Copolymerization of a novel substituted methacrylamide with methyl methacrylate

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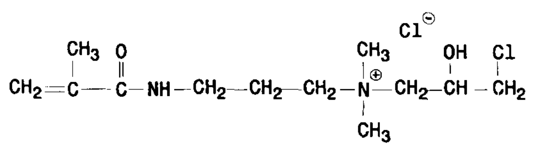
The copolymerization behaviour of the adduct of N',N'-dimethylaminopropyl methacrylamide and epichlorohydrin (DMAPMA-Epi) and methyl methacrylate (MMA) was investigated. The reactivity ratios for the MMA (**1**)/DMAPMA-Epi (**2**) couple in solution, using various regression methods based on the Mayo–Lewis model, are $r_1 = 1.73$ and $r_2 = 0.03$. The Q and e values for DMAPMA-Epi are estimated to be 0.23 and -1.32 respectively. On the basis of the reactivity ratios, theoretical curves for the instantaneous copolymer composition throughout conversion have been calculated.

(Keywords: copolymerization; reactivity ratios; methacrylamide)

Introduction

The monomer N',N'-dimethyl-N'-(3-chloro-2-hydroxypropyl)-N'-methacrylamido-3-propylammonium chloride (DMAPMA-Epi) is the basis for a broad range of commercial applications, such as concrete admixtures, cementitious paints, anti-corrosive coatings and adhesives.



$CH_2{=}C(CH_3){-}C({=}O){-}NH{-}CH_2{-}CH_2{-}CH_2{-}\overset{\oplus}{N}(CH_3)_2{-}CH_2{-}CH(OH){-}CH_2Cl \quad Cl^{\ominus}$

DMAPMA-Epi

For these applications it is copolymerized in emulsion with a variety of acrylic or vinyl ester monomers, yielding polymer latices with high solids content and low viscosity.

Methacrylamide monomers containing quaternary salts have been utilized as monomers in hydrogels. These gels can undergo large volume changes when the swelling medium is altered. Networks containing negative charges undergo much stronger phase transitions than those containing positive charges. One of the reasons for this behaviour is suggested to be 'unfavourable copolymerization parameters' for the monomers containing a positive charge[1]. Copolymer microstructure, namely alternating *versus* block monomer sequences, has a great influence on hydrodynamic dimensions and, subsequently, rheological behaviour[2]. The authors are currently engaged in studies on emulsion polymers containing DMAPMA-Epi, and part of this work has been devoted to an investigation of its copolymerization behaviour.

An important feature of DMAPMA-Epi is that after copolymerization it can be crosslinked at ambient temperatures under alkali conditions. At pH >9 the terminal chlorohydroxyl group reacts to form an epoxide group which can undergo epoxy reactions, resulting in a crosslinked polymer network.

The purpose of this study was to investigate the copolymerization behaviour of the adduct of N',N'-dimethylaminopropyl methacrylamide (DMAPMA) and epichlorohydrin (Epi), and methyl methacrylate (MMA).

Experimental

Synthesis of DMAPMA-Epi. DMAPMA-Epi is synthesized[3] from the monomer DMAPMA. DMAPMA is acidified in aqueous solution by the slow addition of concentrated hydrochloric acid over 2 h, maintaining the temperature below 30°C to prevent polymerization via the double bond. Epichlorohydrin is added slowly over 2.5 h, maintaining the temperature between 30 and 35°C. Unreacted epichlorohydrin and other by-products are removed by liquid/liquid extraction with ethyl acetate. The reaction mechanism is shown in *Figure 1.*

Copolymerization. The nominal compositions of the reaction mixtures used in the reactivity ratio determination are listed in *Table 1.* The reaction mixtures, containing accurately known weights of monomers (MMA and DMAPMA-Epi), initiator (benzoyl peroxide) and solvent (ethanol), were placed in a 50 ml glass test-tube and deoxygenated with nitrogen for 10 min. The tubes were tightly sealed and placed in a thermostated water bath at 60 ± 1°C. After approximately 1.5 h, the reaction mixtures were cooled and precipitated in a seven-fold excess (by volume) of isopropanol and then reprecipitated after dissolving in methanol. The copolymers were then redissolved in methanol for analysis. The experiment was run in duplicate, and in all cases the conversion was measured to be less than 5%.

