Copolymerization of Acrylamide with Cationic Monomers in Solution and Inverse-Microsuspension

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Synopsis

The free radical copolymerization of acrylamide with three of the most commonly used cationic comonomers diallyldimethylammonium chloride, dimethylaminoethylmethacrylate, and dimethylaminoethylacrylate, the latter two quaternized with methyl chloride, was investigated. The polymerizations were carried out with azocyanovaleric acid and potassium persulfate over the temperature range 45–60°C. The copolymer reactivity ratios were determined with the error-in-variables method using residual monomer concentrations, measured by a Nalco HPLC method. This combination of estimation procedure and analytical technique has been found to be superior to any methods used previously for the estimation of reactivity ratios for cationic-acrylamide copolymers.

INTRODUCTION

During the last 20 years, there has been an increasing interest in water-soluble cationic polymers. They are commonly used in the paper industry where they are needed for the adhesion between fillers and the wood fibers[1] and as flocculation aids in waste water treatment.[2] They are also used to a smaller extent in mining and in tertiary oil recovery. These polymers are generally produced by copolymerization of cationic monomers with acrylamide to obtain high molecular weight polyelectrolytes.

While the properties and the application of these cationic homopolymers[3-7] and copolymers[8-11] have been well described by many authors and in several patents,[12-15] there is very little kinetic data available, although the comonomers have been known for almost 30 years.[16] To date only the homo- and copolymerization of diallyldimethylammonium chloride has been extensively investigated.[17-25] For the other copolymers only Tanaka[25] has measured the reactivity ratios. Furthermore, there is only one publication[24] dealing with the production of water-soluble cationic polymers in inverse-emulsion. This investigation was made on the copolymerization of diallyldimethylammonium chloride with acrylamide.

Of all the published papers only Huang et al.[24] quote the error limits of the reactivity ratios and no author provides the joint confidence region. Furthermore, the reactivity ratios published by various authors have quite different

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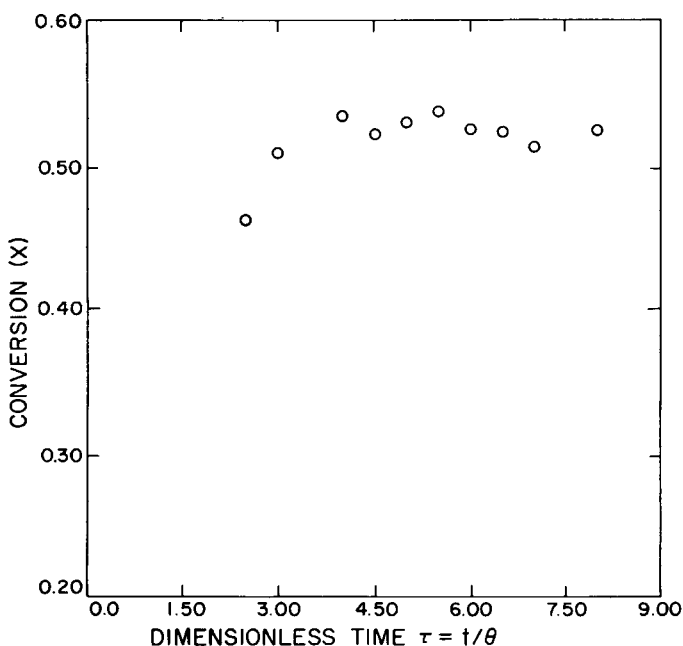
Fig. 1. Dependence of conversion on dimensionless time (τ) for the system AAM/DMAEA. The monomer feed ratio was 1.7:1, and the residence time (θ), was 30 min.

values. One reason for this might be that there were no satisfactory analytical methods available for the accurate determination of the copolymer composition or the residual monomer concentrations. In the present work, the copolymerization of acrylamide (AAM) with the commercially most commonly used cationic comonomers, diallyldimethylammonium chloride (DADMAC), dimethylaminoethyl acrylate quaternized with methyl chloride (DMAEA), and dimethylaminoethyl methacrylate quaternized with methyl chloride (DMAEM), has been investigated. The reactivity ratios were determined using continuous solution polymerization with the error-in-variables method. These measurements were extended to the polymerization in inverse-microsuspension by considering the partitioning of monomer between the aqueous and organic phases. These predicted reactivity ratios were compared with those experimentally determined by inverse-microsuspension.

EXPERIMENTAL

The polymerizations were carried out in solution in a 0.5-L continuous stirred tank reactor. This provided polymers of constant composition and enabled a larger number of samples to be withdrawn than would be possible from a batch reactor. At steady state these samples provided estimates of all errors involved in the calculation of r_1 and r_2. This steady state was obtained after about three mean residence times (Fig. 1).[†] The solution was stirred at

[†] Residence times were 30 min for all reactions with the exception of DADMAC III (41 min) and DMAEM IX to XI (34 min).

300 rpm. The polymerization temperatures were 45 and 60°C, respectively, and 50°C for the polymerization with DADMAC. The monomer concentration was kept low at 0.5 mol/L to maintain low viscosities. The monomer–comonomer feed ratio was varied between 0.3 and 0.7. The initiators were azocyanovaleric acid (ACV, Wako Chemical Co.) and potassium persulfate (KPS, BDH Chemicals). The monomers AAM, DADMAC, DMAEM, and DMAEA were kept as concentrated stabilized solutions and later diluted. A small amount of EDTA solution was added to chelate the stabilizer. The pH value during the polymerization was about 5.2.

The volume of the reactor samples taken was 20 mL, to which 200 μL of a solution containing 1 wt % hydroquinone was added to stop the polymerization. For the polymerization in inverse-microsuspension, the water phase containing the monomer was emulsified in Isopar K as oil phase and stabilized with the nonionic emulsifier sorbitanmonooleate. The phase ratio was 1:1 and the oil phase contained 5.14 wt % stabilizer. The initiator was the oil-soluble azodimethylvaleronitrile (ADVN) (DuPont Co.). The stirring speed was 600 rpm. All other conditions were the same as with the solution polymerization.

