Studies on the kinetics of inverse emulsion polymerization of acrylamide using α-ketoglutaric acid as photoinitiator

Swapan Kumar Ghosh and Broja M. Mandal*
Polymer Science Unit, Indian Association for the Cultivation of Science, Jadavpur, Calcutta 700 032, India
(Received 24 November 1992; revised 23 February 1993)

The kinetics of the inverse emulsion photopolymerization of acrylamide using the water soluble photoinitiator (triplet radical generator) α-ketoglutaric acid (α-KGA), sorbitan monooleate (Span 80) as the emulsifier and toluene as the oil phase has been studied. The rate of polymerization (R_p) can be represented by: $R_p \propto I^{0.5}[C]^{0.5}[M]^{1.28}[E]^{-0.42}$, where I, C, M and E represent the light intensity (313 nm u.v. light), photoinitiator, monomer and emulsifier, respectively. The kinetic results suggest that the polymerization of acrylamide is essentially a microsuspension one. The emulsifier apparently acts as a retarder. The overall activation energy is 10.20 ± 1.58 kJ mol^{-1}. The presence of the gel effect is evident from the increase of molecular weight with conversion and also from the nature of the percentage conversion *versus* time curves. A useful linear relation between high conversion molecular weight and maximum R_p was found to exist. The relation yields the upper limit of the viscosity average molecular weight $[(7.25 \pm 0.48) \times 10^6]$ for 4.5 mol dm^{-3} acrylamide, 6.3% (w/v) Span 80, toluene:water = 53:47 (v/v), a stirring rate of 425 rev min^{-1} and a temperature of 30°C.

(Keywords: inverse emulsion; photopolymerization; acrylamide; α-ketoglutaric acid; microsuspension; kinetics)

INTRODUCTION

Recently we reported that α-ketoglutaric acid (α-KGA) and β-ketoglutaric acid (β-KGA) act as efficient water soluble photoinitiators in the inverse emulsion polymerization of acrylamide[1]. Toluene was used as the oil phase and sorbitan monooleate (Span 80) as the water-in-oil emulsifier. It was found that at the same rates of polymerization the molecular weights of the polymers formed using these initiators are not only greater than those obtained using the water soluble azo initiator 4,4′-azobis-4-cyanopentanoic acid (ACPA) but also greater than those prepared using the oil soluble initiator 2,2′-azobisisobutyronitrile (AIBN). The latter two initiators generate singlet radical pairs on dissociation while the two keto-acids give rise to triplet radical pairs[1]. In the literature[2-5] it has been concluded that polymerization using water soluble initiators proceeds in the emulsified monomer droplets irrespective of whether an aliphatic or an aromatic hydrocarbon is used as the oil phase. Each droplet acts as a small batch reactor so that solution polymerization kinetics operate. Thus the process is essentially a suspension polymerization and in order to emphasize the smallness of the reactor the prefix 'micro' is used so that the process is referred to as 'microsuspension polymerization'[2-7]. It is of interest to study the kinetics of the polymerization using the photoinitiators mentioned above and to examine whether the same kinetics apply as for singlet radical initiated polymerization. It is difficult to carry out quantitative work using β-KGA because of its instability, hence α-KGA has been used in the present kinetics study.

EXPERIMENTAL

Acrylamide (E. Merck) was recrystallized twice from dried and distilled methanol. Commercial distilled water was redistilled over alkaline permanganate once and then plain distilled twice. Toluene was washed with concentrated H_2SO_4 and then with 5% $NaHCO_3$ solution, dried over fused $CaCl_2$ and distilled. Span 80 (Sigma, USA) and α-KGA (E. Merck) were used as received. Acrylamide was dissolved in water to appropriate concentrations. The required amount of Span 80 dissolved in toluene was put into the reactor and the acrylamide solution in water was added to it to attain a water:oil ratio of 47:53 (v/v). The polymerization vessel was a jacketed, Teflon-stoppered cylindrical Corning glass test tube (3.2 cm × 6 cm lower part; 2.2 cm × 12 cm upper part) provided with a stirrer, a N_2 inlet and a Teflon capillary for sample withdrawal. The reaction mixture was sonicated for 10 min. Then the required amount of the initiator was added and the emulsion was deaerated by bubbling oxygen-free N_2 gas for 30 min, while the mixture was stirred at 1000 rev min^{-1}. The temperature was maintained by

