Macromolecules **1990,** *23,* 5161–5163 **5161**

Pulsed Laser Study of the Propagation Kinetics of Acrylamide and Methacrylamide in Water

Introduction. The kinetics of monomer/polymer systems in water are complicated because of competing electrostatic, hydrogen-bonding, and hydrophobic effects. Understanding such kinetics is rendered even more difficult because the literature often contains conflicting data. In the present work, we present studies of the polymerization kinetics of acrylamide in water at low conversion, using the newly established pulsed laser technique. This technique has been shown to yield reliable rate parameters and is more direct than more conventional means such as the rotating sector method. We apply the method to acrylamide, an important water-soluble monomer, whose aqueous-phase polymerization kinetics are far from being well understood. We also apply the technique to methacrylamide, to provide additional data to test against mechanistic hypotheses.

Acrylamide (AAm), methacrylamide (MAAm), and their respective polymers (PAAm and PMAAm) are nonionic in neutral water. However, it is well recognized that amides in solution associate strongly via intermolecular H-bonding to form not only dimers, as is commonly known to occur with carboxylic acids, but also larger aggregates.[1,2] This effect is suspected to give rise to the extraordinarily high values of the propagation rate coefficient k_p that have been reported (ca. 10^4 dm^3 mol^{-1} s^{-1}).[3] By studying various solvent effects, Chapiro et al.[4–6] suggested that H-bonded linear aggregates of monomer could explain the large k_p of AAm and other acrylic monomers. They suggested that polymerization would proceed rapidly within these aggregates because (a) the AAm molecules are favorably aligned and (b) they present high local monomer concentrations. Another possible explanation, the so-called template effect,[7] is similar in concept to that put forward by Chapiro et al., except that propagation is supposed to be preceded by a specific arrangement of monomer molecules, H-bonded along a preexisting polymer chain. Again in this model the monomer molecules are aligned and in close proximity to one another, which might give rise to rapid polymerization.

A necessary step toward testing these models is to obtain accurate data for k_p as a function of temperature. Here we report these values for AAm and MAAm in water, with the remarkable finding for AAm that k_p decreases as temperature increases; i.e., it exhibits an apparent negative activation energy.

Experimental Section. Reagents. AAm (Aldrich, >99%), uranyl chloride (Pfaltz & Bauer, 99%), aqueous perchloric acid (Aldrich, 61%), hydroquinone (Aldrich), and sodium sulfate (Merck) were used as received. MAAm (Aldrich) was recrystallized twice from chloroform. Distilled water, further purified by passing through a Milli-Q filter system (Millipore), was employed throughout.

Photopolymerizations. Cylindrical Pyrex sample tubes charged with aliquots (0.7 cm^3) of aqueous solutions (pH 1) of AAm (0.5 mol dm^{-3}) and MAAm (1 mol dm^{-3}), containing perchloric acid (0.1 mol dm^{-3}) and uranyl chloride (0.01 mol dm^{-3}), were placed in a temperature bath and allowed to equilibrate for 8 min, while being degassed with high-purity argon. The AAm experiments at pH 4 were treated similarly, except that no perchloric acid was added. The pH of all experiments before and after polymerization did not change noticeably. Throughout these preparations ambient light was minimized by using aluminum foil to avoid premature polymerization. Each cell was then placed in a thermostated cell holder ready for polymerization and the temperature monitored with a thermocouple. The runs were carried out over temperatures ranging from 15 to 50 °C.

The pulsed laser system was identical with that described previously.[8] Polymerization was initiated with laser pulses (15 ns) of 35 mJ at 355 nm, generated by a Quantaray DCR2 Nd:YAG laser. The beam, directed vertically from underneath the cell, had a diameter of ca. 9 mm, illuminating the entire reaction volume. The radical flux was approximately 1.8×10^{-6} mol dm^{-3}. Dark times, t_f, were varied between 0.2–0.1 and 1–0.5 s for AAm and MAAm, respectively. A sufficient number of pulses was used to produce ca. 0.4% polymer in the final aqueous solution. Hydroquinone (5 wt % in water) was added to inhibit further polymerization.