For the determination of the copolymer composition several analytical methods were investigated. In the past only titration methods have been described in the literature. The most common of these is colloid titration with toluidene blue as indicator,[26, 27] but recently also conductometric titration[23] and silver nitrate titration[24] have been used. The latter methods are more accurate than the classical colloid titration, which can have large errors, as shown later in this paper. In general, none of the titration methods show satisfactory accuracy. In this paper colloid titration has only been used for comparison with the Nalco HPLC method described in the next paragraph. For the colloid titration a commercial PVSK solution whose correct concentration has been determined by titration against $1/400$ N cetylpryidinium chloride monohydrate solution was used. For the colloid titration 1 mL of copolymer solution containing 200–600 ppm copolymer and one drop toluidene blue was placed on a magnetic stirrer and titrated with the PVSK solution until the opaque solution became clear and the color changed from blue to red-violet. Each titration was performed at least five times.

A Nalco HPLC method has been used and optimized to get quite accurate values for the residual monomer concentration of both comonomers. While for AAM the determination of residual monomer has been reported in the literature[28-30] using Partisil or C-18 columns, nothing has been reported for cationic monomers. In the present study a Waters radial compression system with a CN column (particle size 5 μm, cartridge ID 8 mm), known to separate amines and amides, was used. The HPLC consists of an ERC-3110 degasser (Erma Optical works), a Waters U6K injection system, a filter, and a precolumn (CN) as well as a Beckman 160 UV detector with a zinc lamp at a wavelength of 214 nm. The mobile phase was a mixture of 40 vol % acetonitrile and 60 vol % water, which contained 0.005 mol dibutylaminephosphate. The flow rate was 2 mL/min.

The HLPC was calibrated with standard solutions of the monomers. For AAM, DMAEM, and DMAEA the calibration curve is linear between 1 and 100 ppm (for AAM and DMAEA moderately linear also up to 200 ppm). Sample concentrations can be reproduced with an accuracy of about 1%. For
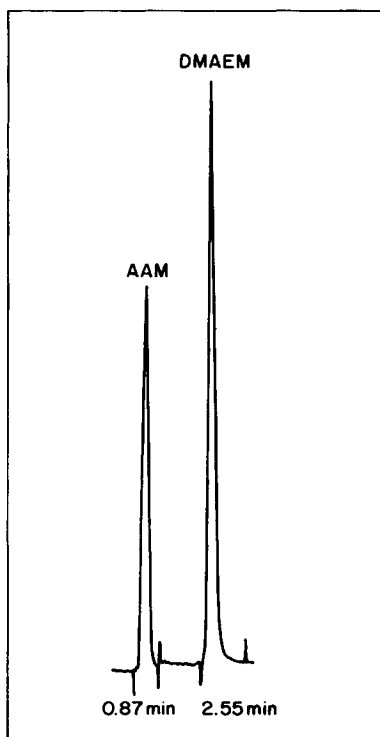
Fig. 2. Example of a HPLC chromatogram for the system AAM/DMAEM. The peaks correspond to a concentration of 47.5 ppm of AAM and 90.1 ppm of DMAEM, respectively.

DADMAC the linear calibration range extends to 600 ppm. But the accuracy of the measurement is smaller, due to a larger difference in the location of the peak maximum and measurement wavelength (214 nm).

For the HPLC measurements all samples were diluted in double distilled deionized water to provide residual monomer concentrations between 10 and 100 ppm. The pH was adjusted to 3. The polymer in the sample was separated by high speed centrifugation (20 min at 11000 g with a Sorvall RC5B Superspeed Centrifuge). Remaining polymer was kept back by the guard column which was changed every 100 injections. This prevented polymer from reaching the CN column, whose packing would otherwise be damaged. The injection volume was 200 μL. Every sample was measured three to five times.

Figure 2 shows an example of a typical chromatogram of AAM and DMAEM. A good separation can be noted. The signal areas can be quantitatively measured within 1% error limits. In this system the AAM signal appears almost at the same time as the signal of the solvent front. Because water shows a negative signal, the area of the water signal has to be added to the area of the acrylamide signal. Furthermore, the hydroquinone used to terminate the reaction and the azoinitiator show small signals at the same retention time. Therefore, these signals have also to be determined separately and subtracted from the acrylamide signal.

^{13}C-NMR spectra were recorded for an 8.06 wt % D_2O solution at 62.89 MHz and ambient temperature on a Bruker WM 250 spectrometer operating at 5.87 T in the pulsed Fourier transform mode with inverse gated decoupling.

The ^{13}C-pulse width and acquisition time were 30.5 ms and 0.442 s, respectively. Each spectrum contained 16 K data points over a frequency of 18518 Hz, with about 2000 acquisitions.

The determination of the partition coefficient of the monomers between the oil and the water phase was done by measuring the concentration of the monomer in the water phase before and after partitioning. Therefore, an off-line UV-spectrophotometer with good resolution and variable wavelength (Gilford Response) was used. The wavelengths used for the measurements were: AAM at 212 nm, DMAEM at 220 nm, DMAEA at 200 nm, and DADMAC at 190 nm. The concentration–absorption dependence was determined by calibration with standard concentrations between 1 and 100 ppm. A series of samples with the phase ratios oil to water of 1 : 1, 2 : 1, and 4 : 1 with oil phases containing zero, 1, 4, or 8 wt % of the emulsifier sorbitanmonooleate were prepared. This was done for each monomer. The samples were shaken often and vigorously during a day to insure equilibrium partitioning was achieved. The water phase contained 1.4 mol monomer/L. For DMAEM the whole series was repeated with 0.5 mol/L. For the UV measurement the water phase was separated after partitioning from the oil phase and emulsifier by centrifugation. First a centrifugation of 10 min was carried out in a Sorvall RC5B superspeed centrifuge at 11000 g, where the oil phase was separated. Afterwards the remaining solution was repeatedly centrifuged in an Eppendorf centrifuge 5415 at 14000 g to separate remaining emulsifier until the water phase was clear.

