

# Aqueous solution polymerization of acrylamide at low conversions: 1. Kinetics and transfer studies

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(Received 8 April 1987; accepted 1 July 1987)

The aqueous polymerization of acrylamide, initiated by 4,4'-azobis-4-cyanovaleric acid, has been studied in the presence of propionamide, and oligoacrylamide, at 30–90°C. Molecular weights were determined viscometrically and transfer constants to propionamide, oligoacrylamide and monomer were evaluated. Exponents expressing the dependency of initial polymerization rate on monomer and initiator concentrations at 50°C were  $1.16 \pm 0.01$  and  $0.52 \pm 0.03$ , respectively.

(Keywords: acrylamide; polyacrylamide; radical polymerization; transfer constants; oligoacrylamide)

## INTRODUCTION

Polyacrylamides, together with the corresponding anionic and cationic copolymers, and derivatives, are the most important series of water soluble polymers for current industrial applications<sup>1,2</sup>. The world demand for polyacrylamides, as their properties are exploited, is expected to grow, as evidenced, for example, by increased use in polymer flooding for enhanced oil recovery<sup>3,4</sup>.

Most of the properties and applications of this set of polymers are strongly dependent on their molecular weight, linearity or degree of branching of the polymer molecules<sup>5–7</sup>.

Surprisingly, there have been relatively few detailed studies of the radical polymerization of acrylamide with controlled branching apart from work by Gleason *et al.*<sup>8</sup>, later confirmed<sup>6,7</sup> and work reported by Kulicke<sup>5</sup>.

In this paper, we report studies of the low conversion aqueous-phase radical polymerization of acrylamide initiated by 4,4'-azobis-4-cyanopentanoic acid (ACV), and compare results with those of other workers. More importantly, the transfer reactions of polyacrylamide radicals with respect to the model compound, propionamide,  $\text{CH}_3\text{CH}_2\text{CONH}_2$  and oligoacrylamide,  $(-\text{CH}_2\text{CH}(\text{CONH}_2))_n$ , have been directly studied and values of transfer constants at 50 and 70°C for propionamide, and 30, 50, 70 and 90°C for oligoacrylamide are reported for the first time. The values of the transfer constants to oligoacrylamide reflect the susceptibility of polyacrylamide molecules to transfer by polymer radical and/or primary radical attack and to consequent branching. Analysis of the experimental data also leads to values for the transfer constants to monomer at 30–90°C.

## EXPERIMENTAL

### Reagents

**Acrylamide.** Acrylamide (BDH Chemicals) was recrystallized twice from chloroform, dried in a vacuum oven at room temperature for 3 days and stored in a

refrigerator until required. The purified acrylamide had a melting point of  $84 \pm 0.5^\circ\text{C}$ . Gel permeation chromatograms in water were recorded both for a fresh monomer solution and for a solution subsequently kept in the dark at room temperature for 4 months. The two chromatograms were identical within experimental error, indicating that no detectable polymerization takes place under these conditions over a period of 4 months.

**4,4'-Azobis-4-cyanopentanoic acid (ACV).** ACV (Aldrich Chemical Co. Ltd.) was purified as follows. The ACV was suspended in distilled water at room temperature, and solid sodium bicarbonate was added until the solid ACV just dissolved. The solution was then acidified with 1 M HCl, until slightly acidic, causing precipitation of the ACV. The solid was filtered off and washed with ice-cold water and dried *in vacuo* at room temperature. Infra-red spectra of AVC (Nujol mull) and nuclear magnetic resonance (n.m.r.) confirmed the structure of ACV. An ultra-violet spectrum of the compound, recorded in water, showed a main absorbance peak at 343.4 nm, which is typical of azo groups. The analysis of ACV is shown in Table 1.

**Propionamide.** Propionamide (BDH Chemicals) was recrystallized twice from benzene and dried *in vacuo* at room temperature (m.p.  $79.0 \pm 0.5^\circ\text{C}$ ). The n.m.r. data are in very good agreement with the literature<sup>9</sup>.

