Aqueous solution polymerization of acrylamide to high conversion: 2. Branching studies

M. H. Rafi'ee Fanood and Maurice H. George
Chemistry Department, Imperial College of Science and Technology, London SW7 2AY, UK
(Received 8 April 1987; accepted 1 July 1987)

Acrylamide, AM, was polymerized radically at 50°C with different concentrations of monomer and 4,4'-azobis-4-cyanovaleric acid, ACV, to high conversions. The polyacrylamides were isolated by precipitation into ethanol. After drying, the limiting viscosity numbers and apparent molecular weights of these polyacrylamides were determined viscometrically in distilled water and 1 M sodium chloride solution. The dependence of limiting viscosity numbers on percentage conversion is discussed, and the significance of polymer branching is assessed.

(Keywords: acrylamide; free-ridical polymerization; polyacrylamide; branching; high molecular weights)

INTRODUCTION

High molecular weight and linear polyacrylamides, PAMs, are finding increasing application in areas such as flocculation and enhanced oil recovery by means of polymer flooding. In commercial production, there is often a need to maximize both the production yield and the linearity of the resultant PAMs. This can be achieved by adjusting polymerization conditions, such as polymerization temperature, monomer and initiator concentrations, and technique of polymerization and possibly by alteration of reactor design.

The objective of the present work was to investigate branching in the radical polymerization of acrylamide at high conversions. The results were analysed by reference to a previous paper in which a detailed study of transfer to oligoacrylamide was reported[1].

EXPERIMENTAL

Reagents

Acrylamide, AM, and 4,4'-azobis-4-cyanovaleric acid, ACV, were purified and characterized as described previously[1].

Sodium chloride (Analar) was supplied by BDH Chemicals Ltd. The source of ethanol and distilled water has been described elsewhere[1].

Apparatus and experimental procedures

Temperature variation during polymerization. A set of standard experiments was carried out to determine the variation of reaction temperature during the polymerization process to high conversions at 50°C. Pyrex glass ampoules were employed, o.d. 24 mm, i.d. 20 mm and 20 cm high.

A method was developed whereby mixtures were thoroughly degassed and introduced into an ampoule of the above type, fitted with a thermometer inserted through a vacuum-tight seal. Each ampoule, sealed off under vacuum, was then placed in a thermostat at 50°C and the reaction temperature was measured as a function of time. Monomer and ACV concentrations were varied and the time, t, to reach any observed maximum temperature was recorded.

Freeze–thaw degradation of PAM samples in aqueous solution. Two low conversion samples of polyacrylamide which had previously been made at 50°C with AM and ACV concentrations of 0.563 and 1.78×10^{-4} mol dm^{-3}, respectively, were chosen to determine the freeze–thaw effect on viscosity. Thoroughly degassed aqueous polymer solutions, 0.1% w/v, were frozen in liquid nitrogen and thawed in warm water at 50°C, three times. The polymer solutions were then diluted with 2 M aqueous NaCl solution in air to give a final polymer solution in 1 M NaCl. Subsequently, viscosity measurements were performed at 25°C to determine limiting viscosity numbers.

Thermal degradation of a PAM sample in aqueous solution at 50°C. A PAM sample of the freeze–thaw experiment, sample I, with an initial limiting viscosity number, $[\eta]$, of 16.20×10^{-2} cm^3 g^{-1} was chosen for the measurements of the purely thermal degradation effect on limiting viscosity numbers, at 50°C. Five sample solutions, 0.1% w/v, were degassed, sealed off *in vacuo* and then left in a thermostatted bath at 50°C for different times. All polymer solutions were then diluted with aqueous 2 M NaCl solution to give a final 1 M NaCl solution for viscosity measurements at 25°C.

The effect of 1 M NaCl solution on limiting viscosity number. Viscosity measurements were carried out at 25°C with PAM samples, both in aqueous and aqueous 1 M sodium chloride solutions, to determine limiting viscosity numbers, so that values could be compared.