RESULTS AND DISCUSSION

The Error-in-Variables Method

The error-in-variables method was used for the estimation of the reactivity ratios. This method was developed by Reilly et al.[31, 32] It was first applied for the determination of reactivity ratios by O'Driscoll and Reilly.[33, 34] In this work, a modified version by Sutton and MacGregor[35] adapted by Gloor[36] for a continuous stirred tank reactor was used. The error-in-variables method shows two important advantages compared to the other common methods for the determination of copolymer reactivity ratios which are statistically incorrect, as for example, Fineman–Ross[37] or Kelen–Tudos.[38] First, it accounts for the errors in both dependent and independent variables; the other estimation methods assume the measured values of monomer concentration and copolymer composition have no variance. Secondly, it computes the joint confidence region for the reactivity ratios, the area of which is proportional to the total estimation error.

The use of a continuous stirred tank reactor permits one to apply the instantaneous copolymer equation for reactivity ratios estimation:

$$F_1 = \frac{r_1 f_1^2 + f_1(1 - f_1)}{(r_1 + r_2 - 2)f_1^2 + 2(1 - r_2)f_1 + r_2} \tag{1}$$

with

$$f_1 = \frac{[M_1]}{[M_1] + [M_2]} \quad \text{and} \quad F_1 = \frac{m_1}{m_1 + m_2}$$

where r_1 and r_2 are the reactivity ratios, $[M_1]$ and $[M_2]$ the monomer concentrations at the outlet of the reactor, and m_1 and m_2 the monomer bound in the copolymer. In this paper the index 1 refers always to the AAM and the index 2 to the cationic monomer. Equation (1) may be written as

$$\text{Residual } (R) = \frac{r_1 f_1^2 + f_1(1 - f_1)}{(r_1 + r_2 - 2)f_1^2 + 2(1 - r_2)f_1 + r_2} - F_1 \qquad (2)$$

and the residual for each observation of a series can be determined. Afterwards, r_1 and r_2 are estimated in a nonlinear regression where the sum of the squared residuals, weighted in relation to the variance, is minimized using Marquardt's procedure. The variance of the residuals can be determined by summing up the products of the partial differential of the residuals to the variables and the variances of the variables:

$$V_R = \left(\frac{\partial R}{\partial [M_1]}\right)^2 V_{M_1} + \left(\frac{\partial R}{\partial [M_2]}\right)^2 V_{M_2} + \left(\frac{\partial R}{\partial F_1}\right)^2 V_{F_1} \qquad (3)$$

V represents the variance and R the residual of eq. (2). The confidence region can be determined by plotting the sum of squares contour for several r_1 and r_2 values, which satisfy the instantaneous copolymer equation for the variables given.

Reactivity Ratios in Solution Polymerization

Tables I–IV list the monomer concentrations and their variances experimentally determined by HPLC as well as the mol fractions of AAM in the

TABLE I
Residual Monomer Concentrations and Mol Fraction of AAM in the Polymer
for the Copolymerization of AAM and DMAEM with KPS at 60°C
in Solution at Various Feed Ratios

Sample no.	$[M_1]$ (AAM) (mol/L)	V_{M_1}	$[M_2]$ (DMAEM) (mol/L)	V_{M_2}	F_1	V_{F_1}
II-Mono	0.384	0.0010	0.116	0.00010	—	—
II-7	0.286	0.0006	0.070	0.00001	0.680	0.0012
II-8	0.291	0.0008	0.071	0.00001	0.675	0.0016
II-10	0.270	0.0005	0.065	0.00002	0.691	0.0010
II-11	0.286	0.0005	0.069	0.00002	0.676	0.0010
III-Mono	0.272	0.0008	0.228	0.00004	—	—
III-8	0.211	0.0005	0.141	0.00002	0.412	0.0016
III-9	0.191	0.0006	0.124	0.00002	0.438	0.0016
III-11	0.204	0.0006	0.132	0.00002	0.415	0.0016
III-12	0.191	0.0005	0.125	0.00002	0.440	0.0016
IV-Mono	0.166	0.0005	0.334	0.00003	—	—
IV-7	0.108	0.0005	0.147	0.00002	0.238	0.0010
IV-9	0.106	0.0006	0.146	0.00001	0.242	0.0012
IV-11	0.106	0.0005	0.146	0.00002	0.242	0.0010
IV-12	0.107	0.0004	0.149	0.00002	0.243	0.0010

TABLE II
Residual Monomer Concentrations and Mol Fraction of AAM in the Polymer
for the Copolymerization of AAM and DMAEM with ACV at 60°C
in Solution at Various Feed Ratios

Sample no.	[M$_1$] (AAM) (mol/L)	V_{M_1}	[M$_2$] (DMAEM) (mol/L)	V_{M_2}	F_1	V_{F_1}
I-Mono	0.384	0.0010	0.116	0.00001	—	—
I-7	0.236	0.0005	0.054	0.00002	0.703	0.0010
I-9	0.240	0.0006	0.055	0.00001	0.702	0.0012
II-10	0.246	0.0006	0.057	0.00001	0.701	0.0012
II-11	0.249	0.0006	0.056	0.00001	0.693	0.0012
V-Mono	0.268	0.0005	0.232	0.00005	—	—
V-9	0.177	0.0007	0.107	0.00002	0.420	0.0014
V-11	0.202	0.0005	0.123	0.00001	0.376	0.0010
V-12	0.193	0.0005	0.115	0.00002	0.392	0.0010
V-13	0.173	0.0004	0.105	0.00003	0.429	0.0010
VI-Mono	0.182	0.0007	0.318	0.00002	—	—
VI-7	0.127	0.0004	0.164	0.00001	0.262	0.0014
VI-8	0.122	0.0003	0.159	0.00002	0.275	0.0014
VI-10	0.130	0.0003	0.172	0.00001	0.262	0.0014
VI-11	0.135	0.0003	0.178	0.00001	0.250	0.0014