**2-Mercaptoethanol.** 2-Mercaptoethanol was supplied by BDH Chemicals Ltd, 99% pure.

**Oligoacrylamide.** Low molecular weight polyacrylamide (oligoacrylamide) was prepared at 50°C by the

Table 1 Analysis of ACV

	Carbon (%)	Hydrogen (%)	Nitrogen (%)
Calculated	51.42	5.75	19.99
Found	51.58	5.74	19.98

0032-3861/88/010128-06\$03.00

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128 POLYMER, 1988, Vol 29, January

radical polymerization of acrylamide in water, initiated by ACV in the presence of mercaptoethanol,  $\text{HS}(\text{CH}_2)_2\text{OH}$ , as transfer agent, and was isolated by precipitation in dioxane. The concentrations of ACV, acrylamide and mercaptoethanol were  $1.775 \times 10^{-3}$ , 6.67 and  $0.33 \text{ mol dm}^{-3}$ , respectively, and there as a 19.6% conversion of monomer for a reaction time of 2 h. The oligomer was dissolved in water and reprecipitated into excess dioxane three times before isolation by filtration using a no. 3 sintered glass crucible.

After washing the filtered oligomer with fresh dioxane, the solid was dried *in vacuo* for 4 days at room temperature. No precipitation was observed when silver nitrate solution was added to an aqueous solution of the oligomer, indicating the absence of free mercaptoethanol.

The number average molecular weight of the oligoacrylamide was 2850, which was determined in aqueous solution using a Knauer vapour pressure osmometer.

#### Solvents

*Dioxane.* 1,4-Dioxane (technical grade) was supplied by BDH Chemicals Ltd.

*Ethanol.* Methylated spirits (Unalco) was used for polymer precipitation.

*Water.* Distilled water was used in all kinetic experiments and was prepared using an autostill ('Four-Plus', Jencons).

#### Apparatus and experimental procedures

*Vacuum line.* A conventional glass high vacuum line incorporating a rotary oil pump and a mercury diffusion pump was used when filling reaction vessels.

*Infra-red spectroscopy.* Infra-red spectra of reagents were determined in Nujol mulls using a Perkin-Elmer 137G grating infra-red spectrometer.

*Ultra-violet spectroscopy.* For ultra-violet spectroscopic work, a Shimadzu recording spectrometer, UV-260, was used.

*Nuclear magnetic resonance (n.m.r.).*  $^1\text{H}$  spectra of reagents were recorded using a Varian XL-100-12 n.m.r. spectrometer.

*Viscometry.* Limiting viscosity numbers,  $[\eta]$ , of polymers were determined in aqueous solution at  $30^\circ\text{C}$  using an Ubbelohde dilution viscometer with a high shear rate<sup>10</sup>.

All solutions for viscosity measurements were prepared from dried polyacrylamide samples by adding solvent and shaking periodically by hand. No additional mechanical shaking, or heating, was used. The polymer concentration range was  $1.0\text{--}4.0 \text{ g dm}^{-3}$ , using distilled water as the solvent. The viscosity measurements were made with fresh samples to avoid ageing effects<sup>5</sup>.

*Vapour pressure osmometry.* The number average molecular weights of oligoacrylamides were determined using a Knauer pressure osmometer (I. H. Knauer Co.).

The number average molecular weight of the oligoacrylamide was measured at  $37^\circ\text{C}$  using distilled water as solvent. The instrument was calibrated with dextrose (D-glucose).

#### General procedures

*Pyrex reaction vessels.* Two types of Pyrex vessel were constructed: Pyrex glass ampoules, o.d. 24 mm (i.d. 20 mm)  $\times$  20 cm high, capillary stems about 22 cm long made of 4 mm bore capillary ended with a B10 socket, used for the polymerization of acrylamide; and Pyrex vessels of volume  $380 \text{ cm}^3$  for preparation of oligoacrylamide.

