Preparation and kinetic characterization of copolymers of acrylamide and poly(ethylene glycol) (meth)acrylate macromonomers

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Novel comb copolymers were prepared by the free-radical copolymerization of acrylamide (AM) and poly(ethylene glycol) (PEG) macromonomers in aqueous solution using potassium persulfate as an initiator. The reactivity ratios of acrylamide (M_1) toward macromonomers (M_2), $r_1 = K_{p11}/K_{p12}$, were estimated at low conversion by using ^1H nuclear magnetic resonance (n.m.r.) spectroscopy and high performance liquid chromatography (h.p.l.c.) techniques. The values of r_1 ranged between 1.35 and 2.2 and were dependent on the PEG pendant chain length in the macromonomers. The reactivity of the macromonomers in copolymerization, characterized by ($1/r_1$), decreased with the PEG pendant chain length. The reactivity of the macromonomer in homopolymerization, expressed as $K_p/K_t^{1/2}$, increased with the PEG pendant chain length. The changes of K_p and K_t are probably caused by the shielding effect on the growing radicals by the macromonomer pendant chains. The molecular weights of the copolymers were found to be sensitive to the polymerization temperature. Higher-molecular-weight ($> 3 \times 10^6$) copolymers were obtained at lower temperatures.

(Keywords: acrylamide; macromonomer; copolymerization)

INTRODUCTION

Poly(ethylene oxide) (PEO) has been widely used in many technologies including waste-water treatment, paper making and polymer processing. PEO with a molecular weight of 4.0×10^6 is effective as a flocculant (retention aid) for the production of newsprint[1,2]. However, the requirement for high molecular weight causes problems in industrial applications. Very-high-molecular-weight PEO chains are susceptible to oxidative and hydrodynamic degradation, resulting in lower molecular weights and lower flocculation efficiencies. Pelton *et al.*[3] proposed more robust structures for high-molecular-weight flocculants consisting of a long polyacrylamide (PAM) backbone with a few short poly(ethylene glycol) (PEG) pendant chains to give comb structures (see *Figure 1*).

One route to the desired comb copolymers is to graft PEG on to polyacrylamide. Possible grafting methods include γ-ray irradiation polymerization[4], redox radical polymerization[5], functional group condensation and coupling through water-soluble carbodiimides[6]. The disadvantages of using these methods include (1) the difficulty in controlling the density of graft and graft chain lengths, (2) the tendency to produce by-products, and (3) the high cost.

For this present work, free radical copolymerization of acrylamide with PEG macromonomers was used to produce the comb copolymer. PEG macromonomers are methoxy PEG esters of acrylic and methacrylic acid. The structures of the PEG macromonomers used in this work are shown in *Figure 2*. Compared with the random grafting methods previously mentioned, the copolymerization reaction potentially provides full control over the pendant chain length, the number of pendant chains per macromolecule and the molecular weight of the copolymers.

A number of recent papers have been published on macromonomer copolymerizations[7,8]. Most of the published work has involved hydrophobic monomers such as styrene and methyl methacrylate (MMA)[9–12]. Few studies have been reported on the copolymerization of PEG macromonomers with hydrophilic monomers such as acrylamide and acrylic acid. Schulz *et al.*[13] synthesized copolymers of nonylphenoxy PEG acrylate and acrylamide. Since nonylphenoxy poly(ethylene oxide) acrylate is surface active, no external surfactant was needed for the preparation of high-molecular-weight acrylamide copolymers with 0.1–5 mol% hydrophobic content from the nonylphenoxy PEG acrylate macromonomer. This work[13] focused on the use of the lowest levels of nonylphenoxy PEG acrylate macromonomer necessary to achieve hydrophobic enhancement of the viscosity. However, no polymerization kinetic measurements were reported.

This present paper describes the preparation of a series of novel acrylamide–PEG macromonomer comb copolymers with well defined structures and the measurement of

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Figure 1 Schematic structure of long PAM having short PEG pendant chains to give a comb copolymer

n= 5 to 40

R = H (A-n macromonomer)

or R = CH₃ (MA-n macromonomer)
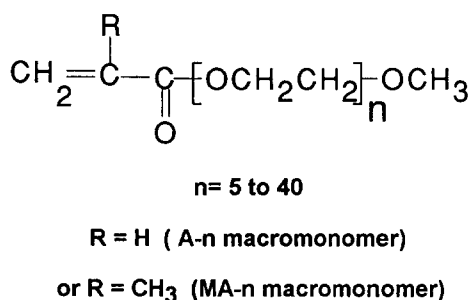
Figure 2 Structure of PEG-(meth)acrylate macromonomer

the reactivities of the PEG macromonomers in copolymerization with acrylamide. N.m.r. spectroscopy and h.p.l.c. were used to elucidate the kinetics of polymerization. The factors studied were influence of the PEG pendant chain length on the reactivity of the macromonomer in homopolymerization and copolymerization, as well as the effect of polymerization temperature on the molecular weight of the copolymers synthesized.

EXPERIMENTAL

Materials

Acrylamide (Aldrich Co.), methoxy poly(ethyleneoxy) ethyl acrylate (R = H in *Figure 2*) (Monomer-Polymer, Inc.), methoxy poly(ethylene glycol) monomethacrylate (R = CH₃ in *Figure 2*) (Polysciences, Inc.), potassium persulfate (KPS) initiator (BDH Chemicals), hydroquinone (BDH Chemicals), sodium dodecyl sulfate (SDS) (BDH Chemicals) and pyrene (Aldrich Co.) were used as supplied. Milli-Q treated distilled water was used to prepare all aqueous solutions.