Polymerization to high conversion at 50°C. Acrylamide was polymerized radically at 50°C at different

0032-3861/88/010134-04$03.00

Table 1 Temperature variation during polymerization of acrylamide at 50°C

Expt. no.	[AM] (mol dm^{-3})	[ACV] (mol dm^{-3})	ΔT_{max} (°C)	Time to reach ΔT_{max} (min)
A1	3.500	1.5×10^{-3}	11.0	13.0
A2	3.500	9.0×10^{-5}	0.9	55.0
A3	0.563	9.0×10^{-5}	0.0	–
A4	0.563	2.7×10^{-3}	0.0	–

Table 2 Freeze–thaw degradation of PAMs in aqueous solution

Sample no.	$[\eta]/100$ cm^3 g^{-1} (in original stock solution)	$[\eta]/100$ cm^3 g^{-1} (after freeze-thaw process)	Reduction in $[\eta]$ (%)
I	16.20	14.13	12.77
II	17.00	14.62	14.00

concentrations of monomer and ACV, to high conversion. Conversion was measured gravimetrically after precipitation into ethanol and drying *in vacuo* at 50°C.

RESULTS AND DISCUSSION

Temperature variation during the polymerization

Table 1 shows the experimental conditions and corresponding maximum temperature changes, ΔT_{max}, during the polymerization of acrylamide at 50°C.

The fact that the temperature increased in experiment A1 by 11°C, compared with 0.9°C in A2, indicates the lack of effective heat transfer in experiment A1. This was due to the formation of a highly viscous polyacrylamide solution in A1, in the early stages of reaction, and presumably a consequent rate acceleration, or so-called gel effect. Experiments A3 and A4 involved lower polymerization rates and were thus isothermal.

Freeze–thaw degradation of PAMs

Table 2 shows that during three freeze–thaw cycles the limiting viscosity numbers of two PAM samples decreased by about 13%. This decrease may be due to backbone degradation consequent on the formation of ice crystals in the polymer matrix, but may also be due to changes in hydrogen bonding during the freeze–thaw process. Kulicke *et al.*[2] have already reviewed the main types of hydrogen bonding that can occur in aqueous PAM solutions and the effects of changes in hydrogen bonding on molecular shapes.

Thermal degradation in aqueous solutions at 50°C

Table 3 shows the effect of thermal degradation at 50°C on the limiting viscosity number of a PAM sample in 1 M sodium chloride solution. It appears that the thermal degradation of the PAM sample, about 6% after 7 h, was much less than that during three freeze–thaw cycles. Other workers[3], using gel permeation chromatography (g.p.c.), have suggested that there is negligible thermal degradation for a PAM with $\bar{M}_w = 2.9 \times 10^6$ after 1 h at 50°C in aqueous solution.

Effect of 1 M NaCal solution on limiting viscosity number

Table 4 shows the limiting viscosity number of PAM samples both in distilled water and 1 M NaCl solution. There is on average an increase in $[\eta]$ of about 18% on changing the solvent from distilled water to aqueous 1 M NaCl solution. Munk *et al.*[4] have reported a 20% increase in $[\eta]$ in 1 M sodium chloride solution, compared with the values in distilled water, for a set of PAM samples with a $\bar{M}_w$ range of 0.26×10^6–11.20×10^6. These molecular weights are close to those involved in the present work. The observed effect may be caused by some rearrangement in hydrogen bonds within the solution, which are responsible for the solubility of PAM in water. Also, it might be caused by the breakage of Z-position H-bonds mentioned in the Kulicke model[2].

It was also shown[4] that the limiting viscosity number increases with increasing ionic strength (increasing the molarity of NaCl).

Polymerization to high conversion at 50°C

Figure 1 shows plots of percentage conversion against reaction time for the present work, curves B and C; data of Hamielec[5] are combined with the present results to give curve A. In general, as expected, the higher the values of [AM] and [ACV], the higher are the initial polymerization rates and the shorter the times to reach high conversions.