*Filling ampoules.* Acrylamide and ACV aqueous stock solutions were made up and stored in the dark in a refrigerator until required for filling reaction ampoules. All filled reaction vessels, connected to a high vacuum line, were subjected to a freeze-thaw process at least three times to remove dissolved air, before they were sealed off *in vacuo*. It was later shown that less than 1% conversion occurred during this freeze-thaw process. After filling and degassing, ampoules were placed in a thermostat for the appropriate time. After reaction, ampoules were quench cooled in liquid nitrogen. No induction periods were observed, indicating that the degassing procedures removed residual oxygen from the reactants.

*Polymer recovery.* Polymer, removed from the reaction ampoules, and related aqueous washings were transferred to a flask containing a trace of hydroquinone and left with added distilled water for several days to obtain a polymer solution. This was then added dropwise to a large excess of ethanol, stirred with a Silverson model 2LR stirrer. The precipitation was performed rapidly, typically lasting only a few minutes, to reduce degradation by stirring<sup>10</sup>.

The precipitated polymer was filtered, using a no. 3 sintered glass crucible, washed with ethanol several times to remove monomer and ACV completely, and dried to constant weight at  $50^\circ\text{C}$  under vacuum. Usually, drying times lasted more than a week. Conversion of monomer to polymer was measured by gravimetry.

In transfer experiments involving propionamide, this transfer agent was readily removed by the above procedure owing to its solubility in ethanol. When oligoacrylamide was involved as transfer agent, however, the high molecular weight polyacrylamide precipitated normally, tending to accumulate around the stirrer shaft. The oligoacrylamide, however, formed a colloidal solution which was thus readily separated from the higher molecular weight material.

*Types of experiment.* The experimental runs were of two kinds, being performed both with and without transfer agents. The runs without transfer agent were made to obtain reliable initial rates of polymerization, gravimetrically, at  $50^\circ\text{C}$  with conversions usually of less than 15%. The runs with transfer agents were made to calculate transfer constants to monomer and transfer agents at  $30\text{--}90^\circ\text{C}$ , and the number average molecular weights of precipitated polymers were calculated from measured limiting viscosity numbers,  $[\eta]$ , using an empirical relation for polydisperse polyacrylamides<sup>11</sup>:

$$[\eta]/100 \text{ cm}^3 \text{ g}^{-1} = 6.8 \times 10^{-4} \bar{M}_n^{0.66} \quad (1)$$

## RESULTS AND DISCUSSION

### Initial rate of polymerization

Initial rates of polymerization,  $R_{p0}$ , were measured at effectively constant monomer and initiator con-

**Table 2** Initial rates of polymerization at 50°C,  $[M]_0 = 3.5 \text{ mol dm}^{-3}$ 

$10^5[\text{ACV}]_0$ ( $\text{mol dm}^{-3}$ )	Reaction time (min)	Conversion (%)	$10^4 R_{p0}^a$ ( $\text{mol dm}^{-3} \text{ s}^{-1}$ )
25.000	5.0	5.60	6.53 (6.20) <sup>b</sup>
25.000	15.0	15.10	5.87
100.000	6.0	15.00	14.58
1.562	50.0	14.00	1.63

<sup>a</sup>  $R_{p0}$  was calculated as  $[M]_0 \times (\Delta X / \Delta t)$ , where  $\Delta X$  is the fractional conversion and  $\Delta t$  is the reaction time

<sup>b</sup> At  $[\text{ACV}]_0 = 2.5 \times 10^{-4} \text{ mol dm}^{-3}$  the average value of  $R_{p0}$  was taken

**Table 3** Initial rates of polymerization at 50°C,  $[\text{ACV}]_0 = 2.5 \times 10^{-4} \text{ mol dm}^{-3}$ 

$[M]_0$ ( $\text{mol dm}^{-3}$ )	Reaction time (min)	Conversion (%)	$10^4 R_{p0}$ ( $\text{mol dm}^{-3} \text{ s}^{-1}$ )
3.500	5.0	5.60	6.53 (6.20) <sup>a</sup>
3.500	15.0	15.10	5.87
2.500	16.0	15.61	4.07
0.416	20.0	15.00	0.52

<sup>a</sup> At  $[M]_0 = 3.5 \text{ mol dm}^{-3}$  the average value of  $R_{p0}$  was taken

centrations,  $[M]_0$  and  $[\text{ACV}]_0$ , respectively.