Herein the macromonomers are represented as MA-*n* or A-*n* where MA refers to the methacrylic ester and A is the acrylic ester. The *n*-value is the average degree of polymerization for the PEG pendant chains. For example, MA-23 represents the PEG macromonomer with *n* = 23 and R = CH₃ (see *Figure 2*). The macromonomer structures have been verified by ^{1}H and [13]C n.m.r. spectroscopic measurements. More details of the characterization of the macromonomers are provided elsewhere[14].

Copolymer characterization and monomer conversion measurements

H.p.l.c. High performance liquid chromatography (h.p.l.c.) was used to measure the residual acrylamide concentration during polymerization[15]. The h.p.l.c. system was fitted with a precolumn (particle size 5 μm,

cartridge i.d. 8 mm, Waters), an ERC-3110 degasser (Erma Optical Works), a U6K injection system (Waters) and a Beckman 160 ultra-violet (u.v.) detector set at 214 nm, where acrylamide gives the maximum absorption. Milli-Q treated distilled water was used as a mobile phase at a flow rate of 2.0 ml min⁻¹.

N.m.r. spectroscopy. A Bruker AC 200 n.m.r. spectrometer (200 MHz, from Bruker Co.) was used to measure the composition of the copolymers. Graft copolymer powder was dissolved in D₂O at a concentration of about 0.5 wt% in thin-walled 5 mm n.m.r. tubes. [1]H chemical shifts were reported relative to the HDO peak at 4.6 p.p.m.

L.a.l.l.s. and g.p.c. Low angle laser light scattering (l.a.l.l.s.) and gel permeation chromatography (g.p.c.) were used to determine the molecular weights of the comb copolymers[16]. The l.a.l.l.s. photometer used was a Chromatrix Model KMX-6, supplied by Thermoseparation Products. Light scattering was measured at 25°C with a He-Ne unit operating system at the red wavelength (633 nm).

G.p.c. was carried out on an LC Model 5000 instrument (Varian), with the column set TSK G 3000 pw, G 5000 pw and G 6000 pw. TSK standard poly(ethylene oxide) samples, SE-2 to SE-150, with $M_w/M_n < 1.17$, were used for calibration.

Homopolymerization

Homopolymerization of the macromonomers was carried out at 40°C in deuterated water in 5 mm n.m.r. tubes using potassium persulfate as the initiator (see *Table 2* for details). Monomer conversion was monitored by proton n.m.r. by following the peak disappearance of the vinylic protons relative to the terminal methoxy group OCH₃.
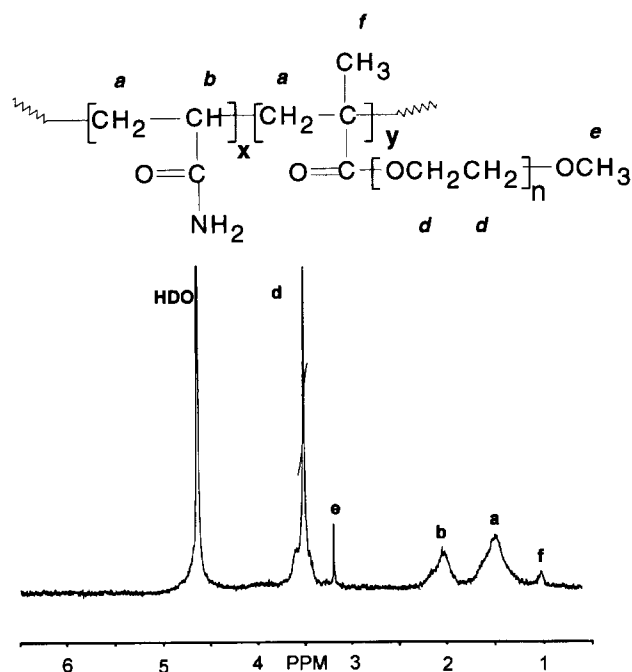
Copolymerization

The copolymerizations were carried out in aqueous solution in a 1 l batch reactor equipped with a mechanical stirring paddle, or in 50 ml test tubes which were stirred with a magnetic stirring bar. The temperature of polymerization was maintained at either 25 or 40°C. Between 2 and 8 h were required for polymerization when using initiator KPS at a concentration of 3.0×10^{-3} mol l⁻¹. *Table 1* summarizes the copolymerization details.

For the systems with a total volume greater than 250 ml, a 20 ml sample was collected every 20 to 30 min during polymerization to permit measurement of the conversion and copolymer compositions. About 1 ml of 0.1% aqueous hydroquinone solution was immediately added to each sample collected to terminate the polymerization. Between 0.2 and 0.5 ml of each sample was needed for h.p.l.c. analysis, with the remainder of the sample being precipitated into acetone.