---

* To whom correspondence should be addressed

0032-3861/93/204287-04

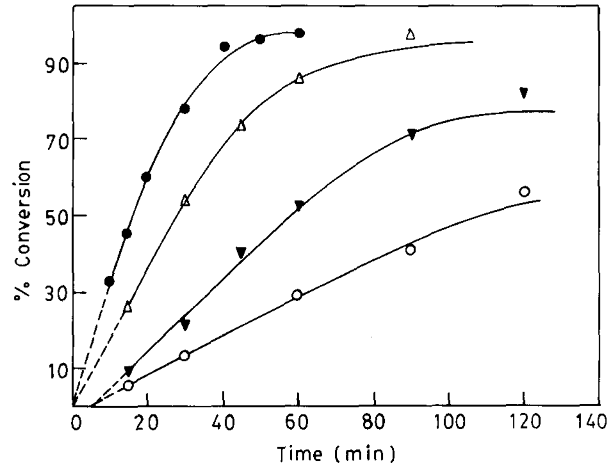

Figure 1 Percentage conversion *versus* time curves in inverse emulsion polymerization of acrylamide using α-KGA photoinitiator at 30°C at different light intensities: (●) 1.0*I*; (△) 0.41*I*; (▼) 0.085*I*; (○) 0.023*I* ($I = 247.6\,\mathrm{J\,m^{-2}\,S^{-1}}$ at 313 nm incident on the surface of the outer jacket of the reaction vessel). Toluene:water = 1.13 (v/v); [acrylamide] = $4.5\,\mathrm{mol\,dm^{-3}}$; Span 80 = 6.3% (w/v) in toluene; [α-KGA] = $6.85\,\mathrm{mmol\,dm^{-3}}$; stirring rate = $425\,\mathrm{rev\,min^{-1}}$

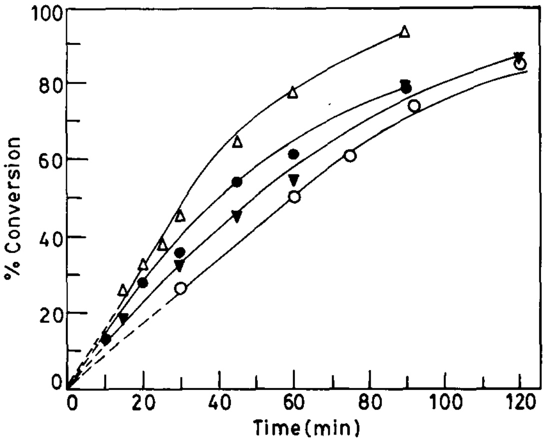

Figure 2 Percentage conversion *versus* time curves in inverse emulsion polymerization of acrylamide at different concentrations of the photoinitiator α-KGA and at a fixed light intensity (0.23*I*, where $I = 247.6\,\mathrm{J\,m^{-2}\,S^{-1}}$) at 30°C: (△) 14.4; (●) 9.9; (▼) 7.2; (○) 4.7 $\mathrm{mmol\,dm^{-3}}$. [Acrylamide] = $1.5\,\mathrm{mol\,dm^{-3}}$; other conditions as in *Figure 1*

passing water from the thermostatically controlled water bath through the jacket of the reaction vessel. The stirrer speed was then decreased to $425\,\mathrm{rev\,min^{-1}}$ and a positive pressure of N_2 was maintained over the reaction mixture.

An Oriel 1000 W Hg-Xe lamp with a potassium chromate and sodium carbonate filter solution (path length 8.0 cm) was used to obtain light with a wavelength of 313 nm. The concentration of the potassium chromate was varied to change the light intensity. The reaction vessel was positioned 50 cm away from the u.v. source. Further details have been given earlier[8]. Aliquots were withdrawn at different times and polyacrylamide was precipitated into acetone. The precipitated polymer was filtered, washed and dried for 48 h at 60°C in a vacuum oven and weighed.

The light intensity incident on the outer surface of the double-walled reaction vessel was calculated from the data given in the manufacturer's manual dealing with the lamp characteristics and from the knowledge of the absorbance of the filter solution at 313 nm and the length of the light path through the filter.