There is no direct evidence from *Figure 1* that a gel-effect rate acceleration occurs during polymerization. However, threre is some evidence that a gel effect does occur during polymerization. Simple theory[6] suggests that $(R_p \times \overline{DP})/[\overline{M}]^2$ should be constant, during a polymerization, and equal to k_p^2/k_t, where R_p, $\overline{DP}$ and $[\overline{M}]$ are, respectively, the overall rate of polymerization, average degree of polymerization and average monomer concentration at any time t. Calculations using the

Table 3 Thermal degradation of PAM at 50°C

Sample no.	Time (h)	$[\eta]/100$ cm^3 g^{-1}	Reduction in $[\eta]$ (%)
I0[a]	0	14.13	0.0
I1	1	14.10	0.21
I2	2	13.33	5.66
I3	3	13.32	5.73
I4	4	13.30	5.87
I5	7	13.27	6.00

[a] The initial $[\eta]$ value at 25°C in 1 M NaCl solution of this PAM sample was 16.20×10^{-2} cm^3 g^{-1}, but it decreased to 14.13×10^{-2} cm^3 g^{-1} after three freeze–thaw cycles

Table 4 Limiting viscosity numbers of PAMs in water and 1 M NaCl solution at 25°C

$[\eta]/100$ cm^3 g^{-1}		
In distilled water	In 1 M NaCl	$\Delta[\eta]$ (%)
13.70	15.80	15.32
17.40	20.70	18.96
17.30	20.80	20.23
17.10	20.50	19.88
17.00	19.70	15.88
12.60	14.90	18.25
10.30	12.30	19.41

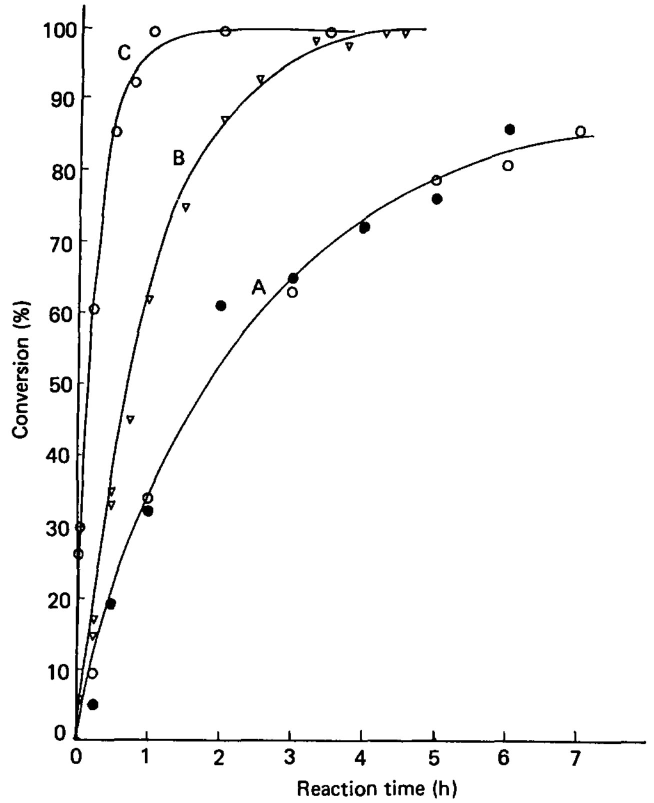

Figure 1 Percentage conversion *versus* polymerization time at 50°C. Curve A: $[M]_0 = 0.563$ mol dm^{-3}, $[ACV] = 1.78 \times 10^{-4}$ mol dm^{-3}; (●) present results; (○) Hamielec's results[5]. Curve B: $[M]_0 = 3.5$ mol dm^{-3}, $[ACV] = 2.5 \times 10^{-4}$ mol dm^{-3}. Curve C: $[M]_0 = 3.5$ mol dm^{-3}, $[ACV] = 1.8 \times 10^{-3}$ mol dm^{-3}