Plots of  $\log R_{p0}$  versus  $\log [M]_0$  at constant initiator concentration,  $[\text{ACV}]_0$ , and  $\log R_{p0}$  versus  $\log [\text{ACV}]_0$  at constant  $[M]_0$  can be drawn using data shown in Tables 2 and 3.

Least-squares analysis gave:

$$R_{p0} \propto [M]_0^a [\text{ACV}]_0^b \propto [M]_0^{1.16 \pm 0.01} [\text{ACV}]_0^{0.52 \pm 0.03}$$

#### Kinetic scheme

The classical kinetic theory was modified by using the reaction scheme described by North<sup>12</sup> and by applying the concept of the 'cage effect'<sup>13-15</sup>.

Under stationary state conditions the rate of initiation,  $I$ , due to decomposition of initiator of concentration  $[C]$  may be written:

$$I = 2k_d[C] \left( \frac{[M]}{k_R/k_x + [M]} \right) \quad (2)$$

where  $k_d$ ,  $k_R$  and  $k_x$  are velocity constants for initiator decomposition, wastage of caged initiator radicals and escape of caged radicals by reaction with monomer, respectively<sup>12</sup>.

The final expression for the rate of polymerization,  $R_p$ , becomes:

$$R_p = -\frac{d[M]}{dt} = \left( \frac{k_p^2}{k_t} \right)^{1/2} \left( \frac{k_d[C][M]}{(k_R/k_x) + [M]} \right)^{1/2} [M] \quad (3)$$

In considering transfer, water has a zero chain transfer constant<sup>14,16</sup>, while transfer to ACV is negligible<sup>16,17</sup>. Termination occurs predominantly by disproportionation<sup>14,16,17</sup>, so that a single termination rate constant,  $k_t$ , may be used in (3), with  $k_p$  the conventional propagation rate constant.

In the presence of added transfer agents (propionamide or oligoacrylamide), the degree of polymerization,  $DP$ ,

may be written:

$$\frac{1}{DP} = \frac{2}{k_p[M]} \left( \frac{k_d k_t [C][M]}{k_R/k_x + [M]} \right)^{1/2} + C_m + C_s \frac{[S]}{[M]} \quad (4)$$

where  $C_m$  is the transfer constant to monomer ( $k_{tm}/k_p$ ),  $C_s$  is the transfer constant to transfer agent ( $k_{tr}/k_p$ ), and  $[S]$  is the concentration of transfer agent. Here  $k_{tm}$  and  $k_{tr}$  are velocity constants for transfer to monomer and transfer agent, respectively.

In this derivation, it is assumed that negligible mutual termination of branched radicals, formed from radical attack on oligoacrylamide or polyacrylamide, occurs.

The observed rate dependence  $R_{p0} \propto [M]_0^{1.16} [\text{ACV}]_0^{0.52}$  in ACV-initiated polymerization gives a  $b$ -value which agrees well with the initiator exponents previously published<sup>14,17</sup>, but differs in the exponent of the monomer concentration,  $a$ . The present result disagrees slightly with that of Cavell<sup>17</sup>, whose value for  $a$  is 1.04. Hamielec *et al.*<sup>14</sup>, using a more sophisticated 'cage effect' scheme, showed that  $R_{p0} \propto [M]_0^{-1.5} [\text{ACV}]_0^{0.5}$  depending upon the level of  $[M]_0$ : at higher monomer concentrations  $R_{p0} \propto [M]_0^{1.0}$ , and at relatively low monomer concentrations  $R_{p0} \propto [M]_0^{1.5}$ . In the present work the range of monomer concentrations was 0.4–3.5  $\text{mol dm}^{-3}$ ; in reference 13 it was 0.563–2.252  $\text{mol dm}^{-3}$ . Hence the present work, which gives a value  $a = 1.16$  agrees well with the value given by Hamielec *et al.*<sup>14</sup> of 1.24.