The copolymer, precipitated with acetone, was washed with toluene to extract unreacted macromonomers. The washed copolymer was dried at 30°C in a vacuum oven for 12 h. The compositions of the purified copolymers were measured by proton n.m.r. Conversion of the macromonomer in each sample was calculated from the composition of the copolymer and the AM conversion. As an example, the n.m.r. spectrum for the AM-MA-23

Table 1 Copolymerization details; concentration of initiator [KPS] = 3×10^{-3} mol l^{-1}

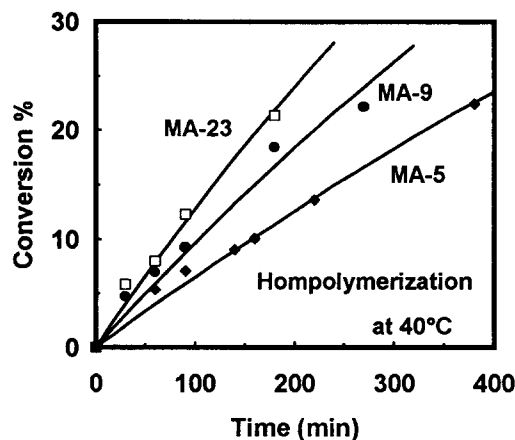| Sample no.	Type of (M)A-n	Weight of AM (g)	Weight of PEG–M (g)	Mole ratio AM/PEG–M	H$_2$O (ml)	T (°C)
43-36	MA-23	9.20	2.84	50	300	40
56-35	MA-23	1.60	0.31	60	35	40
43-176	MA-23	12.80	0.99	200	286	25
56-48	MA-23	2.163	0.259	130	40	20
56-51	MA-9	2.21	0.177	88	40	25
43-71	MA-9	11.08	0.798	100	300	40
56-49	MA-5	2.19	0.166	56	40	25
43-16	A-40	11.36	6.07	50	400	40
23-170	A-40	16.00	8.44	50	475	40
56-36	A-20	1.61	0.369	60	35	40
56-1	A-20	12.82	0.968	200	285	25
43-22	A-10	12.78	1.99	50	385	40
23-160	A-10	16.00	9.99	14	500	40

Figure 3 ^{1}H n.m.r. spectrum of copolymer synthesized from acrylamide and PEG macromonomer MA-9

Figure 4 Conversion *versus* time for the homopolymerization of PEG methacrylate macromonomers with different PEG pendant chain lengths (see *Table 3*). The fitted lines were obtained from the kinetic model summarized by equation (4)

copolymer is shown in *Figure 3*. The composition of the copolymer was estimated by the ratio of the peak areas of OCH$_2$CH$_2$ in the PEG pendant chains to CH–CH$_2$ in the copolymer backbones. The standard deviation, expressed as a percentage of the mean, ranged between 4 and 6% for the same sample when repeats were made.

Solution properties of macromonomers

The luminescence molecule pyrene was used to determine if the macromonomer solutions formed micelles. In this method 1.0 ml of a saturated pyrene aqueous solution was mixed with 1.0 ml of SDS or macromonomer solution. The concentrations of SDS and the macromonomer are given in *Figure 8*. Synchronous scans were conducted using an Aminco Luminescence Spectrometer (SLM Instruments Co.) at 25°C.

RESULTS

Homopolymerization of the macromonomer

Homopolymerizations of the macromonomer were carried out in order to determine kinetic parameters, and the results are shown in *Figure 4*. The points were measured, while the continuous lines were predicted using the following kinetic model.

The rate of expression for R_p in a free-radical homopolymerization obeying the steady-state hypothesis can be written as follows[17]:

$$R_p = -[M]_0 d(1 - X)/dt = (K_p/K_t^{1/2})[M](2fK_d[I])^{1/2}$$

$$(1)$$

where K_p and K_t are the propagation and termination rate constants, f is the initiator efficiency, $[M]_0$ is the initial monomer concentration, and X is the monomer conversion at time t. [M] and [I] are, respectively, the monomer and initiator concentrations at time t, while K_d is the decomposition rate constant of the initiator. For potassium persulfate at pH 7, the Arrhenius equation for

Table 2 $K_p/K_t^{1/2}$ data obtained from MA–PEG macromonomers, with polymerization being carried out in an n.m.r. tube with D_2O at 40°C; data are compared with those of MMA and AM

Sample	[M] × 10⁻² (mol l⁻¹)	n of PEG	[I] (mmol l⁻¹)	$K_p/K_t^{1/2}$
MA-5	25.2	5	1.81	0.474[a]
MA-9	8.44	9	3.55	0.504[a]
MA-23	3.85	23	3.83	0.663[a]
MA-67	4.5	67	0.45[b]	2.46[b]
MMA	–	–	–	0.077[c]
AM	–	–	–	5.57[d] or 5.19[e]

[a] $K_p/K_t^{1/2}$ values were obtained from fitting the kinetic model (equation (4)) to the experimental data by using the least-linear-squares approach
[b] Data taken from Ito *et al.*[20]. Polymerization was carried out at 60°C in D_2O with the initiator 4,4′-azobis(4-cyanovaleric acid) (AVA); $K_d = 4.58 \times 10^{-5}$ s⁻¹ for AVA was chosen in the calculation; $K_p/K_t^{1/2}$ value was estimated from dX/dt at $t = 0$
[c] Data taken from Kamachi *et al.*[21]. Methyl methacrylate was polymerized at 30°C in benzene with the initiator 2,2′-azobisisobutyronitrile (AIBN)
[d] Data taken from Kim[22]
[e] Data calculated from the equation $K_p/K_t^{1/2} = 57\exp(-1500/2T)$[23]

K_d is given by[18]:

$$K_d = 3.53 \times 10^{16} \exp(-33\,320/RT)\,\text{s}^{-1} \qquad (2)$$

and for isothermal polymerization:

$$[I] = [I]_0 \exp(-K_d t) \qquad (3)$$

When diffusion-controlled termination does not occur (K_t is only a function of temperature), integrating equation (1) gives the following expression:

$$\ln(1 - X) = \qquad (4)$$
$$- (K_p/K_t^{1/2})(8f[I]_0/K_d)^{1/2}[1 - \exp(-K_d t/2)]$$

Two standard assumptions were made[19]. The first was that the stationary-state hypothesis was valid for radical reactions. The second assumption was the long-chain approximation, which is that the chain lengths were sufficiently large that the total rate of monomer consumption may be equated to the rate of monomer

consumption by the propagation reactions alone. $K_p/K_t^{1/2}$ values were obtained by fitting equation (4) to the experimental conversion data. The results are summarized in *Table 2* and the predicted conversion curves are compared with the experimental data in *Figure 4*. As a comparison, $K_p/K_t^{1/2}$ values were also estimated from the literature[21–23].