present data for curve B in *Figure 1* give values of $(R_p\overline{DP})/[M]^2$ which generally increase to a maximum of about 8.4 dm^3 mol^{-1} s^{-1} after about 35% polymerization and then progressively decrease. This suggests a decrease in k_t after about 35% conversion. Similar calculations using the present data in curve A also show evidence for a maximum value of $(R_p\overline{DP})/[M]^2$ over a conversion range 32–61%. Curve C in *Figure 1* represents data recorded under non-isothermal conditions.

Figure 2 shows plots of limiting viscosity, $[\eta]$, measured in distilled water or 1 M NaCl solution against percentage conversion for several experiments and includes some results from Hamielec *et al.*[5]

The general shape of all curves in *Figure 2* is the same, with a maximum limiting viscosity number, $[\eta]_{max}$, attained after 32–43% conversion. The initial increase in $[\eta]$ with percentage conversion is considered to be due to the gel effect, which has been discussed in a previous section. There is relatively little increase in $[\eta]$ with percentage conversion in curves A and B because the gel effect at low initial monomer and initiator concentrations would not be expected to be large. There is a dramatic increase in $[\eta]$ for experiments with high initial monomer concentrations, however, even with varying initial initiator concentrations.

Comparision of *Figure 2* curves E and C, for which the initial monomer concentrations were equal (3.5 mol dm^{-3}), indicates, as expected, that the higher $[\eta]$ values were obtained at lower initiator concentrations.

The dramatic decrease in $[\eta]$ with increasing conversion after the maximum is presumably due to the increased branching occurring by transfer to continuously increasing amounts of polymer. The branching process occurs whenever polymer is present. This is discussed in more detail in the following section. However, at the percentage conversion corresponding to $[\eta]_{max}$, in *Figure 2*, most of the polymer molecules are only lightly branched, so the results show that as branching becomes more important with increasing conversions, $[\eta]$ decreases. The situation is complicated since the branching reaction produces not only polyacrylamides of higher molecular weight but also an increased fraction of polymers[7] of low molecular weight.

Branching calculations

The smoothed-out values of the transfer constants per repeat unit of acrylamide in oligoacrylamide at different temperatures[1] can be used to calculate the number of branches per polyacrylamide molecule, assuming no change in transfer constants with increase in molecular weight. Use is made of the equation[8]

$$\rho = -C_p[1 + (1/\alpha)\ln(1-\alpha)] \qquad (1)$$

where C_p is the transfer constant to polymer per monomeric repeat unit, α is the fractional conversion of monomer and ρ is the number of branches per monomeric repeat unit in the polymer chain.