The values of  $a$  and  $b$  are relatively close to the theoretical values predicted by the simplest kinetic scheme with no cage effect; 1.0 and 0.5 respectively.

The fact that the monomer exponent  $a$  in the present work has a value of 1.16, only slightly greater than unity, suggests that the cage effect is not very important. This is confirmed by the transfer results, which are discussed next.

#### Transfer studies

A series of transfer experiments were performed under conditions such that  $[\text{ACV}]^{1/2}/[M]$  values were maintained constant, so that an analysis of the results could be made firstly using the most simple equation<sup>12</sup>:

$$\frac{1}{DP} = \frac{2}{k_p[M]} (F k_t k_d [\text{ACV}])^{1/2} + C_m + C_s \frac{[S]}{[M]} \quad (5)$$

and secondly using the more exact equation for  $1/\overline{DP}$ , which has already been presented in equation (4).  $F$  in equation (5) represents the unknown value of initiator efficiency, so the use of equation (4) is preferred.

A plot of  $1/\overline{DP}$  versus  $[S]/[M]$  and also

$$\frac{1}{DP} - \frac{2}{k_p[M]} \left[ \frac{k_d k_t [\text{ACV}][M]}{(k_R/k_x) + [M]} \right]^{1/2}$$

versus  $[S]/[M]$ , with  $[\text{ACV}]^{1/2}/[M]$  maintained constant, then enables the determination of  $C_s$  (from equation (5)) and  $C_s$  and  $C_m$  (from equation (4)), respectively, at different temperatures by least-squares analysis.

Typical plots for oligoacrylamide and propionamide are shown in Figure 1. All plots of  $1/\overline{DP}$  versus  $[S]/[M]$

were linear, irrespective of whether S was propionamide or oligoacrylamide. The absence of curvature suggested that  $F$  is not strongly dependent on  $[M]$ . Plots of the left-hand side of equation (4) versus  $[S]/[M]$ , using values of  $k_d$ ,  $k_t$ ,  $k_p$  and  $(k_R/k_x)$  given in the literature, also gave linear plots, as in Figure 1, with slopes in very good agreement with those obtained from  $1/DP$  versus  $[S]/[M]$  plots.

The values of  $k_t^{1/2}/k_p$  (using the notation of this paper) and  $k_d^{1/2}$  at different temperatures which were needed were

calculated from the equations:

$$k_p/k_t^{1/2} = 196.6 \exp(-8379/RT) \text{ dm}^{3/2} \text{ mol}^{-1/2} \text{ s}^{-1/2} \quad (6)$$

$$k_d = 7.7 \times 10^{13} \exp(-120124/RT) \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \quad (7)$$

(refs. 18 and 14, respectively). From the data of ref. 14 it was established that:

$$k_R/k_x = 1.237 \times 10^{-3} \exp(17908/RT) \text{ mol dm}^{-3} \quad (8)$$

Activation energies and differences are in joules per mole.

$C_s$  for propionamide and oligoacrylamide, and  $C_m$ , using equation (4), were calculated at different temperatures using the methods described above.

For oligoacrylamide, the transfer constant per molecule was divided by the number of repeat units in the oligomer molecule to obtain the transfer constant per repeat unit. For example,  $C_s$ , the transfer constant to oligoacrylamide was  $108.28 \times 10^{-5}$  at  $30^\circ\text{C}$ , and the molecular weight of the oligoacrylamide was 2850. Hence the transfer constant per repeat unit of  $-\text{CH}_2-\text{CH}(\text{CONH}_2)-$  was  $(108.28 \times 10^{-5} \times 71.08)/2850$ , equal to  $2.70 \times 10^{-5}$ , since the molecular weight of the repeat unit was 71.08. Tables 4 and 5 show the experimental conditions and results for transfer to propionamide and oligoacrylamide, respectively. The transfer constants to propionamide and oligoacrylamide are in Table 6, with the related values of  $C_m$ , at different temperatures.