TABLE III
Residual Monomer Concentrations and Mol Fraction of AAM in the Polymer
for the Copolymerization of AAM and DMAEA with ACV at 60°C
in Solution at Various Feed ratios

Sample no.	[M$_1$] (AAM) (mol/L)	V_{M_1}	[M$_2$] (DMAEA) (mol/L)	V_{M_2}	F_1	V_{F_1}
I-Mono	0.315	0.0014	0.185	0.00001	—	—
I-7	0.123	0.0007	0.055	0.0002	0.595	0.0028
I-8	0.138	0.0005	0.064	0.00007	0.594	0.0028
I-10	0.187	0.0007	0.095	0.0001	0.586	0.0028
I-11	0.228	0.0013	0.122	0.0001	0.578	0.0028
II-Mono	0.402	0.0018	0.098	0.0003	—	—
II-6	0.177	0.0006	0.020	0.0003	0.743	0.0036
II-7	0.176	0.0007	0.019	0.0001	0.742	0.0036
II-8	0.178	0.0005	0.021	0.0002	0.744	0.0036
II-9	0.179	0.0019	0.020	0.0002	0.742	0.0038
III-Mono	0.402	0.0018	0.098	0.0003	—	—
III-10	0.3745	0.0014	0.085	0.0008	0.675	0.0036
III-11	0.3855	0.0013	0.090	0.0009	0.674	0.0036
VI-Mono	0.183	0.0005	0.317	0.0003	—	—
VI-8	0.050	0.0007	0.110	0.0002	0.391	0.0014
VI-9	0.050	0.0006	0.110	0.00008	0.390	0.0016
VI-10	0.054	0.0008	0.110	0.0002	0.385	0.0016
VI-11	0.050	0.0006	0.103	0.0004	0.383	0.0012

TABLE IV

Residual Monomer Concentrations and Mol Fraction of AAM in the Polymer
for the Copolymerization of AAM and DADMAC with ACV at 50°C
in Solution at Various Feed Ratios

Sample no.	$[M_1]$ (AAM) (mol/L)	V_{M_1}	$[M_2]$ (DADMAC) (mol/L)	V_{M_2}	F_1	V_{F_1}
I-Mono	0.247	0.0018	0.253	0.0004	—	—
I-11	0.234	0.0003	0.251	0.0002	0.867	0.0022
I-13	0.178	0.0001	0.2395	0.0005	0.836	0.0023
I-15	0.181	0.0004	0.240	0.00008	0.836	0.0022
V-Mono	0.3556	0.00002	0.1444	0.0002	—	—
V-10	0.352	0.0002	0.1442	0.0001	0.943	0.0004
V-12	0.309	0.00008	0.141	0.0002	0.934	0.0004
VI-Mono	0.1196	0.00005	0.3805	0.00008	—	—
VI-8	0.109	0.00005	0.376	0.0001	0.702	0.00015
VI-10	0.098	0.00009	0.370	0.00006	0.672	0.00018
VI-11	0.1053	0.00009	0.379	0.0002	0.905	0.00029

TABLE V

Reactivity Ratios of the Polymerization of Acrylamide with Different
Cationic Monomers at Various Conditions[a]

Monomer system	r_1 (AAM)	r_2 (cationic)	Initiator	Temperature (°C)
AAM/DMAEM	0.49 ± 0.15	2.46 ± 0.40	ACV	60
AAM/DMAEM	0.61 ± 0.07	2.52 ± 0.19	KPS	60
AAM/DMAEM	0.43 ± 0.18	2.39 ± 0.38	ACV	45
AAM/DMAEA	0.29 ± 0.07	0.34 ± 0.09	ACV	60
AAM/DMAEA	0.33 ± 0.09	0.40 ± 0.11	ACV	45
AAM/DADMAC	6.4 ± 0.4	0.06 ± 0.03	ACV	50

[a]ACV = azocyano valericacid, KPS = potassium persulfate.

copolymer and its variances for the copolymerization of AAM with DMAEM
using ACV and KPS as initiators, with DMAEA at 60°C and with DADMAC
at 50°C. From these data the reactivity ratios and their confidence regions
were calculated. The same calculation was performed for the copolymerization
at 45°C with the reactivity ratios obtained listed in Table V. Figures 3–5
show the 95% confidence regions of these reactivity ratios. The 95% confidence
regions for the copolymerization of AAM and DMAEM with ACV and KPS
overlap extensively and the reactivity ratios determined with the two initia-
tors are not significantly different. A slight difference can be explained by the
fact that KPS is charged and, therefore, interactions with the cationic
monomer are possible. The temperature variation causes also only slight
changes in the reactivity ratios, as is to be expected. An azeotropic point is
only observed for the system AAM/DMAEA.

The accuracy of the reactivity ratios determined by HPLC and colloid
titration are compared in Figure 6. The errors involved in colloid titration are
several orders of magnitude larger than for HPLC. Furthermore, the individ-
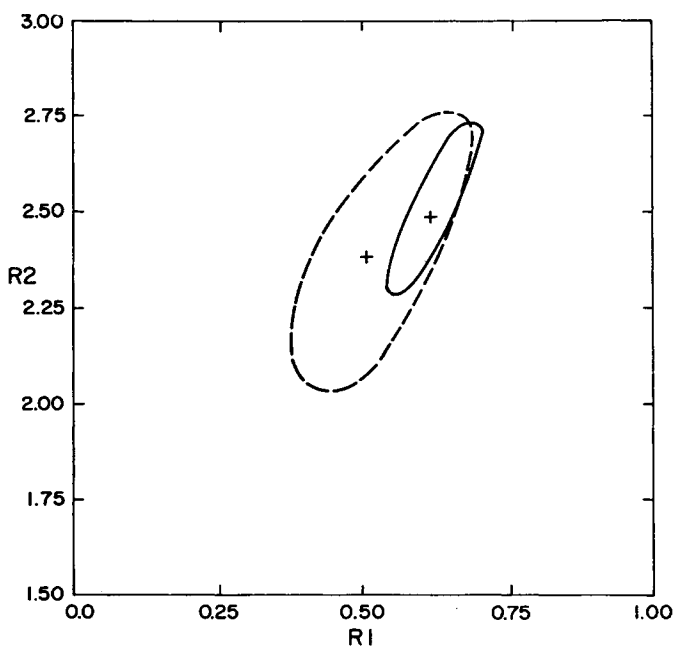ual 95% confidence intervals from colloid titration surround zero, which