Compared to the values obtained for macromonomers, the reactivity of acrylamide, expressed as $K_p/K_t^{1/2}$, was six to eight times higher. For macromonomers with different pendant chain lengths, the reactivity increased with the pendant chain length. For example, $K_p/K_t^{1/2}$ for MA-23 was 0.663, but only 0.474 for MA-5. An even higher value for MA-67 was obtained by Ito *et al.*[20] (polymerization conditions for MA-67 are shown in *Table 2*). Compared with methyl methacrylate (MMA) polymerized in benzene, polymerization of the PEG–methacrylate macromonomer conducted in water was of an order of magnitude faster.

Copolymerization

Conversion data for the copolymerizations of AM and macromonomers with different PEG chain lengths and
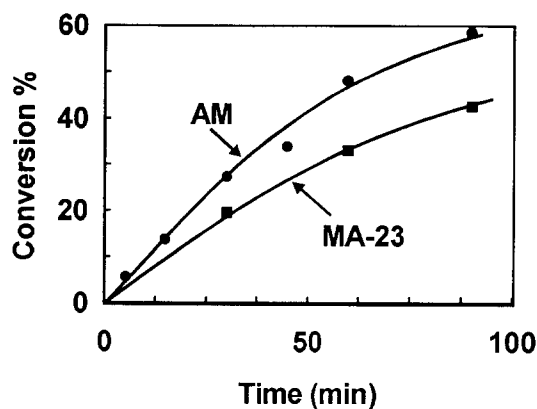
Figure 5 Conversion curves for AM and PEG-methacrylate macromonomer with PEG pendant chain length of 23. The corresponding recipe for copolymerization is given as recipe 43-36 in *Table 1*

Table 3 Conversion data for AM and macromonomers

Sample no.	t (min)	Conversion of AM (%)	Conversion of (M)A-n (%)	Type of (M)A-n	(M)A-n in copolymers[a] (mol%)
43-22	35	24.9	18.4	A-10	1.41
23-160	60	28.4	18.6	A-10	4.83
56-36-2	40	12.2	8.32	A-20	1.09
56-1-4	130	38.6	23.2	A-20	0.32
43-16-12	210	83.7	50.8	A-40	1.21
23-170-5	190	63.7	28.4	A-40	0.88
56-49-2	20	15.5	12.4	MA-5	1.51
43-63-8	250	69.9	53.0	MA-9	1.62
51-56-1	20	7.83	6.42	MA-9	1.0
43-176-2	30	19.3	13.4	MA-23	0.33
43-36-6	90	58.6	42.6	MA-23	1.36
56-35-1	20	13.8	9.65	MA-23	0.83

[a] Average molecular weights of the macromonomers were calculated by using the average chain length of PEG in the macromonomers, obtained from proton n.m.r. measurements
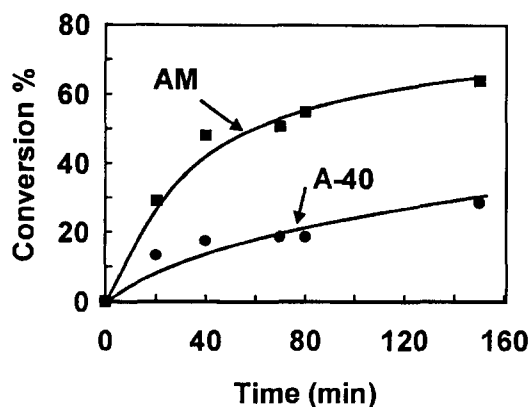
Figure 6 Conversion curves for AM and PEG-acrylate macromonomer with PEG pendant chain length of 40. The corresponding recipe for copolymerization is shown in 23-170 in *Table 1*
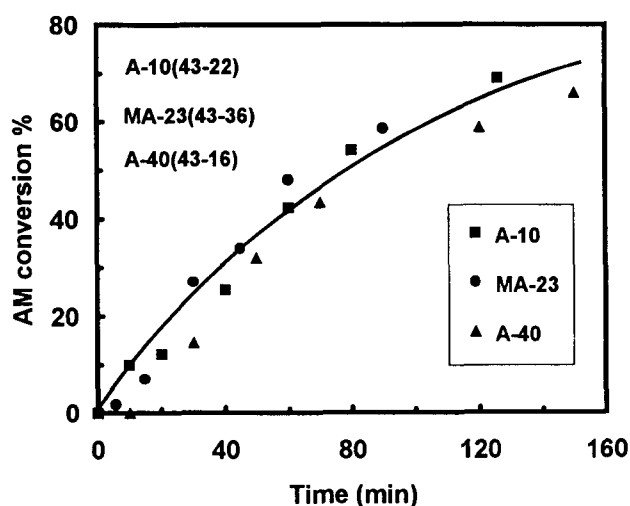

Figure 7 AM conversion in copolymerization of AM with macromonomer with different PEG pendant chains length. Molar ratios of AM to macromonomers were 50 for all samples. Polymerizations were carried out at 40°C with the recipes (43-16, 43-22 and 43-36) shown in *Table 1*

the corresponding compositions of the copolymers are summarized in *Table 3*. The conversion of acrylamide was always higher than that of the macromonomers. This suggests that the reactivity of acrylamide was higher than the PEG acrylate macromonomers under the same polymerization conditions. These results are also consistent with the $K_p/K_t^{1/2}$ values shown in *Table 2*.