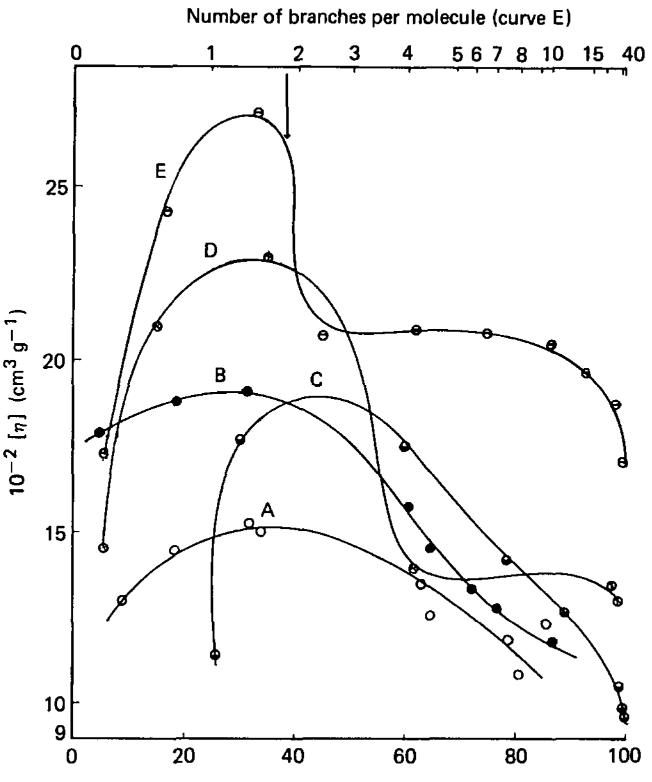

Figure 2 Limiting viscosity number $[\eta]$ versus percentage conversion at 50°C. Curves A, B: $[M]_0 = 0.563$ mol dm^{-3}, $[ACV] = 1.78 \times 10^{-4}$ mol dm^{-3}; (●) present work, viscosity measurements in 1 M NaCl solution at 25°C; (○) Hamielec's data[5], viscosity measurements in water. Curve C: $[M]_0 = 3.5$ mol dm^{-3}, $[ACV] = 1.8 \times 10^{-3}$ mol dm^{-3}; viscosity measurements in 1 M NaCl solution at 25°C. Curves D and E: $[M]_0 = 3.5$ mol dm^{-3}, $[ACV] = 2.5 \times 10^{-4}$ mol dm^{-3}; (⊗) viscosity measurements in distilled water at 30°C; (⊖) viscosity measurements in 1 M NaCl solution at 25°C

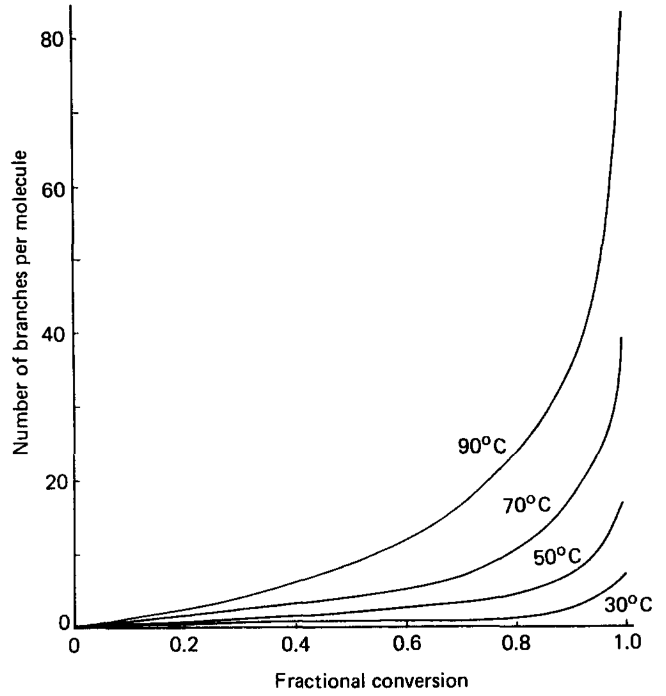

Figure 3 Number of branches *versus* fractional conversion calculated for a polyacrylamide sample of $\bar{M}_n = 5 \times 10^6$ using extrapolated values of C_s obtained from a least-squares plot of ln C_s *versus* $1/T$

The calculated values of the number of branches *versus* fractional conversion for a polyacrylamide of overall number average molecular weight of 5×10^6 are shown in *Figure 3* for different polymerization temperatures.

The rapid increase in the overall number of branches in the polymer molecules at high conversions reflects the increases in the polymer/monomer ratio in the system.

There is expected to be a broadening of molecular weight distributions with increasing conversion, as first pointed out by Bamford and Tompa[7,9]. This broadening could give rise to increased $\bar{M}_w/\bar{M}_n$ values with increasing conversion. However, Hamielec *et al.*[5] have measured $\bar{M}_w/\bar{M}_n$ values even at high conversions and report values close to the theoretical value of 2.0 (for disproportionation) even at conversions of 85%. Some calculations can also be performed using the data shown in *Figure 2* (curve E) to give some idea of the number of branches per polymer molecule at different conversions.