Fig. 3. Joint confidence regions for the reactivity ratios in the system AAM/DMAEM at 60°C: (—) with KPS as initiator; (- - - -) with ACV as initiator.
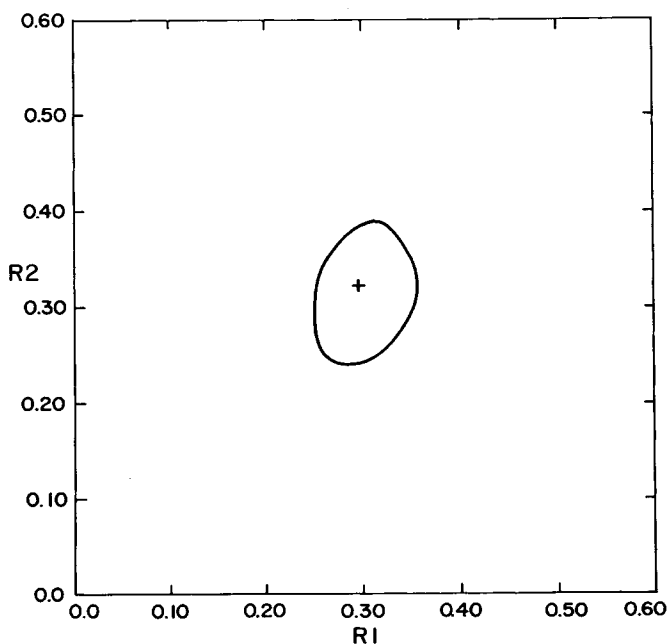

Fig. 4. Joint confidence region for the reactivity ratios in the system AAM/DMAEA at 60°C with ACV as the initiator.
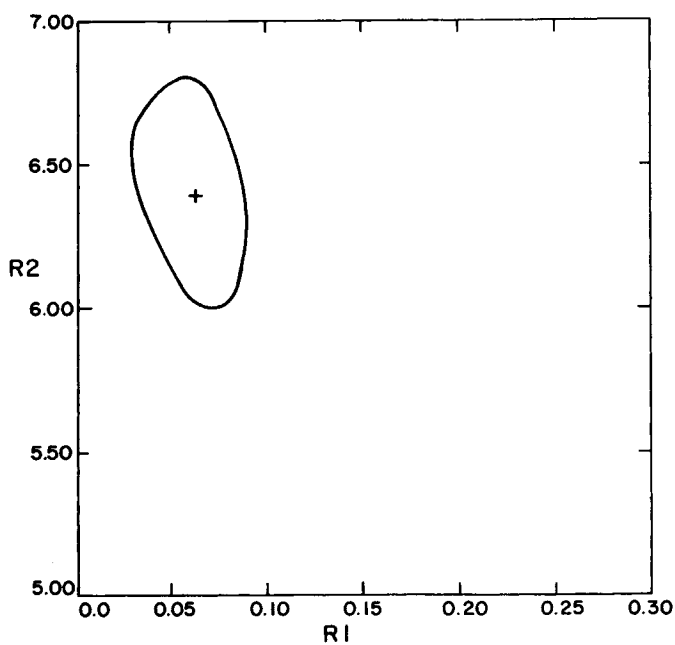
Fig. 5. Joint confidence region for the reactivity ratios in the system AAM/DADMAC at 50°C with ACV as the initiator.
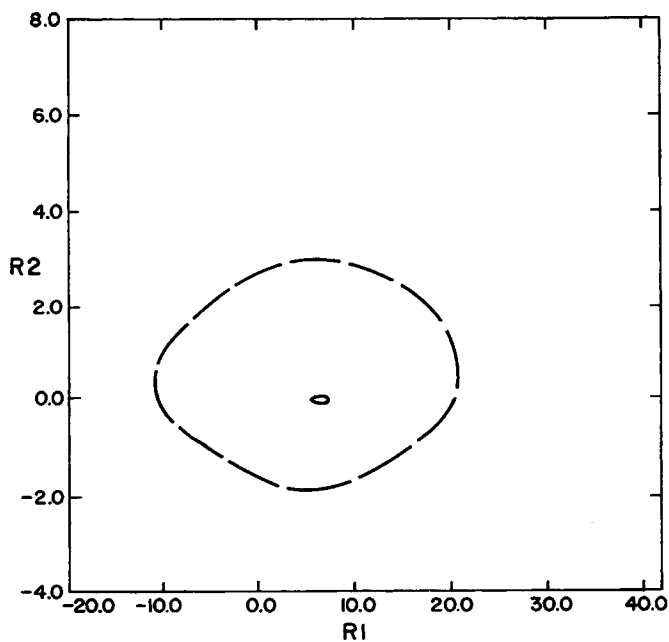

Fig. 6. Comparison of the joint confidence regions obtained by HPLC (—) and colloid titration (- - - -) for AAM/DADMAC at 50°C.

TABLE VI

Comparison of the Reactivity Ratios Determined by Different Authors for the Copolymerization of Acrylamide with Diallyldimethylammonium Chloride

r_1	r_2	Monomer concentration (mol/L)	Temperature (°C)	Range of feed ratios (f_1)	Author(s)
6.4 ± 0.4	0.06 ± 0.03	0.5	50	0.3 → 0.7	This work
6.7	0.58	1.5	20	0.1 → 0.9	Tanaka[25]
6.62[a]	0.074[a]	3.0	35	0.11 → 0.89	Wandrey and Jaeger[23]
7.14[a]	0.22[a]	4.0	35	0.2 → 0.72	Wandrey and Jaeger[23]
7.54[b]	0.049[b]	5.75	47	0.2 → 0.8	Huang et al.[24]

[a] These are average values, since r_1 and r_2 were observed to depend on the feed ratio.
[b] Determined in inverse-emulsion polymerization.

implies that inferences based on such data are arbitrary and insignificant. Therefore, reactivity ratios which have been determined from colloid titration measurements must be regarded with extreme skepticism. We recommend using the reactivity ratios determined by the EVM–HPLC method.