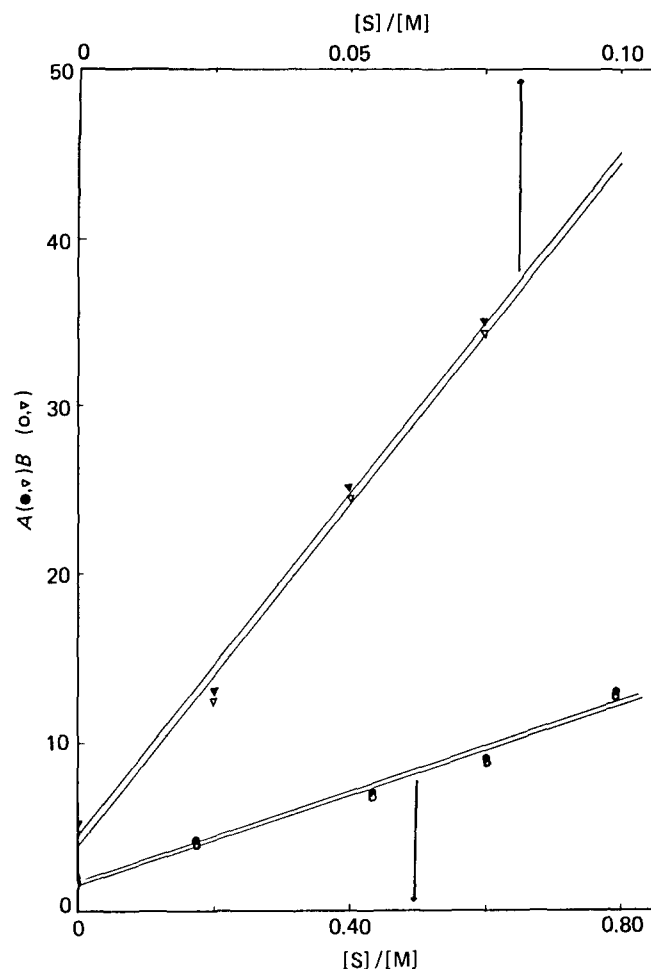


Figure 1 Transfer to oligoacrylamide ( $\blacktriangledown, \nabla$ ) and propionamide ( $\bullet, \circ$ ) at  $70^\circ\text{C}$ .  $A = 10^5/DP$  (filled symbols)

$$B = 10^5 \left\{ \frac{1}{DP} - \frac{2}{k_p[M]} \left[ \frac{k_d k_t [\text{ACV}][M]}{(k_R/k_x) + [M]} \right]^{1/2} \right\} \quad (\text{open symbols})$$

Table 4 Transfer to propionamide at 50 and  $70^\circ\text{C}$ <sup>a-c</sup>

[M] (mol dm <sup>-3</sup> )	[S] (mol dm <sup>-3</sup> )	[η]/100 cm <sup>3</sup> g <sup>-1</sup>		10 <sup>5</sup> /DP		B <sup>d</sup>	
		50°C	70°C	50°C	70°C	50°C	70°C
2.500	0.000	13.40	14.80	2.21	1.90	1.996	1.728
2.286	0.400	9.82	8.80	3.54	4.18	3.329	4.010
2.000	0.883	7.64	6.25	5.18	7.02	4.973	6.852
1.857	1.125	6.77	5.30	6.22	9.01	6.016	8.844
1.714	1.365	5.75	4.16	7.97	13.01	7.769	12.846

<sup>a</sup> Conversion < 15% in all experiments

<sup>b</sup>  $[\text{ACV}]^{1/2}/[M] = 6.32 \times 10^{-3} \text{ dm}^{3/2} \text{ mol}^{-1/2}$  in all experiments at  $50^\circ\text{C}$

<sup>c</sup>  $[\text{ACV}]^{1/2}/[M] = 1.58 \times 10^{-3} \text{ dm}^{3/2} \text{ mol}^{-1/2}$  in all experiments at  $70^\circ\text{C}$

$$^d B = 10^5 \left\{ \frac{1}{DP} - \frac{2}{k_p[M]} \left[ \frac{k_d k_t [\text{ACV}][M]}{(k_R/k_x) + [M]} \right]^{1/2} \right\}$$