Compositional analysis. The copolymer composition was measured using ^{13}C n.m.r. on a Bruker AM500 n.m.r.

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spectrometer operating at 125.77 MHz. Inverse gated decoupling, as well as composite pulse ^1H decoupling, was used to obtain quantitative spectra. The acquisition time was 557 ms with a 75° pulse angle and a relaxation delay of 4 s.

The concentration of the samples was approximately 10–20 wt% copolymer in methanol. At this concentration the spectra are dominated by solvent peaks, resulting in only a fair signal-to-noise ratio.

Peak sizes were measured using an integrator function on a PC-based spectrum analyser program. Each peak was measured 10 times and averaged.

The DMAPMA-Epi proportion in the copolymers was obtained from the two peaks in the region around $\delta = 66$ ppm, peak 1 in *Figure 2*. No unique peaks suitable for quantitative analysis were found for MMA. As such, the MMA content was calculated by difference from peaks at $\delta = 52$ and 45 ppm, peaks 2 and 3, respectively, in *Figure 2*. Residual DMAPMA-Epi monomer in the samples was measured from the peak at $\delta = 140$ ppm and found to be very small in most cases. The absence of residual MMA monomer was assumed.

Results and discussion

Reactivity ratio calculation. The reactivity ratios were calculated using the procedures of Fineman–Ross[4], Kelen–Tüdös[5], curve fitting[6], and the error-in-variables model (EVM)[7]. The results are listed in *Table 2*.

The ellipse in *Figure 3* is the joint 95% confidence

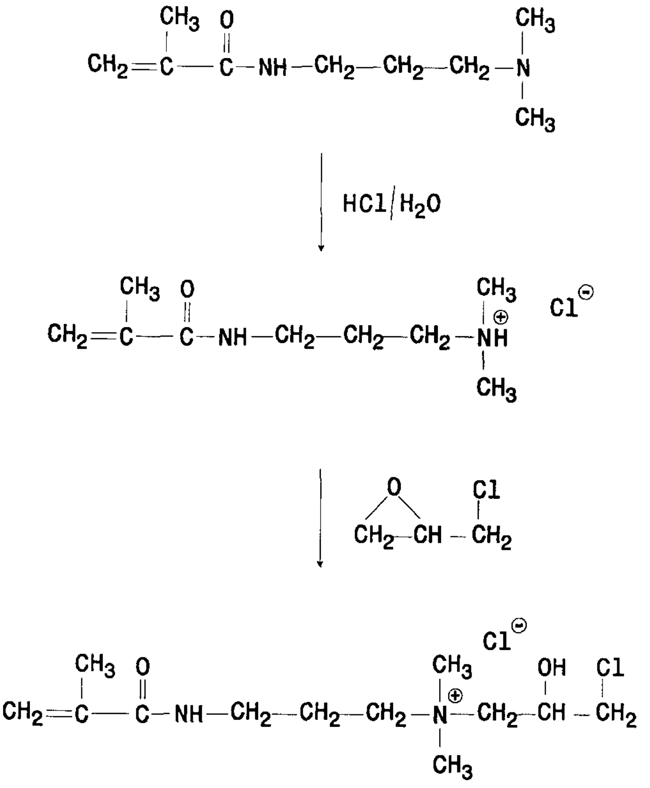

Figure 1 Mechanism for DMAPMA-Epi synthesis from DMAPMA

Table 1 Composition of reaction mixtures

	Sample number					
	1	2	3	4	5	6
Initiator, BP (g)	0.05	0.05	0.05	0.05	0.05	0.05
Solvent, EtOH (g)	12.6	13.5	14.3	15.1	15.9	16.7
MMA (g)	1.0	2.0	3.0	4.0	5.0	6.0
DMAPMA-Epi (g)	16.4	14.5	12.7	10.9	9.1	7.3

Table 2 Reactivity ratios for MMA (1)/DMAPMA-Epi (2)

Procedure	r_1	r_2
Fineman–Ross[4]	1.60	−0.06
Kelen–Tüdös[5]	1.67	−0.01
Curve fitting[6]	1.78	0.04
EVM[7]	1.73	0.03