Polymer characterization

The molecular weights were determined by viscometry. The polymer was purified by dissolution in water. For this purpose, the polymer was kept for 1 week in contact with water to which sodium azide (0.1% w/v) was added to prevent microbial degradation. The dissolved polymer was precipitated into acetone. The polymer was then dried for 48 h in a vacuum oven at 60°C.

The intrinsic viscosity was determined at 25°C using 0.5 M NaCl solution as solvent. The intrinsic viscosity was shear corrected. The molecular weights were calculated using the Mark–Houwink equation for which K and α data of Klein and Conrad[9] were used. The values are 7.19×10^{-5} and 0.77, respectively (concentrations in $\mathrm{g\,dl^{-1}}$).

RESULTS

The photoinitiator allows polymerization to be carried out at lower temperatures than are required for thermally dissociable initiators like AIBN. *Figure 1* shows the percentage conversion *versus* time curves at different light intensities at 30°C with the α-KGA concentration remaining the same in all cases. The initial rate of polymerization (R_p) for each of the experimental sets was determined from the initial slope of the curves shown in *Figure 1*. It was found that R_p decreased with a decrease in light intensity. The light intensity is indicated here as the relative light intensity incident on the outside surface of the double-walled reactor facing the light source. The intensity was in the range of $5.69–247.6\,\mathrm{J\,m^{-2}\,s^{-1}}$ at 313 nm. Double logarithmic plots of R_p *versus* I were linear with slopes of 0.5 (correlation coefficients of 0.99 and 0.96 at 30 and 50°C, respectively). *Figure 2* shows the percentage conversion *versus* time curves for a fixed light intensity but varying photoinitiator concentrations ([C]) at a lower monomer concentration ([M] = $1.5\,\mathrm{mol\,dm^{-3}}$). Double logarithmic plots of R_p *versus* [C] were linear with slopes of 0.5 (correlation coefficients of 0.99 and 0.98 for [M] = 1.5 and $4.5\,\mathrm{mol\,dm^{-3}}$, respectively). *Figure 3* shows the percentage conversion *versus* time plots at various [M] values. In these experiments [M] in the aqueous phase was varied

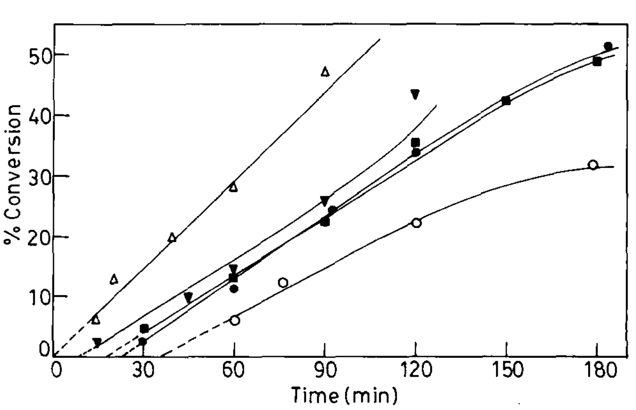

Figure 3 Percentage conversion *versus* time curves for various concentrations of acrylamide in the aqueous phase at 30°C: (○) 0.5; (■) 1.0; (●) 1.5; (▼) 2.0; (△) 2.5 $\mathrm{mol\,dm^{-3}}$. [α-KGA] = $3.7\,\mathrm{mmol\,dm^{-3}}$. Toluene:water = 1.13 (v/v); Span 80 = 6.3% (w/v) in toluene; light intensity = 0.20*I* (where $I = 247.6\,\mathrm{J\,m^{-2}\,S^{-1}}$)

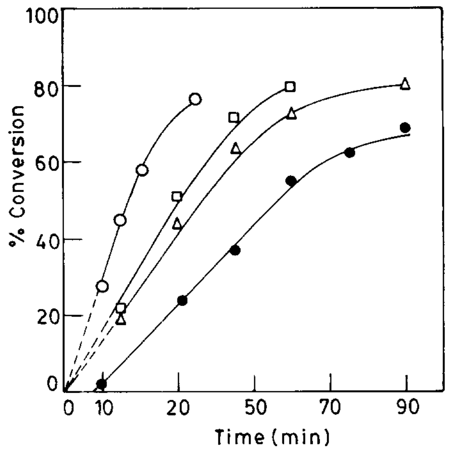

Figure 4 Percentage conversion *versus* time curves in inverse emulsion polymerization of acrylamide with various concentrations of emulsifer [Span 80 (w/v)] in toluene at 30°C: (●) 9.0; (△) 6.3; (□) 3.0; (○) 1.4%. Toluene:water = 1.13 (v/v); [acrylamide] = 3.5 mol dm^{-3}; [α-KGA] = 5.0 mmol dm^{-3}; light intensity = 0.41*I* (where *I* = 247.6 J m^{-2} S^{-1})