The data for AM and macromonomer conversion *versus* time are plotted in *Figures 5* and *6*. In both cases the AM was consumed more quickly than the macromonomers.

Figure 7 shows AM conversion curves obtained in the presence of three different macromonomers. The similarity of the AM polymerization behaviour in *Figure 7* suggested that the reactivity of AM was independent of the type of macromonomer at mole ratios of AM to macromonomer greater than 50. In contrast, the macromonomers with different PEG pendant chain lengths behaved differently, as shown in *Figures 5* and *6*. MA-23 reached a higher conversion than A-40 under the same conditions. For example, the conversion of MA-23 was

$\sim 42\%$ after 1.5 h of polymerization time, whereas the conversion of A-40 was $\sim 20\%$ after the same period.

Reactivity of macromonomers toward acrylamide

For binary copolymerization which follows the terminal model, the instantaneous copolymer composition equation may be expressed as follows:

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1]}{[M_2]} \frac{r_1[M_1] + [M_2]}{[M_1] + r_2[M_2]} \quad (5)$$

where M_1 is acrylamide and M_2 is the macromonomer. Reactivity ratios are defined as $r_1 = K_{p11}/K_{p12}$ and $r_2 = K_{p22}/K_{p21}$, where the rate constant nomenclature is illustrated with the following reactions:

$$\sim M_1 \bullet + M_1 \xrightarrow{K_{p11}} \sim\sim M_1\bullet \quad (6)$$

$$\sim M_1 \bullet + M_2 \xrightarrow{K_{p12}} \sim\sim M_2\bullet \quad (7)$$
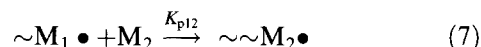
With a very large molar excess of acrylamide, i.e. $[M_2]/[M_1] \ll 1$, equation (5) can be reduced to the simple form:

$$\frac{d[M_1]}{d[M_2]} = r_1 \frac{[M_1]}{[M_2]} \quad (8)$$

This equation can be used to estimate r_1 for macromonomers with different PEG chain lengths. The reciprocal $(1/r_1)$ is a measure of the reactivity of the macromonomer towards the polyacrylamide radical. The parameter r_2 cannot be estimated due to the extremely low concentrations of macromonomer that are used.

It was assumed that the drift in copolymer composition was negligible at low monomer conversions ($< 25\%$), and the instantaneous composition was approximately equal to the composition in the accumulated copolymer. Under these conditions, equation (8) can be expressed in the following form:

$$r_1 = \frac{\ln(1 - X_1)}{\ln(1 - X_2)} \quad (9)$$

where X_1 and X_2 are the conversions of acrylamide and PEG macromonomer, respectively.

Table 4 shows r_1 data obtained by applying equation (9) to the experimental conversion data. The results indicated that the reactivity of the macromonomer, measured by $1/r_1$, increased as the PEG pendant chain lengths decreased. For example, the average $1/r_1$ for MA-5 was 0.74, while $1/r_1$ for MA-23 was 0.63. Similarly, the average $1/r_1$ for A-10 was 0.735, and for A-40 it was 0.45.

Table 4 Values of r_1 estimated from low-conversion data; error estimations are based on standard deviations of n.m.r. composition measurements

Macromonomer	n of PEG	Reactivity ratio r_1
PEG–MA-5	5	1.35 ± 0.11
PEG–MA-9	9	1.39 ± 0.15
PEG–MA-23	23	1.58 ± 0.13
PEG–A-10	10	1.36 ± 0.04
PEG–A-20	20	1.63 ± 0.18
PEG–A-40	40	2.20 ± 0.11

Table 5 Molecular-weight data for the comb copolymers

Sample no.	$M_w \times 10^{-6}$	Polymerization temperature (°C)	Mole feed ratio $M_1:M_2$	Type of macromonomer
43-36	1.2[a]	40	50:1	MA-23
43-48	1.0[b]	40	25:1	MA-23
PAM	1.06[c]	40	–	–
43-129	3.7[b]	20	99:1	MA-23
43-176	3.4[b]	25	200:1	MA-23
56-48	4.5[a]	20	130:1	MA-23
56-51	5.1[a]	25	88:1	MA-9
PAM	5.3[d]	25	–	–