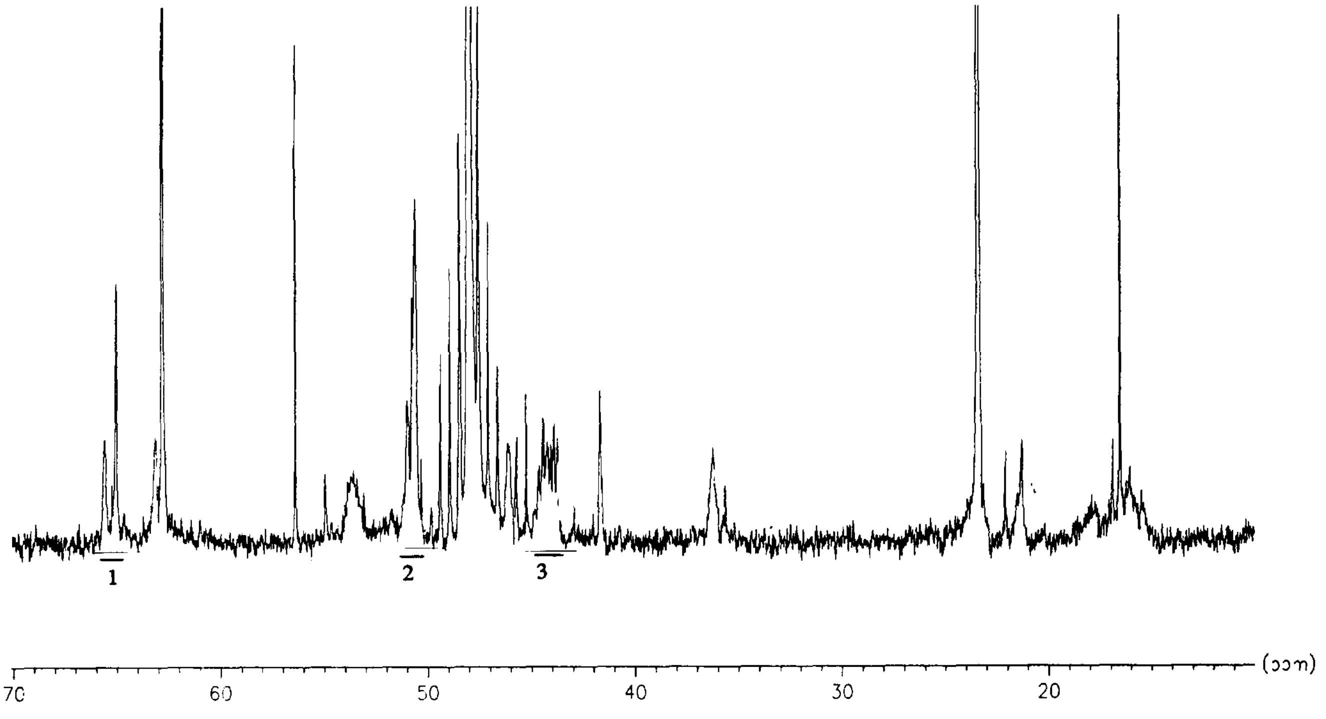

Figure 2 ^{13}C n.m.r. spectrum of sample number 2 in CH_3OH. Residual IPOH present from precipitation of copolymer

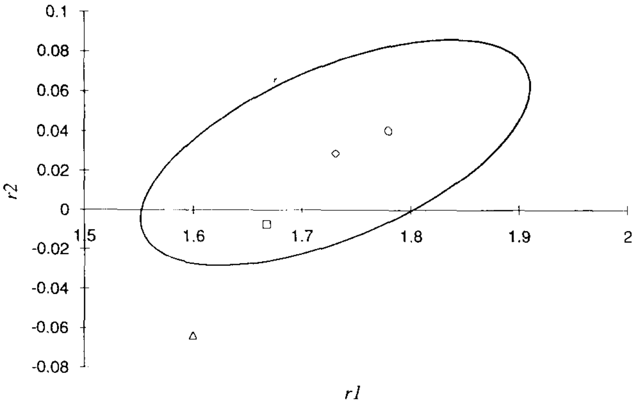

Figure 3 Comparison of calculated reactivity ratios: △, Fineman–Ross; □, Kelen–Tüdös; ○, curve fitting; ◇, EVM. The ellipse shows the 95% confidence interval as calculated by EVM

interval for the reactivity ratios as calculated by EVM. The Kelen–Tüdös and curve fitting results are well within this region, but the Fineman–Ross result is significantly different.