For the system AAM/DADMAC, good agreement with the results of Wandrey and Jaeger was found (Table VI). According to the results obtained by these authors at various monomer concentrations, and those obtained for a monomer concentration of 0.5 mol/L in this work, the reactivity ratios of both monomers increase slightly with increasing monomer concentration.

^{13}C-NMR measurements confirmed that five member rings were formed in the copolymerization of DADMAC and AAM. A typical NMR spectra is shown in Figure 7. The assignments agree with those made by Lancaster et al. for DADMAC homopolymers.[39] It is also shown that the compositions obtained by HPLC and NMR agree reasonably well. However, the time required
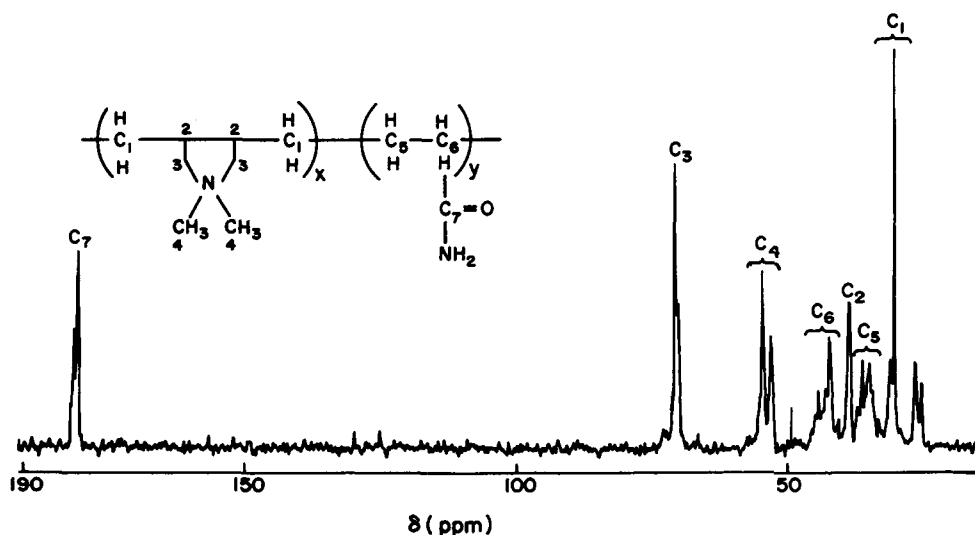

Fig. 7. ^{13}C-NMR spectra of an AAM/DADMAC copolymer with peak assignments. F_1 = 0.680 by HPLC and 0.639 by NMR.

for an NMR analysis is about 20 h and it is obviously not suitable for routine measurement of a series of samples. One HPLC measurement takes, by comparison, only about 3 or 4 min. The determination of the sequence length distribution may be possible by ^{13}C-NMR as has already been described for other systems in the literature.[40] Further investigations are necessary to confirm this for these cationic copolymers.

Modification of the Reactivity Ratios for Polymerization in Inverse-Microsuspension

Inverse-microsuspension polymerization[41, 42] consists of the dispersion of a water soluble monomer, in solution, in a continuous oil phase, which is usually paraffinic. The initiator may reside in either the aqueous or the organic phase, although the latter is more common.

According to Schuller,[43] the reactivity ratios for a copolymerization in a heterophase system, such as inverse-microsuspension, can be calculated from the reactivity ratios obtained in solution when one has knowledge of the partition coefficients of the monomers between the continuous and dispersed
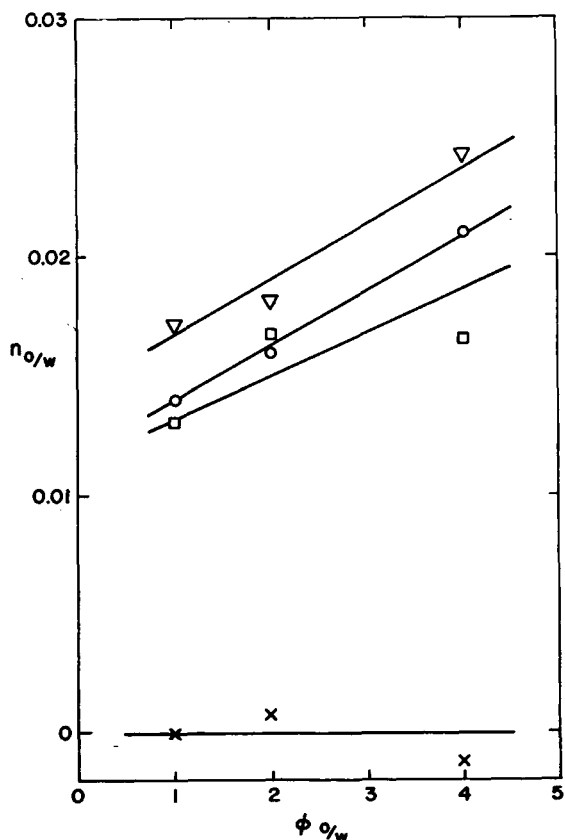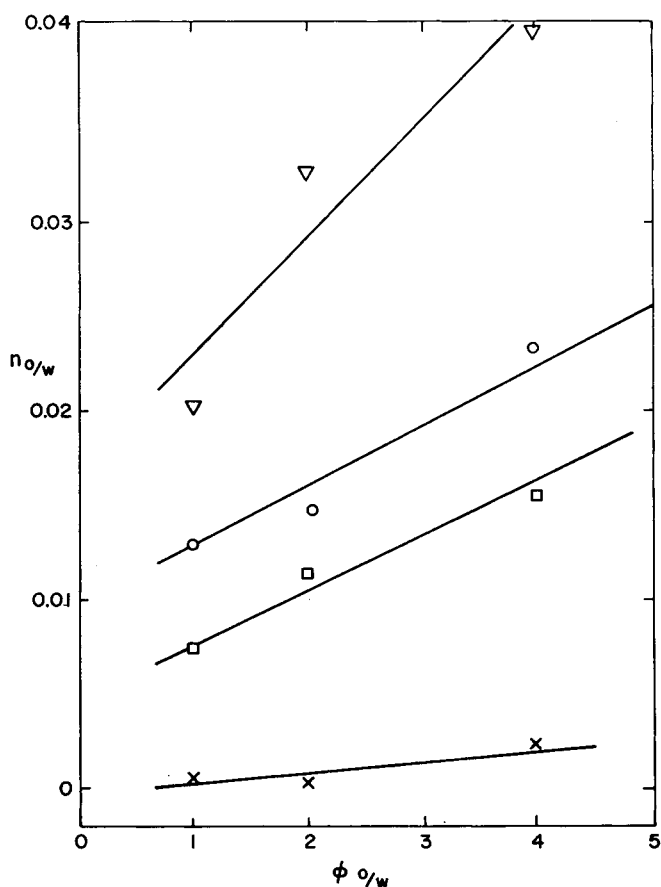
Fig. 8. Partition coefficient (n) of AAM in water-in-oil emulsions as a function of the phase ratio of oil to water ($\phi_{o/w}$): ($\times$) without emulsifier; ($\square$) with 1 wt % SMO; ($\bigcirc$) with 4 wt % SMO; (∇) with 8 wt % SMO.