Molecular weights were determined by size-exclusion chromatography at 22 °C on a Waters M-6000A chromatograph equipped with a Linear-Ultrahydrogel column (Waters) and an R400 refractive index detector. Poly(ethylene oxide) (PEO) standards (Pressure Chemicals and Toya Soda) were employed in conjunction with the universal calibration procedure, using the Mark–Houwink parameters [°C, 10^3K (cm^3 g^{-1}), α] for PEO[9] [25, 17, 0.75; 30, 4.9, 0.78] for PAAm[10] [25, 11, 0.80], and for PMMAm[9] [30, 2.1, 0.76].

Results and Discussion. These studies used the pulsed laser technique recently developed by Olaj and co-workers.[11–13] This is the first use of this method to determine k_p for water-soluble monomer systems. The underlying principles of this technique are as follows: the photopolymerizable system is subjected to periodic pulses of ultraviolet laser light, which generate a flux of primary radicals within a relatively short time interval (ca. 10^{-8} s). Some of these radicals propagate while others undergo bimolecular termination either between themselves or with propagating radicals. With every laser pulse the population of surviving radicals (initiated by a preceding pulse) decreases because their termination is enhanced by the accompanying flux of primary radicals. Those that terminate at this time will have propagated to a degree of propagation ν_p

$$\nu_p = k_p[M]t_f \qquad (1)$$

where [M] denotes the concentration of monomer and t_f is the dark time between pulses (some radicals may survive more than one period, leading to higher order "harmonics"). Hence, if one is able to determine the degree of polymerization of those radicals terminated by the next pulse, k_p can be determined directly by using eq 1, without any further assumptions. In practice, ν_p is determined from size-exclusion chromatography [SEC]. Olaj et al. have demonstrated that the inflection point on the low molecular weight side of the polymer peak corresponds to ν_p.

Polymerization of AAm and MAAm was photoinitiated by using uranyl chloride. Although the mechanism of the photoinitiation step is not understood, this is of no consequence here if the burst of primary radicals is formed on a time scale much shorter than t_f. Values of k_p were calculated from eq 1. Due to the high k_p values of AAm and MAAm and limited laser power at high frequencies, low monomer concentrations were necessary to maintain ν_p within the SEC calibration range. Unfortunately, this led to a significant decrease of [M] during polymerization: 12% for AAm and 4% for MAAm. The value of [M] used to evaluate k_p from eq 1 was therefore treated as an average over the initial and final values, viz., 0.94 and 0.98 of the initial values for AAm and MAAm, respectively.

The values we obtain for k_p at 25 °C are entirely consistent with previous work. At pH 1 we find 1.6×10^4

0024-9297/90/2223-5161$02.50/0

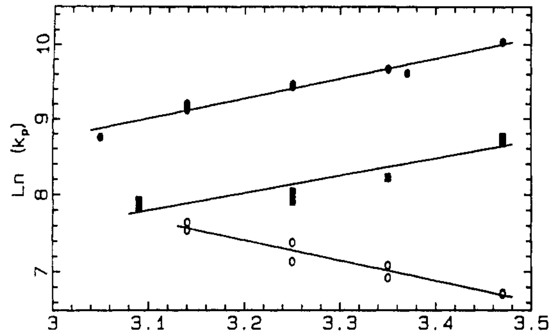

Figure 1. Arrhenius plots for the propagation rate coefficient k_p (dm^3 mol^{-1} s^{-1}) of AAm at pH 1 (●) and pH 4 (■) and of MAAm at pH 1 (○).

M^{-1} s^{-1} for AAm, compared to 1.7 × 10^4 M^{-1} s^{-1} reported by Currie et al.,[14] and 1.1 × 10^3 M^{-1} s^{-1} for MAAm, compared to 0.8 × 10^3 M^{-1} s^{-1} (pH unspecified) by Dainton and Sisley.[15] Our most important result concerns the temperature dependence of these values. These are presented as Arrhenius plots in Figure 1. Whereas MAAm (lowermost line) shows normal behavior, and an activation energy of 20 ± 2 kJ/mol, the traces for AAm at pH 1 and 4 are remarkable. They show a positive slope, indicating that k_p increases as temperature decreases. There is a precedent for this result. More than a decade ago, Kothandaraman and Gnanasundaram reported a decrease in the rate of polymerization (R_p) between 30 and 60 °C for AAm initiated with Co(III) and Mn(III) complexes.[16,17] Our results imply a negative apparent activation energy (-20 ± 2 kJ/mol) for AAm polymerization in water at both pH 1 and 4.

