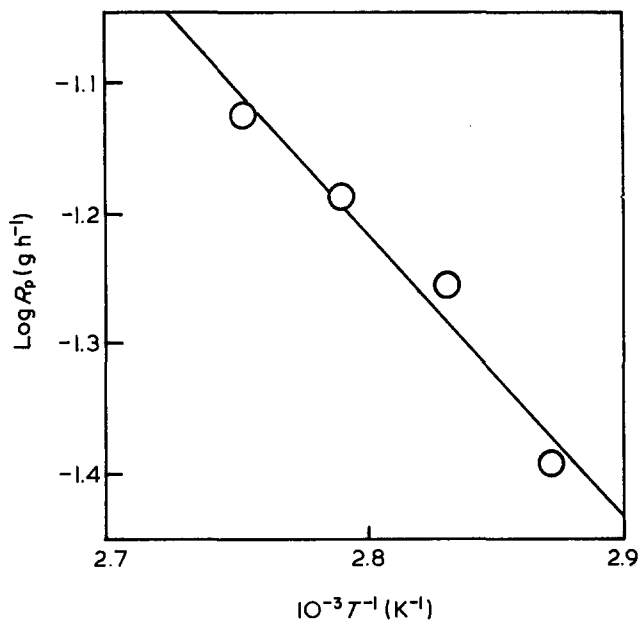


Figure 3 Arrhenius plots for the polymerization of MMA with poly(Q-DMAEM-Cl)

Table 3 Polymerizations of St and MMA without shaking^a

Monomer	Conversion (%)	
	Water layer	Monomer layer
MMA	12.59	0.70
St	0.89	1.64
AN	6.82	0

^a Monomer, 3 cm³; poly(Q-DMAEM-Cl)-1, 0.04 g; H₂O, 10 cm³; 85°C; 3 h

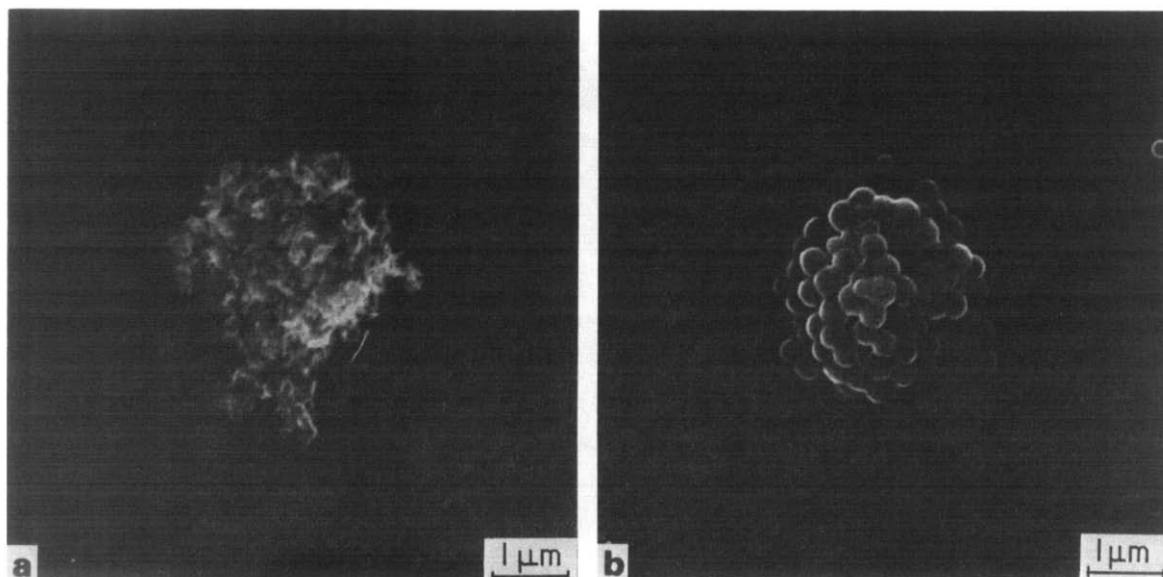


Figure 4 Surface views of poly(Q-DMAEM-Cl). Poly(Q-DMAEM-Cl)-1, 0.04 g; H₂O, 10 cm³; 85°C; 3 h without shaking. After the polymerization the system diluted with 500 cm³ of H₂O. (a) Before polymerization; (b) after polymerization