Fig. 9.   Partition coefficient (n) of DMAEM in water-in-oil emulsions as a function of the phase ratio of oil to water ($\phi_{o/w}$): ($\times$) without emulsifier; ($\square$) with 1 wt % SMO; ($\bigcirc$) with 4 wt % SMO; ($\triangledown$) with 8 wt % SMO.

phases. For a quite arbitrary series of phase ratios, these may be expressed as

$$r_1' = r_1 \frac{1 + 1/\beta\psi}{1 + 1/\alpha\psi} \qquad r_2' = r_2 \frac{1 + 1/\alpha\psi}{1 + 1/\beta\psi} \qquad (4)$$

where ψ is the phase ratio, α the partition coefficient of monomer 1 between oil and water phase, and β the partition coefficient of monomer 2 between oil and water phases for an inverse system. Therefore, the partition coefficient for all monomers had to be determined in the presence of different stabilizer concentrations by UV measurements as described in the experimental part. For DMAEM this was done for two levels of monomer concentrations to verify that, in the concentration range of interest, the partition coefficient is independent of the monomer concentration. The resulting values of the partition coefficient are plotted as a function of the phase ratio and the stabilizer concentration in Figures 8–11. In most cases the stabilizer has a solubilizing effect on the monomer in the oil phase. The strongest effect can be seen for DMAEM. Only for DADMAC does the stabilizer not have such an
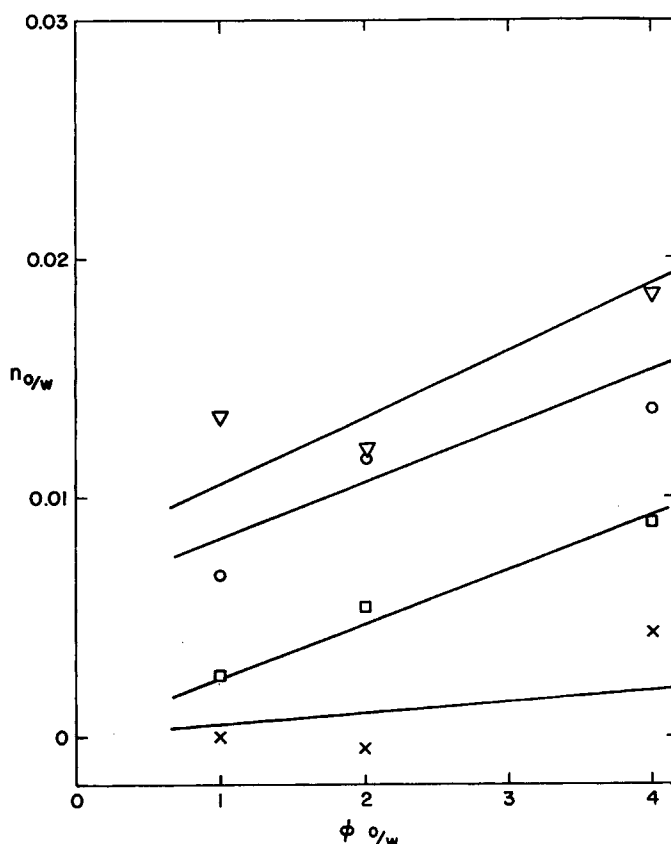
Fig. 10. Partition coefficient (n) of DMAEA in water-in-oil emulsions as a function of the phase ratio of oil to water ($\phi_{o/w}$): ($\times$) without emulsifier; ($\square$) with 1 wt % SMO; ($\bigcirc$) with 4 wt % SMO; ($\triangledown$) with 8 wt % SMO.