Apparent negative activation energies normally indicate the existence of a bound complex on the reaction pathway whose dissociation is enhanced at elevated temperatures. The reaction scheme may be envisaged as

$$\mathrm{R}^\bullet + \mathrm{AAm} \overset{K_{eq}}{\rightleftarrows} (\mathrm{R}^\bullet\cdots\mathrm{AAm}) \xrightarrow{k_p(\mathrm{true})} \mathrm{RAAm}^\bullet \qquad (2)$$

where K_{eq} is an equilibrium constant and k_p(true) is the rate coefficient for the true propagation step. The apparent propagation rate coefficient, k_p(app), may then be represented by

$$k_p(\mathrm{app}) = K_{eq}k_p(\mathrm{true}) \sim \exp[-\Delta H^\circ/RT] \times \exp[-\Delta H^\ddagger/RT] \qquad (3)$$

where ΔH° is the enthalpy change for preassociation and $\Delta H^\ddagger$ is the activation enthalpy of the propagation state. The apparent activation energy ($E_{app} = \Delta H^\circ + \Delta H^\ddagger$) will be negative whenever ΔH° is negative and $|\Delta H^\circ| > \Delta H^\ddagger$.

Although eq 2 seems to imply only binary complexes, we have no reason to exclude larger aggregates of AAm favored by Chapiro, which would lead to an enhanced local concentration ($[\mathrm{M}]_{local}$) of AAm in the vicinity of the propagating radicals. This idea generates a kinetically equivalent expression

$$k_p(\mathrm{app}) = k_p(\mathrm{true})[\mathrm{M}]_{local}/[\mathrm{M}]_{total} \qquad (4)$$

where ΔH° now refers to the enthalpy associated with cluster formation.

Our results do not provide any insights into the molecular origin of the ΔH° term, which may very well be influenced by enhanced structuring of water in the vicinity of the complex. Future experiments involving polymerization in the presence of acetamide or urea may provide information on this point.

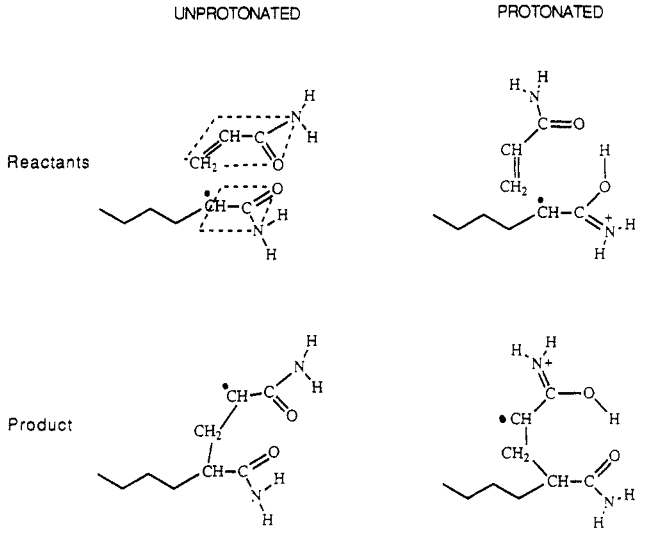

Figure 2. Proposed reaction pathways for the unprotonated and protonated propagating radical, the latter believed to be appropriate under low pH conditions. Neither model is intended to suggest that larger aggregates of AAm are not involved in the reaction.