The *Q* and *e* values[8] for DMAPMA-Epi were calculated to be 0.23 and −1.32, respectively, from literature values for MMA[9]. The large negative value for *e* indicates a degree of repulsion between like monomer groups.

Theoretical predictions. Using the reactivity ratios calculated by EVM, theoretical predictions are made about compositional drift during copolymerization and monomer sequence length distribution.

(a) Compositional drift. For almost all copolymerizations, the monomer feed and copolymer compositions are different. The large disparity between the reactivity ratios results in considerable compositional drift as the copolymerization proceeds to high conversion. The Skeist[10] equation is used to determine the instantaneous copolymer composition as a function of conversion for any given monomer feed:

$$\ln \frac{[\mathrm{M}]}{[\mathrm{M}_0]} = \int_{f_1^0}^{f_1} \frac{\mathrm{d}f_1}{F_1 - f_1} \qquad (1)$$

where [M] is the monomer concentration, f_1 is the fraction of monomer 1 in the monomer feed, and F_1 is the fraction of monomer 1 in the copolymer. This equation has been integrated by Meyer and Lowry[11] to give the following expression, which relates the degree of conversion to changes in the feed composition and reactivity ratios:

$$x = 1 - \frac{\mathrm{M}}{\mathrm{M}_0} = 1 - \left(\frac{f_1}{f_1^0}\right)^{\alpha}\left(\frac{f_2}{f_2^0}\right)^{\beta}\left(\frac{f_1^0 - \delta}{f_1 - \delta}\right)^{\gamma} \qquad (2)$$

The zero superscripts indicate initial quantities and the other symbols are given by:

$$\alpha = \frac{r_2}{1 - r_2}$$
$$\beta = \frac{r_1}{1 - r_1}$$
$$\gamma = \frac{1 - r_1 r_2}{(1 - r_1)(1 - r_2)} \qquad (3)$$
$$\delta = \frac{1 - r_2}{2 - r_1 - r_2}$$

Figure 4 shows the variation in instantaneous copolymer composition with conversion at five different monomer feed compositions, as calculated by equation (2). Copolymers are richer in MMA during the early part of polymerization for all starting compositions. This reverses as the reaction proceeds, resulting in homopolymerization of DMAPMA-Epi at high conversions.

For the specific case $f_1 = 0.5$ in *Figure 4*, the copolymer composition remains almost constant (within 10%) until conversion reaches 70%. When conversion reaches 85% all the MMA has been consumed, causing the reaction to become a homopolymerization of DMAPMA-Epi. Therefore, in applications where a homogeneous copolymer is desired, a semicontinuous feed strategy is required, similar to that adopted for MMA/*N*-vinyl-2-pyrrolidone copolymerization[12].

(b) Sequence length distribution. The sequence length distribution of each monomer in the copolymers can be predicted from probability functions[13]. *Figure 5* shows how the sequence length distribution changes with monomer feed composition.

Sequence length is the number of like monomer units joined consecutively. *N*(*i*) is the number fraction of each sequence length in the copolymer. These two axes combined give the sequence length distribution at a

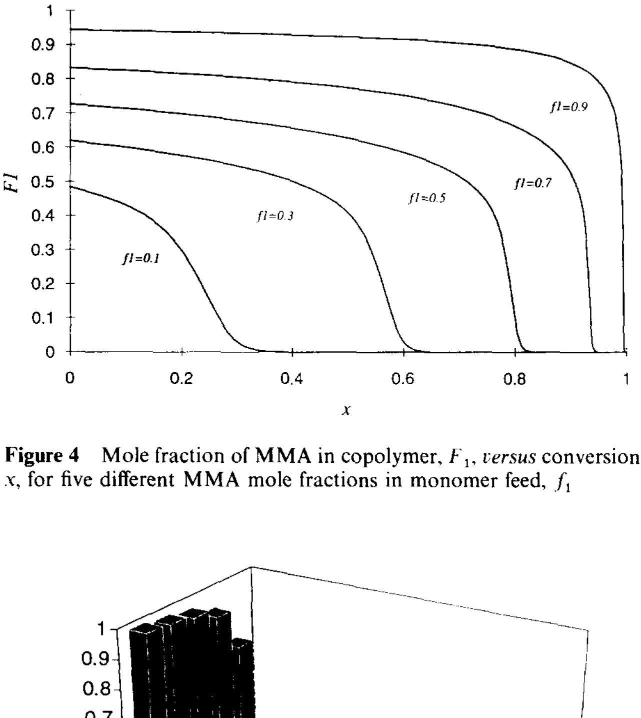

Figure 4 Mole fraction of MMA in copolymer, F_1, *versus* conversion, x, for five different MMA mole fractions in monomer feed, f_1