The value of $[\eta]_{max}$ in *Figure 2* (curve E) is 27.2×10^{-2} cm^3 g^{-1}. Since most molecules at the conversion corresponding to $[\eta]_{max}$ are linear, the Munk $[\eta]$–$\bar{M}_w$ equation, valid in 1 M NaCl solutions[4], can be used as an approximation to give a corresponding weight average molecular weight of 16 233 100. Assuming a theoretical value of $\bar{M}_w/\bar{M}_n$, the corresponding value of $\bar{M}_n$ is 8 116 550 at a conversion of 33.0%, corresponding to $[\eta]_{max}$.

Hamielec[5,10] has also predicted that $\bar{M}_w$ does not change markedly with percentage conversion. Hence, assuming that the $\bar{M}_n$ value of 8 116 550 ($\overline{DP} = 114\,189$) also does not change, the number of branches per polymer molecule for curve E is as shown on a second axis in *Figure 2*.

For good solvents, the ratio of the limiting viscosity number of a branched polymer molecule, $[\eta]_b$, to that of a linear polymer molecule of the same molecular weight, $[\eta]_l$, is given by[11]:

$$[\eta]_b/[\eta]_l = g^{1/2}(\alpha_{\eta,b}/\alpha_{\eta,l})^3 \qquad (2)$$

where α_η denotes the expansion factor of the viscosity radius compared with that under θ-conditions and g is the ratio of the mean square radius of gyration for branched to linear polymer molecules under θ-conditions. There is some evidence[11] that for polystyrene star molecules $(\alpha_{\eta,b}/\alpha_{\eta,l})^3$ is only slightly greater than unity, but the value for PAMs is unknown. Again, the value of g for PAM is unknown theoretically, but $[\eta]_b/[\eta]_l$ has been found[2] to be equal to 0.6 for PAMs of overall weight average molecular weight 1.8×10^6 with 20 branches of weight average molecular weight 48 000.

If the variation of $\bar{M}_w$ is small in the present experiments, then in the experiment corresponding to curve E of *Figure 2*, for 20 branches per molecule, $[\eta]_b$ is 19.0×10^{-2} cm^3 g^{-1} and $[\eta]_l = [\eta]_{max} = 27.2 \times 10^{-2}$ cm^3 g^{-1}. This leads to a value of $[\eta]_b/[\eta]_l$ of 0.7, in reasonable agreement with the above value[2].

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.

REFERENCES

1 Rafi'ee Fanood, M. H. and George, M. H. *Polymer* 1988, **29**, 128
2 Kulicke, W. M., Kniewske, R. and Klein, J. *Prog. Polym. Sci.* 1982, **8**, 373
3 Klein, J. and Westerkamp, A. *J. Polym. Sci.* 1981, **19**, 707
4 Munk, P. A., Williams, P. and Hoffman, D. E. *Macromolecules* 1980, **13**, 871
5 Ishige, T. and Hamielec, A. E. *J. Appl. Polym. Sci.* 1973, **17**, 1479
6 North, A. M. 'The Kinetics of Free Radical Polymerisation', Pergamon Press, Oxford, 1966
7 Bamford, C. H., Barb, W. G., Jenkins, A. D. and Onyon, P. F. 'The Kinetics of Vinyl Polymerization by Radical Mechanisms', Butterworths, London, 1958
8 Flory, P. J. 'Principles of Polymer Chemistry', Cornell University Press, Ithaca, New York, 1953
9 Bamford, C. H. and Tompa, H. *J. Polym. Sci.* 1952, **10**, 345
10 Kim, C. J. and Hamielec, A. E. *Polymer* 1984, **25**, 845
11 Yamakawa, H. 'Modern Theory of Polymer Solutions', Harper and Row Publications, New York, 1971