A possible model for the association complex is presented in Figure 2. It does not explicitly treat the details of larger AAm aggregates that might be present, but it allows for the idea of a hydrogen-bonded complex between AAm and the propagating radical, and it builds upon an idea first suggested by Gromov et al.[18] to explain the pH sensitivity of k_p. Gromov suggested that, at low pH, the propagating radical could undergo protonation to yield the cation radical shown in the right-hand column of Figure 2. This species is thought to be more reactive toward the free-radical addition step and is also suitable for a hydrogen-bonding interaction with the incoming AAm. Note that the propagating species here is the cation radical. It remains to be seen if the similar E_{app} values found at pH 1 and 4 are simply a coincidence or whether ΔH° and $\Delta H^\ddagger$ values are similar for the protonated and unprotonated propagating species.

In the case of MAAm, the large value of k_p compared to other monomers, and the relatively small value of E_p (e.g., styrene, 30 kJ/mol), suggest that a complex or an aggregate is also involved in its polymerization. Here, presumably, the α-methyl group imposes steric and hydrophobic constraints. These act to disrupt the binding within the complex and to slow down the polymerization rate compared to AAm.

Acknowledgment. We thank NSERC Canada and the Australian Research Grants Scheme for their financial support. A Commonwealth Postgraduate Scholarship Research Award for P.P. is gratefully acknowledged.

References and Notes

(1) Susi, H. *Structure and Stability of Biological Macromolecules*; Timasheff, S. N., Fasman, G. D., Eds.; Marcel Dekker: New York, 1969; Chapter 7.

(2) Badger, R. M.; Rubalcava, H. *Proc. Natl. Acad. Sci. U.S.A.* **1954**, *40*, 12.

(3) Brandrup, J.; Immergut, E. H. *Polymer Handbook*, 3rd ed.; Wiley: New York, 1989.

(4) Chapiro, A. *Pure Appl. Chem.* **1972**, *30*, 77.

(5) Chapiro, A. *Eur. Polym. J.* **1973**, *9*, 417.

(6) Chapiro A.; Perec-Spritzer, L. *Eur. Polym. J.* **1975**, *11*, 59.

(7) Tan, Y. Y. *Comprehensive Polymer Science*; Pergamon: Oxford, 1989; Vol. 3, Chapter 19.

(8) Davis, T. P.; O'Driscoll, K. F.; Piton, M. C.; Winnik, M. A. *Macromolecules* **1989**, *22*, 2785.

(9) Molyneux, P. *Water-Soluble Synthetic Polymers: Properties and Behavior*; CRC Press Inc.: Boca Raton, FL, 1985; Vol. I, pp 39 and 104.

(10) Klein, J.; Conrad, K.-D. *Makromol. Chem.* **1980**, *181*, 227.

(11) Olaj, O. F.; Bitai, I.; Gleixner, G. *Makromol. Chem.* **1985**, *186*, 2569.

(12) Olaj, O. F.; Bitai, I.; Hinkelmann, F. *Makromol. Chem.* **1987**, *188*, 1689.

(13) Olaj, O. F.; Bitai, I. *Angew. Makromol. Chem.* **1987**, *155*, 177.

(14) Currie, D. J.; Dainton, F. S.; Watt, W. S. *Polymer* **1965**, *6*, 451.

(15) Dainton, F. S.; Sisley, W. D. *Trans. Faraday Soc.* **1963**, *59*, 1369.

(16) Kothandaraman, H.; Gnanasundaram, P. *Makromol. Chem.* **1977**, *178*, 1979.

(17) Gnanasundaram, P.; Kothandaraman, H. *Eur. Polym. J.* **1979**, *15*, 399.

(18) Gromov, V. F.; Galperina, N. I.; Osmanov, T. O.; Khomikovkii, P. M.; Abkin, A. D. *Eur. Polym. J.* **1980**, *16*, 529.

Philippe Pascal, Donald H. Napper, and Robert G. Gilbert*

Department of Physical and Theoretical Chemistry
University of Sydney, N.S.W. 2006, Australia

Mark C. Piton and Mitchell A. Winnik*

Department of Chemistry and Erindale College
University of Toronto, Toronto, Ontario, M5S 1A1 Canada

Received May 21, 1990

Revised Manuscript Received August 29, 1990

---

* To whom correspondence should be addressed.