Table 5 Transfer to oligoacrylamide at different temperatures<sup>a-d</sup>

[M] (mol dm <sup>-3</sup> )	[S] (mol dm <sup>-3</sup> )	[η]/100 cm <sup>3</sup> g <sup>-1</sup>				10 <sup>5</sup> /DP				B <sup>e</sup>			
		30°C	50°C	70°C	90°C	30°C	50°C	70°C	90°C	30°C	50°C	70°C	90°C
0.416	0.0000	11.00	10.40	7.69	3.15	2.98	3.24	5.31	19.8	2.780	2.411	4.588	19.255
0.381	0.0095	7.62	—	4.12	1.50	5.20	—	13.20	61.0	5.008	—	12.499	60.468
0.331	0.166(5)	5.74	3.51	2.69	—	7.99	16.80	25.20	—	7.803	16.033	24.525	—
0.309	0.0231	4.64	2.98	2.16	0.80	11.03	21.50	35.00	152.0	10.853	20.757	34.345	151.500
0.285	0.0285	4.04	2.55	—	0.70	13.60	27.30	—	194.0	13.429	26.579	—	193.512

<sup>a</sup> In most experiments, conversion < 25%

<sup>b</sup>  $[\text{ACV}]^{1/2}/[M] = 3.8 \times 10^{-2} \text{ dm}^{3/2} \text{ mol}^{-1/2}$  in all experiments at 30 and  $50^\circ\text{C}$

<sup>c</sup>  $[\text{ACV}]^{1/2}/[M] = 9.49 \times 10^{-3} \text{ dm}^{3/2} \text{ mol}^{-1/2}$  in all experiments at  $70^\circ\text{C}$

<sup>d</sup>  $[\text{ACV}]^{1/2}/[M] = 2.4 \times 10^{-3} \text{ dm}^{3/2} \text{ mol}^{-1/2}$  in all experiments at  $90^\circ\text{C}$

<sup>e</sup> B is defined in Table 4

## Activation energies

Using the values for  $C_s$  per repeat unit for oligoacrylamide shown in Table 6, the activation energy difference,  $\Delta E$ , between transfer and propagation,  $E_{tr} - E_p$ , was calculated to be  $40250 \pm 7500 \text{ J mol}^{-1}$  from a plot of  $\ln C_s$  versus  $10^3 K/T$ . Thus

$$C_s = \frac{k_{tr}}{k_p} = \frac{A_{tr}}{A_p} \exp[-(E_{tr} - E_p)/RT] \quad (9)$$

where  $A_{tr}$  and  $A_p$  are the frequency factors for transfer and propagation, respectively. By direct calculation,  $\Delta E$  for propionamide was  $29600 \text{ J mol}^{-1}$ .

The higher  $\Delta E$  value for transfer to oligoacrylamide than for transfer to propionamide may be related to the increased steric hindrance involved in the radical transfer to polymer.

In Table 7 the values given in the literature for transfer constants,  $C_s$ , to oligo(vinyl acetate) and oligo(methyl methacrylate) are compared with the results of the present work. The activation energies for the transfer process,  $\Delta E$ , are also shown in Table 7. The acrylamide radical may be considerably less reactive than radicals from vinyl acetate and methyl methacrylate. The low reactivity of the polyacrylamide radical would be expected on the basis of resonance stabilization, possibly H-bond formation in that radical, which is responsible for the higher activation energy,  $\Delta E$ , for transfer involving oligoacrylamide. Clearly, however, the absolute value of the velocity constant for transfer,  $k_{tr}$ , will depend on the reactivities of both radical and oligomer.