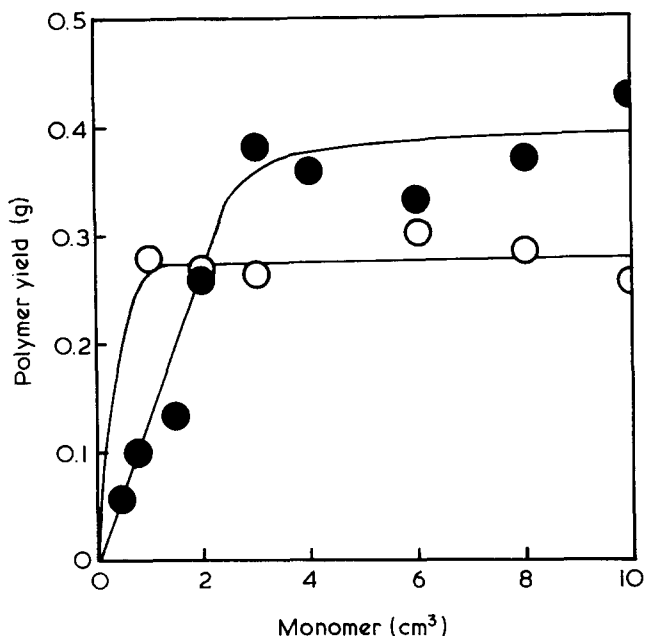


Figure 5 Polymer yield versus amount of monomer. Poly(Q-DMAEM-Cl)-1, 0.04 g; H₂O, 10 cm³; 85°C; 3 h; with shaking; ○, MMA; ●, AN

Effect of amount of poly(Q-DMAEM-Cl) on the polymerization

The polymerizations of MMA and AN were carried out in water at 85°C with shaking, with various amounts of poly(Q-DMAEM-Cl). The results are shown in Figure 6. It is clear that the conversions of MMA and AN increase with the amount of poly(Q-DMAEM-Cl).

Figure 7 shows the effect of the amount of poly(Q-DMAEM-Cl) on the efficiency of grafting (E.G.) and \bar{P}_n of homopolymer produced in the polymerization of MMA. Although E.G. increased with the amount of poly(Q-DMAEM-Cl), \bar{P}_n of poly(MMA) was almost independent of the amount of poly(Q-DMAEM-Cl).

Initiation mechanism

As mentioned previously, the monomer is incorporated into HA and there, polymerization commences. According to the concept of hard and soft hydrophobic area (HA) and monomers^{6,7}, a hard HA prefers to incorporate a hard monomer and a soft HA prefers to incorporate a soft monomer. Poly(Q-DMAEM-Cl) can be considered to form the soft HA in the water layer. The hardness or softness of a monomer can be represented by its solubility in water. Figure 8 shows the relation between the corrected conversion and the solubility of monomer⁶. As the solubility of monomer is parallel to the conversion,

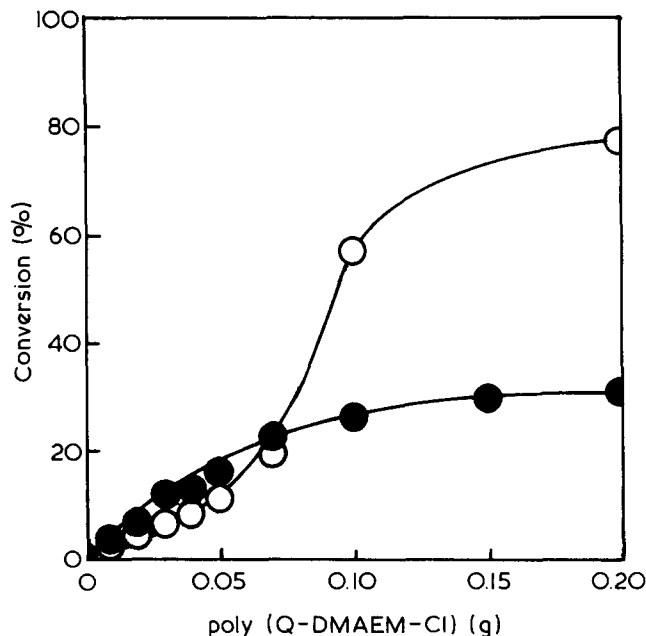


Figure 6 Effects of the amount of poly(Q-DMAEM-Cl)* on the polymerizations of MMA and AN. Monomer, 3 cm³; H₂O, 10 cm³; 85°C; 3 h; with shaking; ○, MMA; ●, AN; *poly(Q-DMAEM-Cl)-1. *Corrected conversion = [Conversion in the presence of poly(Q-DMAEM-Cl)] - [Conversion in the absence of poly(Q-DMAEM-Cl)]