[a] Data obtained from g.p.c. measurements
[b] Data obtained from l.a.l.l.s. measurements
[c] Number-average molecular weight obtained from ref. 24; $[AM] = 0.5\,\text{mol}\,\text{l}^{-1}$; $[KPS] = 2.5 \times 10^{-3}\,\text{mol}\,\text{l}^{-1}$
[d] Number-average molecular weight obtained from ref. 24; $[AM] = 0.5\,\text{mol}\,\text{l}^{-1}$; $[KPS] = 1.0 \times 10^{-3}\,\text{mol}\,\text{l}^{-1}$
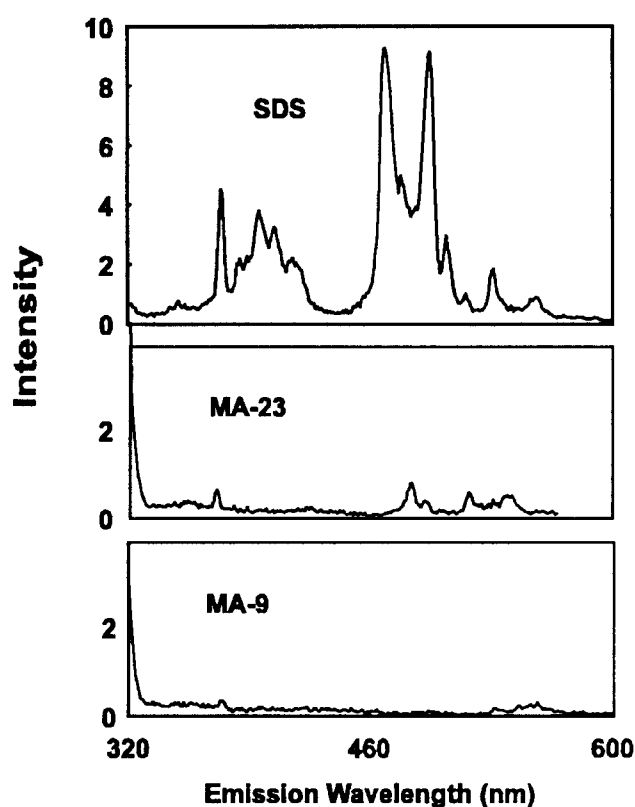
Figure 8 Fluorescence spectra of pyrene in SDS, MA-9, MA-23 and water. Concentrations of SDS, MA-9 and MA-23 in aqueous solution were 11.8, 11.4 and 8.86 mmol l^{-1}, respectively

Influence of polymerization temperature on the molecular weight of copolymers

Copolymerizations were carried out at 25 and 40°C in order to investigate the temperature effect on the copolymer molecular weight. The results (see *Table 5*) suggested that the molecular weight of the copolymer was temperature dependent. Copolymers with a molecular weight higher than 3×10^6 were obtained when aqueous solution copolymerizations were carried out at a temperature of 25°C or lower. Polymerization at 40°C gave copolymers with molecular weights of approximately 1.0×10^6.

PEG pendant chain length did not influence the molecular weights of copolymers. The molecular weights of acrylamide homopolymers obtained at 25 and 40°C are compared with those of the copolymers in *Table 5*. The PAM molecular weights herein are number-average values, which were determined from intrinsic viscosity measurements. Therefore, the molecular weights of the PAM homopolymers are similar to those of the copolymers.

Solution properties of macromonomers

It has been reported in the literature that macromonomers can form micelles in water. This would influence the polymer structure and complicate the kinetic interpretation[20]. To check for this possibility, fluorescence measurements were performed using pyrene as a probe. *Figure 8* shows the fluorescence emission spectra of pyrene in aqueous sodium dodecyl sulfate (SDS), which is known to form micelles. The strong emissions indicate the presence of hydrophobic domains capable of enhancing the solubility of pyrene. In contrast, neither of the two macromonomer solutions showed any evidence of pyrene solubilization (see *Figure 8*).

DISCUSSION

The results from this present work have indicated that the reactivities of macromonomers in aqueous solution polymerizations are PEG pendant chain length dependent. It is of interest to note that the influences of the PEG pendant chain lengths in macromonomers on their polymerization behaviour or reactivities are different in homopolymerization and copolymerization reactions. This may reveal that the mechanisms of polymerization involved are not the same. A discussion of the possible mechanisms for both homo- and copolymerization is presented below.

Homopolymerization

In homopolymerization, the $K_p/K_t^{1/2}$ values obtained using conversion measurements increased as the PEG pendant chain lengths (n) increased. This trend could have resulted from the increasing of K_p or the decreasing of K_t with pendant chain length n, or both simultaneously.

(a) **(b)**

Figure 9 Schematic description of shielding effect on propagating radicals. (a) Radical shielded by a growing polymer chain, i.e. growing chain effect; (b) radical shielded by a pendant chain in the macromonomer, i.e. pendant chain effect

It is clear that K_t falls more rapidly with n than K_p increases (if it does at all).

The interpretation of the effect of pendant chain length on K_p and K_t can follow two approaches: (a) a shielding effect of the pendant group on the growing radicals, and (2) micelle formation of the macromonomers.

The shielding effect on the radicals can simultaneously reduce termination by combination and propagation of radical centres located on the macromonomers. Research on the kinetics of polymerization of macromonomers has already revealed this[25]. We assume that there are two kinds of shielding effects in macromonomer homopolymerization: (1) a backbone chain effect, which is the influence of the whole growing polymer chain on the end radical, and (2) the pendant chain effect, which is the influence of the PEG pendant chain on the growing radical. *Figure 9* shows schematically these two kinds of effects.

For the first situation, i.e. for the shielding effect caused by the entire growing polymer chain backbone, several models dealing with the dependence of the termination rate constant K_t on the chain lengths of two reacting radical chains have already been developed[26,27]. A simplified model for the effect of segmental diffusion was expressed as follows[28]:

$$K_{t(n,m)} = K_{to(n,m)}^{-\alpha} \qquad (10)$$

where $K_{t(n,m)}$ is the specific rate constant of termination between two radicals of size n and m and $K_{to(n,m)}$ is a constant; α is a parameter which describes the chain length dependence of K_t. The aqueous solution polymerizations carried out herein are too dilute for polymer translation diffusion to be a limiting factor.