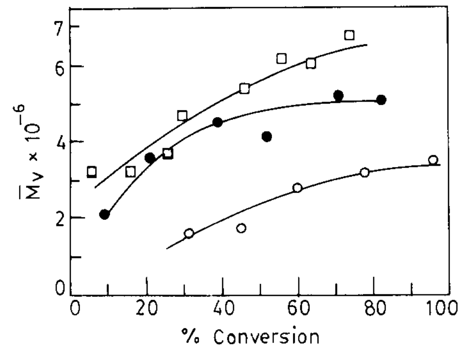

Figure 5 Variation of $\bar{M}_v$ with percentage conversion. The reaction conditions are the same as in *Figure 1* with different light intensities: (□) 0.023*I*; (●) 0.085*I*; (○) 1.0*I*

whilst the phase ratio was kept constant. The double logarithmic plot of R_p *versus* [M] was linear with a slope of 1.28 (correlation coefficient 0.99). *Figure 4* shows that the polymerization rate decrease with increased Span 80 concentrations, and a double logarithmic plot of R_p *versus* emulsifier concentration ([E]) was linear with a slope of −0.42 (correlation coefficient 0.98). These results yield the following rate equation:

$$R_p \propto I^{0.5}[C]^{0.5}[M]^{1.28}[E]^{-0.42} \qquad (1)$$

with respect to monomer found in the present study, namely 1.28, differed from the results of Baade and here for three different light intensities). The increase is sharp in the lower conversion region and the molecular weight tends to level off at a higher conversion level ($\gtrsim$70%). *Figure 6* shows that the high conversion molecular weight ($\bar{M}_v$) decreases linearly with increase in initial R_p (correlation coefficient 0.82) and the following relation between R_p and $\bar{M}_v$ holds for [M] = 4.5 mol dm^{-3} at 30°C:

$$\bar{M}_v = (7.25 \pm 0.48) \times 10^6 - (2.18 \pm 0.37) \times 10^9 R_p \qquad (2)$$

Figure 7 shows that increasing the concentration of emulsifier decreases the molecular weight of the polymers formed. *Table 1* shows the effect of temperature on photopolymerization over the temperature range 20–50°C. It is evident from the results that R_p increases with temperature, e.g. an increase from 20 to 50°C brings about a 50% increase in rate. An Arrhenius plot for R_p yields an overall activation energy (E_{overall}) of 10.20 ± 1.58 kJ mol^{-1}. The molecular weight also increases with increase in temperature (*Table 1*).

DISCUSSION

The kinetic features such as the square root dependence of R_p on light intensity as well as on photoinitiator concentration are typical of solution polymerization kinetics involving mutual bimolecular termination of polymer radicals. In view of the considerable amount of light scattering by the emulsion the exponent of the light intensity conforming to the normal value of 0.5 may appear surprising. The result may suggest that the scattering decreases the light absorption by the same factor at the different light intensities. Baade and Reichert[3] also found a square root dependence

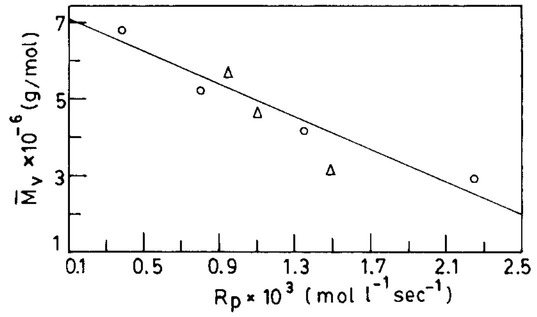

Figure 6 Plot of high conversion $\bar{M}_v$ *versus* maximum R_p: (○) light intensity varied; (△) photoinitiator concentration varied