The activation energy difference between transfer to monomer and propagation,  $\Delta E'$ , equal to  $E_{im} - E_p$ , was calculated from the present  $C_m$  data (Table 6) and also from the above results and the rather scattered values given in the literature for  $C_m$ , which are reported at  $25^\circ\text{C}$

**Table 6** Transfer constants to monomer ( $C_m$ ), propionamide and oligoacrylamide,  $C_s$ , at different temperatures<sup>a</sup>

Temp. (°C)	Transfer agent	$10^5 C_m$	$10^5 C_s^b$
30	Oligoacrylamide	$(2.55 \pm 0.18)$	$(2.70 \pm 0.07)$
50	Oligoacrylamide	$(2.91 \pm 0.82)$	$(5.99 \pm 0.30)$
70	Oligoacrylamide	$(3.79 \pm 1.01)$	$(10.10 \pm 0.52)$
90	Oligoacrylamide	$(18.27 \pm 1.43)$	$(43.84 \pm 0.55)$
50	Propionamide	$(1.98 \pm 0.15)$	$(7.00 \pm 0.30)$
70	Propionamide	$(1.49 \pm 0.54)$	$(13.30 \pm 1.08)$

<sup>a</sup> Values of  $C_s$  and  $C_m$  obtained from a plot based on equation (4)

<sup>b</sup> Values of  $C_s$  are calculated for oligoacrylamide per repeat unit  $-\text{CH}_2-\text{CH}(\text{CONH}_2)-$

as  $1.2 \times 10^{-5}$  (ref. 19),  $1.6 \times 10^{-5}$  (ref. 17),  $2 \times 10^{-5}$  (ref. 20),  $0.79 \times 10^{-5}$  (ref. 21); at  $40^\circ\text{C}$  as  $1.2 \times 10^{-5}$  (ref. 21); and at  $50^\circ\text{C}$  as  $1.45 \times 10^{-5}$  (ref. 14).

Values of  $\Delta E'$  were:  $27420 \pm 12100 \text{ J mol}^{-1}$ ;  $23150 \pm 6850 \text{ J mol}^{-1}$ ; and  $21250 \pm 6850 \text{ J mol}^{-1}$ . These values are all considerably higher than the value of  $\Delta E'$  of  $6730 \text{ J mol}^{-1}$  reported elsewhere<sup>18</sup>.

Theoretically, at any fixed temperature, the value of  $C_m$  should be constant, irrespective of whether oligoacrylamide or propionamide was used in the determination of  $C_m$ . However, Table 6 indicates that  $C_m$ , determined when oligoacrylamide was involved, appears higher than when propionamide was used. The apparent differences may be due, in part, to the difficulty of determining values of  $C_m$  from intercepts, which involves considerable errors.

The  $C_m$  value for an *N*-substituted acrylamide *N,N*-dimethylacrylamide, at  $50^\circ\text{C}$  in toluene initiated with AIBN is reported<sup>22</sup> as  $1.5 \times 10^{-4}$ . This higher value of  $C_m$  than for the acrylamide system may be related to the relative unreactivity of the polyacrylamide radical caused by resonance stabilization and H-bonding.

## ACKNOWLEDGEMENTS

The authors gratefully acknowledge Allied Colloids Ltd, Bradford, for financial support for equipment and materials and for many valuable discussions during the course of this work.

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**Table 7** Values of chain transfer constants to oligomer,  $C_s$ , and related activation energies for some vinyl polymers

Monomer <sup>a</sup>	Polymer <sup>a</sup>	$10^3 C_s$							$E_{tr} - E_p = \Delta E$ (kJ mol <sup>-1</sup> )	Reference
		30°C	40°C	50°C	60°C	70°C	80°C	90°C		
VA	PVA	—	3.2	—	4.8	—	—	—	16.74	23 <sup>b</sup>
MMA	PMMA	—	—	—	0.210	—	0.248	—	8.12	24 <sup>b</sup>
AM	PAM	0.027	—	0.0599	—	0.1010	—	0.4384	$40.25 \pm 7.45$	Present work

<sup>a</sup> VA, PVA: vinyl acetate and oligo(vinyl acetate), respectively.

MMA, PMMA: methyl methacrylate and oligo(methyl methacrylate), respectively.

AM, PAM: acrylamide and oligoacrylamide, respectively

<sup>b</sup> Initiator: AIBN and solvent: benzene

*Solution polymerization of acrylamide (1): M. H. Rafi'ee Fanood and M. H. George*

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