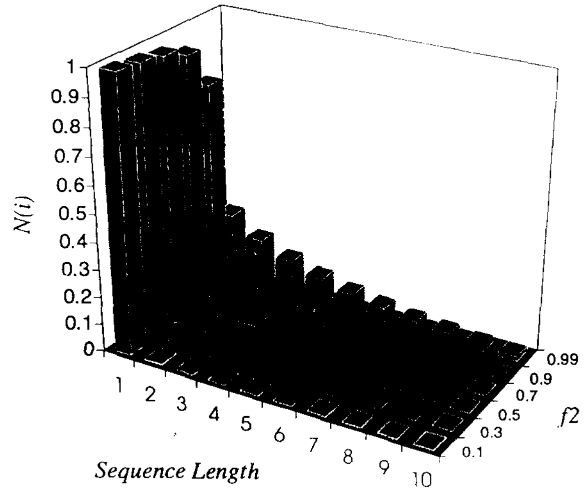

Figure 5 Sequence length distribution of DMAPMA-Epi as a function of its mole fraction in the monomer feed, f_2

unique monomer feed composition. The third axis, f_2, shows how the sequence length distribution changes with respect to the instantaneous mole fraction of DMAPMA-Epi in the monomer feed.

Sequence length distribution can be determined using *Figure 5*. At low f_2, DMAPMA-Epi exists almost entirely as isolated units. The change in sequence length distribution can be predicted as a function of conversion. As copolymerization proceeds f_2 increases, resulting in a broadening of the DMAPMA-Epi sequence length distribution.

Conclusions

The monomer reactivity ratios for MMA (**1**)/DMAPMA-Epi (**2**) using the Mayo–Lewis model were found to be $r_1 = 1.73$ and $r_2 = 0.03$. The different methods used to calculate the reactivity ratios gave good agreement. During copolymerization the MMA monomer is consumed faster than DMAPMA-Epi, causing compositional drift during reaction. The copolymers are initially rich in MMA. However, as conversion proceeds MMA is consumed and there is a shift to DMAPMA-Epi-rich copolymers. The Q and e values determined for DMAPMA-Epi are 0.23 and -1.32, respectively.

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References

1 Ilavsky, M., Bouchal, K. and Hrouz, J. *Polym. Bull.* 1990, **24**, 619
2 McCormick, C. L. and Chen, G. S. *J. Polym. Sci.* 1982, **20**, 817
3 Shih, Y. and Iovine, C. P. US Patent no. 4,489,192, 1984
4 Fineman, M. and Ross, S. D. *J. Polym. Sci.* 1950, **5**, 259
5 Kelen, T. and Tüdös, F. *J. Macromol. Sci. Chem.* 1975, **A9**, 1
6 Heatley, F., Ga-er, Yu, Booth, C. and Blease, T. G. *Eur. Polym. J.* 1991, **27**, 573
7 Reilly, P. M. and Patino-Leal, H. *Technometrics* 1981, **23**, 221
8 Alfrey, T. Jr and Price, C. C. *J. Polym. Sci.* 1947, **2**, 101
9 Brandrup, J. and Immergut, E. H. (Eds) 'Polymer Handbook' 3rd edn, Interscience, New York, 1989, p. II/268
10 Skeist, I. *J. Am. Chem. Soc.* 1946, **68**, 1781
11 Meyer, V. E. and Lowry, G. G. *J. Polym. Sci. A* 1965, **3**, 2843
12 Liu, Y., Huglin, M. B. and Davis, T. P. *Eur. Polym. J.* 1994, **30**, 457
13 Odian, G. 'Principles of Polymerisation' 2nd edn, Wiley-Interscience, New York, 1981, Ch. 6, p. 441