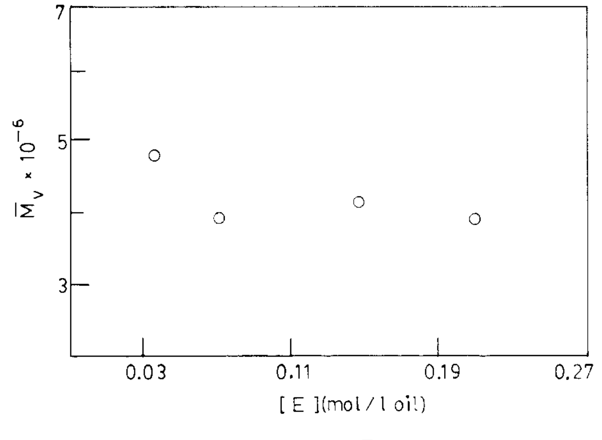

Figure 7 Variation of high conversion $\bar{M}_v$ with [E]. Conditions as in *Figure 4*

Table 1 Effect of temperature on R_p and $\bar{M}_v$ in the inverse emulsion photopolymerization of acrylamide[a]

Temperature (°C)	R_p ($\times 10^3$) (mol l^{-1} s^{-1})	$\bar{M}_v$ ($\times 10^{-6}$) (g mol^{-1})
50	1.50	4.44
40	1.35	4.50
30	1.25	4.24
20	1.00	3.08

[a] Toluene:water = 1.13 (v/v); [acrylamide] = 4.5 mol dm^{-3}; Span 80 = 6.3% (w/v) in toluene; [α-KGA] = 6.05 mmol dm^{-3}

on initiator concentration using thermally dissociable water soluble azo initiators such as 2,2′-azobis-*N*-(2-hydroxyethyl)butyramidine. The emulsifier used by them was the same as the one used here. The reaction order with respect to monomer found in the present study, namely 1.28, differed from the results of Baade and Reichert who found the order to be unity. However, Hunkeler *et al.*[5] reported a monomer order of 1.25. A monomer order higher than unity was also reported for solution polymerization of acrylamide by Riggs and Rodriguez[10] and by Ishige and Hamielec[11] who reported values of 1.25 and 1.24, respectively, using the water soluble initiators $K_2S_2O_8$ and ACPA. The kinetics thus conform to the view that the polymerization occurs in the monomer solution droplets. The polymerization therefore may be justifiably termed microsuspension polymerization. Earlier workers studying solution polymerization kinetics explained the higher monomer order by modifying the classical kinetic theory of free radical polymerization on the basis of the hypothesis that some of the caged initiator radicals are captured by the monomer, i.e. the monomer competes with the secondary cage recombination[10,11]. Such a quantitative treatment is not repeated here.

Our results differ from those of Baade and Reichert[3] in yet another respect. A negative exponent for [E] was obtained by us while they reported the polymerization rate to be independent of [E]. The emulsifier is the same in both cases. The decrease in both R_p and $\bar{M}_v$ with [E] found in the present work tends to suggest that the emulsifier is acting as a retarder. One may argue that the emulsifier might participate in the photochemistry of the initiation and yield odd results. This however turned out to be incorrect since similar results were obtained (not included here) when polymerization was carried out using the water soluble thermally dissociable initiator ACPA. The difference between our results and those of Baade and Reichert with respect to the emulsifier exponent remains unexplained.

The effect of temperature on the photoemulsion polymerization is in line with what one would expect for solution polymerization. In photoinitiation, the rate of initiation (R_i) is independent of temperature and since the solution polymerization kinetics operate here, R_p changes with a change in the value of $(k_p/k_t)^{1/2}$ at fixed [M], I, [C] and [E] where k_p and k_t are rate constants for the propagation and termination reactions, respectively. The overall activation energy, $E_{\text{overall}} = 10.20 \pm 1.58\ \text{kJ mol}^{-1}$, determined from the Arrhenius plot therefore refers to $E_p - \frac{1}{2}E_t$. This is comparable to the literature[12] values reported for solution polymerization of acrylamide in water. For example, Kim and Hamielec[12] give $8.38\ \text{kJ mol}^{-1}$ for the value of $E_p - \frac{1}{2}E_t$. Furthermore, in the absence of a significant transfer reaction, the molecular weight would be given by R_p/R_i. Since R_p increases with temperature while R_i remains constant, the molecular weight increases with temperature (as shown in *Table 1*).