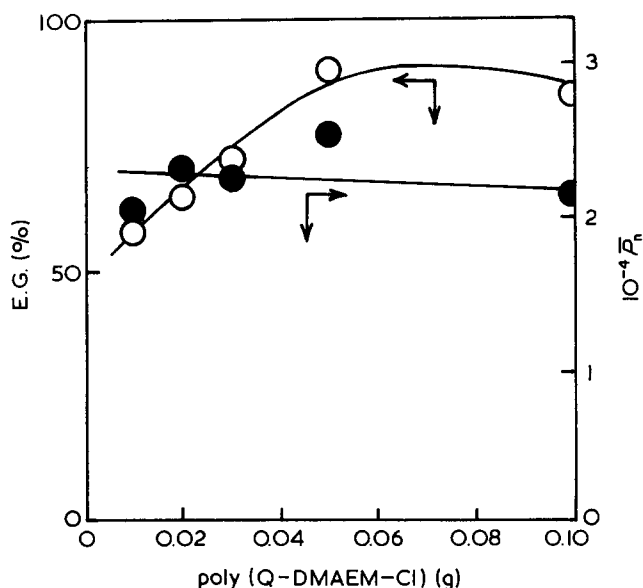


Figure 7 Effects of the amount of poly(Q-DMAEM-Cl)* on the efficiency of grafting and \bar{P}_n of poly(MMA). MMA, 3 cm³; H₂O, 10 cm³; 85°C; 3 h; with shaking; *poly(Q-DMAEM-Cl)-1. *Corrected conversion = [Conversion in the presence of poly(Q-DMAEM-Cl)] - [Conversion in the absence of poly(Q-DMAEM-Cl)]

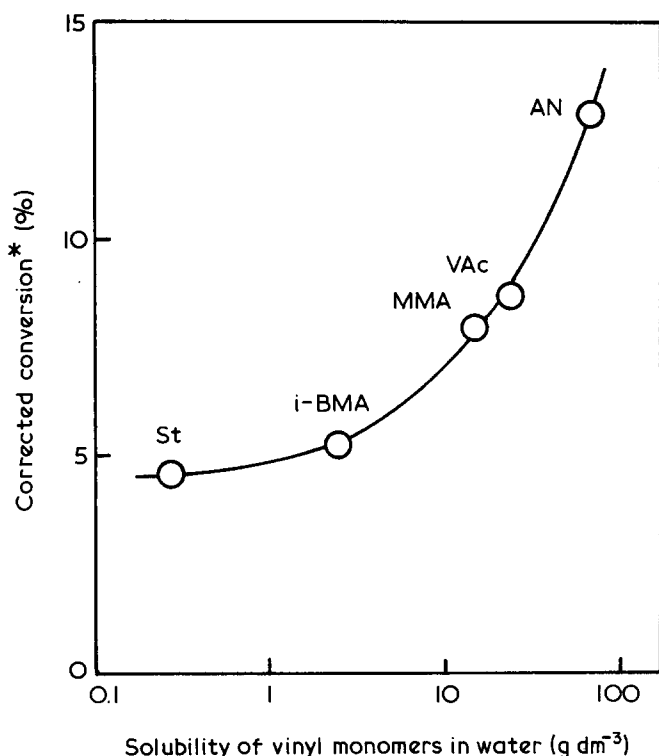
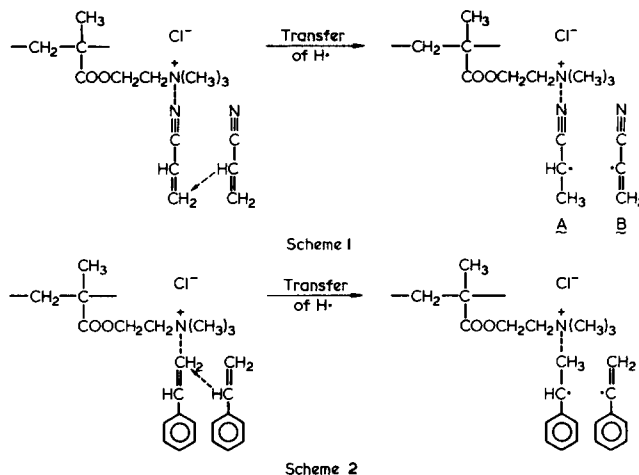


Figure 8 Corrected conversion* versus solubility of vinyl monomer. MMA, 3 cm³; H₂O, 10 cm³; 85°C; 3 h; with shaking. *Corrected conversion = [Conversion in the presence of poly(Q-DMAEM-Cl)] - [Conversion in the absence of poly(Q-DMAEM-Cl)]

the concept of hard and soft HA and monomers is considered to be applicable to the explanation of the relation.

The initiation mechanism is assumed to be as follows: First, the electron-rich part of the monomer is adsorbed on the plus-charged ammonium nitrogen atom in poly(Q-DMAEM-Cl). Then the adsorbed monomer reacts with a free monomer as shown in Schemes 1 or 2. The present mechanism is consistent with that for the uncatalysed polymerization of AN in the aqueous solution of polyethyleneglycol (PEG) where radicals of A and B were detected by the spin-trapping method^{10,11}. Therefore, the hydrogen-transfer mechanism also seems to be applicable to the present case, being similar to the case of PEG.



ACKNOWLEDGEMENT

The authors express sincere thanks to Mitsubishi Rayon Co. Ltd. for providing monomeric Q-DMAEM-Cl.

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