effect. However, for all monomers the solubility in the oil phase is very low. Due to this the calculated values of the reactivity ratios in inverse-microsuspension are only slightly different from those determined in solution. For comparison some copolymerizations in inverse-microsuspension have been carried out. The monomer concentrations and their variances as well as the mole fractions of AAM in the polymer and its variance for these experiments are listed in Table VII. The reactivity ratios for this system were found to be $r_1 = 0.43 \pm 0.06$ and $r_2 = 1.43 \pm 0.26$. While the reactivity ratio for AAM agrees very well with that found via solution polymerization, there is a great difference for the reactivity ratio of DMAEM in inverse-microsuspension and solution, even after the correction with the partition coefficient, as shown in Figure 12. Because it is known from the literature[44] that the addition of a cationic monomer to a cationic end group of the growing polymer radical is strongly influenced by electrostatic interactions, it is believed that this step in inverse-microsuspension is slower than in solution. This may be explained by the presence of a small amount of oil in the water phase, which may change the dielectric constant or the quarternization equilibrium. In such cases Schuller's model is not applicable since it does not consider changes in the
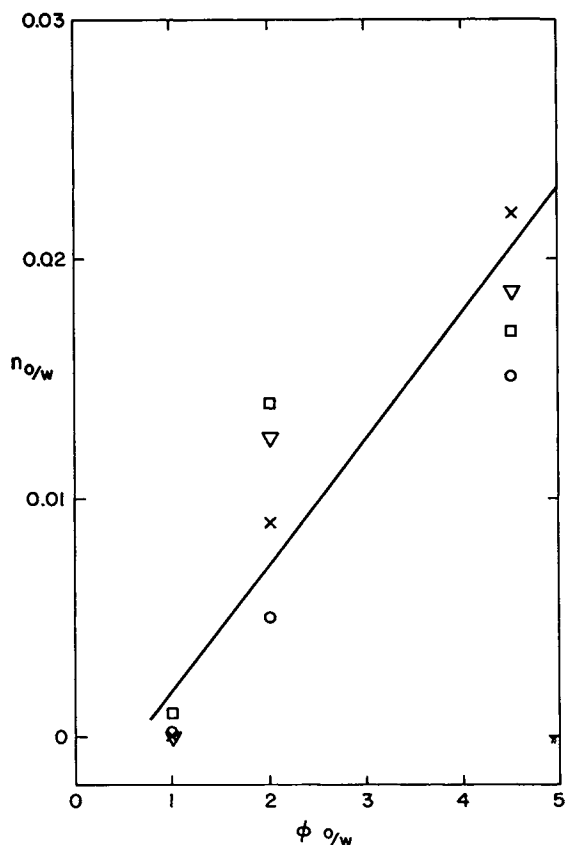
Fig. 11. Partition coefficient (n) of DADMAC in water-in-oil emulsions as a function of the phase ratio of oil to water ($\phi_{o/w}$): ($\times$) without emulsifier; ($\square$) with 1 wt % SMO; ($\bigcirc$) with 4 wt % SMO; ($\triangledown$) with 8 wt % SMO.

TABLE VII
Residual Monomer Concentrations and Mol Fraction of AAM in the Polymer
for the Copolymerization of AAM and DMAEM with ADVN at 60°C
in Inverse-Microsuspension at Various Feed Ratios

| Sample no.	[M$_1$] (AAM) (mol/L)	V_{M_1}	[M$_2$] (DMAEM) (mol/L)	V_{M_2}	F_1	V_{F_1}
IX-Mono	0.382	0.00005	0.118	0.0002	—	—
IX-4	0.248	0.000003	0.054	0.0002	0.678	0.0004
IX-6	0.238	0.00000001	0.051	0.0002	0.682	0.0004
IX-8	0.234	0.000004	0.051	0.0002	0.687	0.0004
IX-10	0.234	0.0000002	0.050	0.0002	0.685	0.0004
X-Mono	0.294	0.000001	0.206	0.0002	—	—
X-5	0.197	0.0000006	0.109	0.0002	0.497	0.0004
X-7	0.191	0.00000006	0.104	0.0002	0.502	0.0004
X-9	0.192	0.0000008	0.104	0.0002	0.500	0.0004
X-11	0.189	0.000006	0.102	0.00023	0.502	0.00043
XI-Mono	0.176	0.000001	0.324	0.0104	—	—
XI-5	0.118	0.000003	0.163	0.0002	0.245	0.0106
XI-7	0.119	0.000006	0.174	0.0006	0.275	0.011
XI-9	0.120	0.0000005	0.169	0.0004	0.265	0.0108
XI-11	0.123	0.00003	0.167	0.0004	0.252	0.0108
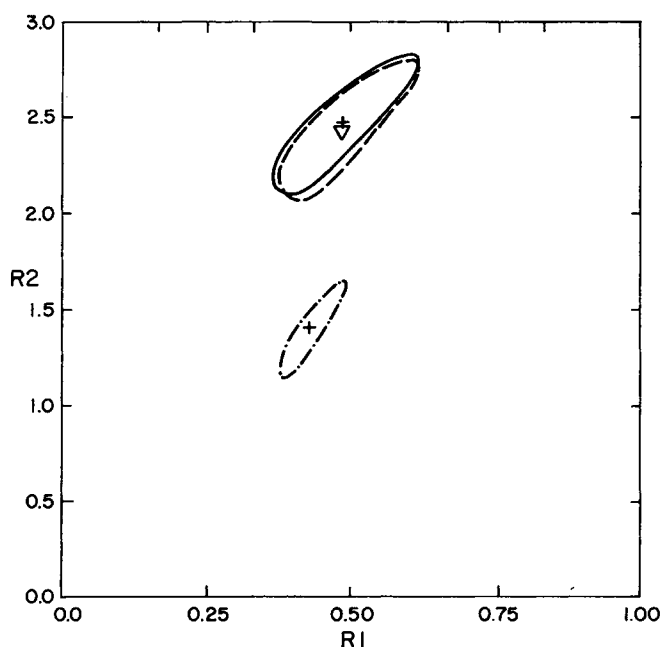
Fig. 12. Comparison of the joint confidence regions for the reactivity ratios in the system AAM/DMAEM for the polymerization in solution and inverse-microsuspension (—) solution polymerization; (– · – · –) inverse-microsuspension polymerization; (- - - -) calculated for inverse-microsuspension from solution polymerization data considering the partitioning of the monomers between the oil and water.

propagation rate constant with reaction conditions. Therefore, to rigorously understand reactivity ratios in a polyelectrolyte system such as this, we must determine the effect of pH, salt concentration, counterion type, and soluble organics on the individual propagation constants. Here further investigations are necessary and these are in progress.

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