The variation of $\bar{M}_v$ with conversion as shown in *Figure 5* is similar to that reported by Hunkeler *et al.*[5] for the inverse emulsion polymerization of acrylamide effected by the oil soluble thermally dissociable initiator AIBN. The increase in molecular weight with conversion is indicative of the existence of the 'gel effect'. The tapering of the molecular weight at higher conversion may arise from two opposing effects, namely, the increase of molecular weight due to the gel effect is opposed by the molecular weight decrease brought about by the depletion of [M]. Hunkeler *et al.*[5] attributed the molecular weight tapering to the latter, reaching the limiting value dictated by monomer transfer[5]. That the limiting molecular weight is not reached in our system is evident from *Figure 6*, which shows that the high conversion $\bar{M}_v$ decreases with increase in the initial R_p (which is also the maximum R_p). The high conversion $\bar{M}_v$ and R_p relation [equation (2)] is a useful working relation. It follows from the relation that the maximum viscosity average molecular weight achievable at $4.5\ \text{mol dm}^{-3}$ acrylamide concentration and at 30°C $(7.25 \pm 0.48) \times 10^6$ under the experimental conditions of 6.3% (w/v) Span 80 and a stirrer speed of $425\ \text{rev min}^{-1}$.

The influence of the gel effect is also evident in the percentage conversion *versus* time curves. The linear portions of the curves extend to very high conversion levels (~50–60%). Under normal conditions the R_p would have decreased with increasing conversion due to decreasing [M] and this would have been evident from ~10% conversion level. However, in the present case this decrease is fortuitously compensated by the increased rate of conversion with increasing polymer concentration (conversion) caused by the gel effect up to a very high conversion level. However, the gel effect in acrylamide polymerization is not as great as in the polymerization of acrylates or methacrylates. According to Ishige and Hamielec[11] the gel effect in acrylamide polymerization is even less important than in the case of styrene polymerization. They, and others, found that the gel effect decreases with decreasing [M].

In conclusion, it follows from this study that the triplet radical initiated polymerization follows essentially the same kinetics as holds for singlet radical initiated polymerization.

ACKNOWLEDGEMENTS

We are grateful to the Department of Science and Technology, Government of India for financial support. SKG thanks the Council of Scientific and Industrial Research, Government of India for a senior research fellowship. Thanks are also due to Professor S. N. Bhattacharyya for helpful discussions.

REFERENCES

1 Ghosh, S. K., Nazimuddin, M. and Mandal, B. M. *Makromol. Chem. Rapid Commun.* 1992, **13**, 583

2 Baade, W. and Reichert, K. H. *Eur. Polym. J.* 1984, **20**, 505

3 Baade, W. and Reichert, K. H. *Makromol. Chem., Rapid Commun.* 1986, **7**, 235

4 Vanderhoff, J. W., DiSteffano, F. V., El-Aasser, M. S., O'Leary, R., Schaffer, O. M. and Visioli, D. L. *J. Dispersion Sci. Technol.* 1984, **5**, 323

5 Hunkeler, D., Hamielec, A. E. and Baade, W. *Polymer* 1989, **30**, 127

6 Kurenkov, V. A. and Myagchenkov, V. A. *Polym. — Plast. Technol. Eng.* 1991, **30**, 367

7 Graillat, C., Pichot, C. and El-Aasser, M. S. *J. Polym. Sci., Polym. Chem. Edn* 1986, **24**, 427

8 Nazimuddin, M., Das, A. R., Mandal, B. M. and Bhattacharyya, S. N. *Eur. Polym. J.* 1990, **26**, 837

9 Klein, J. and Conrad, K.-D. *Makromol. Chem.* 1980, **181**, 227

10 Riggs, J. P. and Rodriguez, F. *J. Polym. Sci. A1* 1967, **5**, 3151

11 Ishige, T. and Hamielec, A. E. *J. Appl. Polym. Sci.* 1973, **17**, 1479

12 Kim, C. J. and Hamielec, A. E. *Polymer* 1984, **25**, 845