Pendant PEG chains located near a growing radical may influence both the propagation rate constant K_p and the termination rate constant K_t. The increase of $K_p/K_t^{1/2}$ with pendant chain length is a result of the more rapid decrease of K_t compared to K_p with the increase in pendant chain length. For example, K_p of MA-23 might be smaller than that of MA-5. However, an even smaller K_t value for MA-23 (due to the pendant chain shielding effect) results in a larger $K_p/K_t^{1/2}$ value for MA-23. The radical lifetime for MA-23 may also be longer than that of the radical for MA-5 due to the smaller K_t.

The dependence of the reaction rate on chain length has been reported for other macromonomer systems. For example, in the homopolymerization of PMMA macromonomer in toluene with AIBN as an initiator, Masuda *et al.*[25] determined K_p and K_t values by using electron

spin resonance (e.s.r.) and found that K_t decreased much faster than K_p as the molecular weight of the macromonomer increased. It was suggested that the highly crowded pendant chain segment resulted in a very slow segmental-diffusion-controlled termination.

Similar work with the styrene macromonomer, carried out by Tsukahara *et al.*[29], showed a significant effect of the molecular weights of the macromonomers on the diffusivity of the macromonomer in radical polymerization. Data from Tsukahara *et al.*[29] indicated that when the degree of polymerization (DP) of the styrene macromonomer was increased from 54 to 59, K_p decreased from 18 to $41 \, mol^{-1} \, s^{-1}$. Meanwhile, the coupling termination rate constant K_t decreased from 9400 to $13001 \, mol^{-1} \, s^{-1}$. However, the $K_p/K_t^{1/2}$ value for the styrene macromonomer with a DP of 54 was 0.196, which was still higher than the $K_p/K_t^{1/2}$ value of 0.111 for a styrene macromonomer with a DP of 59. These results differ from the current observations but still show that K_t falls faster than K_p with an increase in macromonomer chain length.

An alternative explanation for the effect of PEG pendant chain length on $K_p/K_t^{1/2}$, proposed by Ito *et al.*[20], was that the macromonomers formed micelles in water. Homogeneous polymerization kinetic expressions cannot apply to systems where one of the monomers is present as micellar aggregates. Ito *et al.* indicated that the micelles formed because of the amphiphilic structure of the macromonomer[20]. They used light scattering data obtained by using nonpolymerizable models[30] to estimate the critical micelle concentration (c.m.c.) and micellar sizes. The hydrophobic heads of the model compounds used by Ito and coworkers were benzyl and isobutyroyl, which will form hydrophobic domains or micelles much more easily than the methacrylate heads used in this work. The c.m.c. values for the models of the PEG vinylbenzyl macromonomers ranged from 1.8 to $7.1(\times 10^{-5})$ M and the aggregation numbers were between 19 and 1800.

Fluorescence probes have been widely applied in micelle characterization[31,32]. For example, Turro and Yekat proposed an excimer fluorescent method to estimate the c.m.c. and the aggregation number for the SDS micellar system[33]. Geetha *et al.*[34] used this method to characterize macromonomer A-9. They claimed that the aggregation number was 20 and the c.m.c. was 1.2×10^{-4} M. We believe that the conclusion that A-9 forms micelles is wrong for the following reasons.

Conventional PEG-based surfactants which readily form micelles have a hydrophobic head containing eight or more carbon atoms. Structures with smaller head groups either form micelles at very high concentrations or not at all. For example, Elworthy *et al.*[35] found the c.m.c. value for $OH(CH_2)_4EO_3$ (EO is $-CH_2CH_2-O-$) to be 0.8 M in aqueous solution at 20°C; molecules with smaller head groups were not reported. Similarly, Corkill *et al.*[36] found the c.m.c. value for $OH(CH_2)_6EO_3$ to be 0.1 M at 25°C, and Donbrow and Jan[37] found the c.m.c. value for $OH(CH_2)_6EO_5$ to be 0.09 M at 20°C. Macromonomer A-9 has a head group based on three carbon atoms so it is inconceivable that micellization could occur. In support of this argument is our pyrene solubilization data for MA-9 and MA-23 (see *Figure 8*) which showed no evidence for micellization of the three-carbon-head macromonomer.

Copolymerization

In copolymerization the reactivities of the macromonomers are a function of pendant chain length. The reactivity of the macromonomer toward the polyacrylamide radical in copolymerization, as estimated by $1/r_1$, was found to decrease with increasing PEG pendant chain length. The majority of propagating radicals during copolymerization were acrylamide radicals because the molar concentration of AM was at least 20 times greater than that of the macromonomer. As a result, the reactivity of the macromonomers toward polyacrylamide radicals was controlled mainly by the effect of pendant chain length on the propagation constant.

The propagation rate constant K_{p12} in equation (7) describes the kinetic process of macromonomers reacting with polyacrylamide radicals. The segmental diffusion of the pendant chains on individual macromonomers may limit the propagation rate with polyacrylamide radicals. In other words, K_{p12} may be higher for macromonomers with short pendant chains, as compared to macromonomers with long pendant chains. Whereas K_{p11} for acrylamide is independent of the macromonomer pendant chain lengths. Therefore, the $r_1 (= K_{p11}/K_{p12})$ change was caused only by K_{p12}, which is a function of the pendant chain length of the macromonomer.

Decreased reactivity with increasing PEG chain length has been reported for the copolymerization of PEG macromonomers with styrene in benzene. Ito *et al.*[38] explained the results by postulating a repulsion between incompatible PEG and polystyrene. In the copolymerization of PEG macromonomers with maleic anhydride (MAn), Suzuki and Tomono[39] observed similar effects of PEG on the molecular weight. These authors suggested that one reason was the competitive complex formation of MAn with the ether oxygen in the macromonomer, resulting in lower reactivities of the macromonomers with longer PEG chains.

Since the total amount of macromonomer used in copolymerization was much lower than that used in homopolymerization, the possibility of micelle formation by macromonomers appears to be even less likely. Therefore, macromonomer behaviour in copolymerization is mainly determined by its individual structure (or pendant chain length) and not due to aggregation of the macromonomers to form micelles.

The molecular weight of the copolymer was found to be affected by the polymerization temperature, with higher temperatures giving lower copolymer molecular weights. This result is the same as that found for acrylamide homopolymerization, since low levels of macromonomers in copolymer chains may not significantly affect the molecular weight. Chain transfer to monomer and initiator have been found to be the major reasons for the lowering of the molecular weight at higher polymerization temperatures, and many earlier researches have revealed this. For example, the ratio of the rate constant for chain transfer to monomer to the propagation rate constant $(C_m = K_{fm}/K_p)$ in AM homopolymerization at 25°C was found to be 2.0×10^{-5}, as reported by Cavell and Gilson[40] and Fadner and Morawetz[41]. At a higher temperature (40°C) the ratio became 5.8×10^{-4}, as reported by Chou[42]. By using the least-squares estimating method, Shawki and

Hamielec[16,24] gave more accurate values of K_{fm}/K_p, which were 9.10×10^{-6} at 25°C and 2.04×10^{-5} at 40°C. Therefore, higher chain transfer constants at higher temperatures led to lower molecular weights. The same trends were found for chain transfer to initiator. Shawki and Hamielec[16] reported K_{fi}/K_p values of 1.58×10^{-3} and 4.41×10^{-3}, corresponding to 25°C and 40°C, respectively.

The molecular weights obtained for the copolymers (*Table 5*) were lower than those of the acrylamide homopolymers obtained at the same temperatures. A higher initiator concentration used in the copolymer synthesis ($[I] = 3.0 \times 10^{-3} \, \text{mol} \, l^{-1}$) was one reason. Another possible reason is that chain transfer to macromonomers is easier than chain transfer to acrylamide. This explanation has been proposed by Schulz *et al.*[13].

Microstructure of the copolymers

The performance of the copolymers in applications such as flocculation could depend upon the chain microstructure. The distribution of pendant chains was characterized by the mean sequence lengths, μ_1 and μ_2, calculated by using the following equations[43]:

$$\mu_1 = 1 + r_1[M_1]/[M_2] \qquad (11)$$

$$\mu_2 = 1 + r_2[M_2]/[M_1] \qquad (12)$$

where the subscript 1 refers to acrylamide and subscript 2 refers to the macromonomer. For example, sample 56-35 in *Table 1* has $[M_1]/[M_2] = 1/50 - 1/200$, equation (12) predicted that $\mu_2 \cong 1.0$. This meant that the PEG pendant chains were separated by ~50 to 100 acrylamide repeat backbone units in the copolymers produced in this work.

The use of a semi-batch polymerization process[21] is a more effective approach to minimize composition drift and is also more effective in the utilization of costly macromonomers. One possible semi-batch feed policy, i.e. Policy I, is the addition of all macromonomer and sufficient AM (to give the desired composition F_1, i.e. mol% of AM in the copolymers) to the reactor at time zero. Thereafter, the AM is fed to the reactor with a time-varying feed rate so as to maintain $[M_1]/[M_2]$ and F_1 constant with time. This method should provide copolymer chains with the same composition. An alternative policy is called monomer-starved feed policy. With this method, the mixtures of AM and macromonomers at desired ratios are fed to a reactor. The addition rate is controlled at a lower rate so that $[M_1] = [M_2] \sim 0$ and the copolymer composition which is spontaneously formed is the same as the feed composition. In order to maintain the initiator concentration constant in an isothermal polymerization, the initiator e.g. potassium persulfate, can also be continuously fed to the reactor as an aqueous solution during polymerization.

CONCLUSIONS

The main conclusions drawn from this work are as follows:

1. Copolymers of AM and PEG macromonomers can be prepared by homogeneous free-radical polymerization in aqueous solution.

2. The reactivity of the macromonomer (M_2) toward acrylamide (M_1) was pendant chain length dependent in both homopolymerization and copolymerization of the macromonomer. In copolymerization, longer PEG pendant chain lengths gave lower reactivities, as characterized by ($1/r_1$). The homopolymerization rate of macromonomers increases as the PEG pendant chain lengths increase, as estimated by $K_p/K_t^{1/2}$.

3. The shielding effect caused by pendant chains of macromonomers on growing polymer radicals was proposed for interpreting the kinetic mechanism in polymerizations and it was observed that shielding reduced the radical/radical termination rate more than the propagation rate.

4. The molecular weights of the copolymers synthesized were sensitive to the polymerization temperature. Higher molecular weights were obtained at lower temperatures, which is similar to the trend found in AM homopolymerization. The pendant chain length in the macromonomer did not show a significant effect on the molecular weights of the copolymers.

5. Each PEG pendant chain, on average, was separated by 100 AM repeat units at a feed ratio of $[M_1]/[M_2] \sim$ 60. Semi-batch polymerization can provide a more effective approach for minimizing composition drift, along with a more effective use of costly macromonomers.

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