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Pulsed Laser Study of the Propagation Kinetics of Acrylamide and Its Derivatives in Water

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ABSTRACT: The pulsed laser polymerization method has been applied to aqueous acrylamide (AAm) in the absence and presence of 3 mol dm^{-3} propionamide to obtain the propagation rate coefficient (k_p) as a function of temperature. Below *ca.* 50 °C in the absence of propionamide, k_p decreases with increasing temperature. It is proposed that this is due to the existence of an H-bonded intermediate complex along the reaction coordinate, which at low temperatures enhances propagation but which breaks down at higher temperatures. In the presence of propionamide or above 50 °C in the absence of propionamide, the temperature dependence of k_p behaves normally, supporting the proposition. Assuming that the high-temperature rate represents "normal" propagation in the absence of the formation of complex, $k_p = 7 \times 10^6$ dm^3 mol^{-1} s^{-1} $\exp[-(21 \pm 2\ kJ\ mol^{-1})/RT]$. Analysis of these results suggests that the driving force behind the proposed intermediate complex could be H-bonding in nature. Studies of k_p for α-methyl- and *N*-methyl-substituted AAm derivatives indicate that the former imposes greater constraints upon the propagation pathway than the latter.

Introduction

The kinetics of aqueous-phase polymerization of acrylamide (AAm) are complex and have given rise to many, sometimes conflicting, postulates in the literature. However, an understanding of these kinetics and the component mechanism is important for the control of product and processes involving acrylamide polymerization, such as inverse emulsion and inverse microemulsion systems; moreover, insight gained for this system should prove useful in understanding water-based polymerizations.

Much of the work aimed toward understanding acrylamide polymerization kinetics has used data, such as conversion/time curves, where initiation, propagation, and termination events are simultaneously active. The problem is that each of these three is individually complex (e.g., it has been suggested[1] that the initiation step is a hybrid of several different types of reactions). One way to obviate such difficulties is through systems whereby each of these three events can be studied essentially independently of the others. Here we apply the technique of pulsed-laser polymerization to obtain data for the aqueous-phase propagation rate coefficient; the advantage of this technique (discussed in detail below) is that it enables this rate coefficient to be obtained in an essentially assumption-free manner without having to disentangle the influence of other kinetic events.

The work presented here continues our preliminary temperature study of the aqueous-phase propagation kinetics of AAm at low conversion,[2] which invoked the concept of an intermediate bound complex to explain an apparent negative temperature dependence observed for k_p below 50 °C. The proposed binding force behind this complex was said to involve H-bonding of the AAm (*e.g.*, self-association) and perhaps the polymeric radical. In the present paper this k_p study is extended to scrutinize the nature of such a complex by examining a broader temperature range, the effect of molecules capable of disrupting the H-bonding (*viz.*, urea and propionamide), and the magnitude of k_p for α-methyl- and *N*-methyl-substituted AAm. We had suggested[2] that methacrylamide may also propagate via an intermediate complex but to a lesser extent, while the α-methyl perhaps imposes steric and hydrophobic constraints which disrupt the complex. By determining k_p for N-substituted AAm derivatives, these types of constraints and the hypothesis that *direct* H-bonding exists between the amide O and the amide H can also be tested.

The pulsed laser polymerization (PLP) technique[3,4] used in these studies has been shown[5] to yield reliable values of k_p for various monomer systems, including AAm, and is more direct than conventional means such as the SIP (spatially intermittent polymerization) method.[6] In summary, the action of pulsing a laser beam through a monomer solution containing a photoinitiator produces a population of polymer chains which tend to have a degree of polymerization ν_p, given by

$$\nu_p = k_p[M]t_f \tag{1}$$

where [M] is the concentration of monomer and t_f the dark time between pulses (some radicals produced by this method may survive more than one period, leading to values of $2\nu_p$, $3\nu_p$, *etc.*). Hence, if one can determine the value of ν_p by size-exclusion chromatography (SEC), k_p can be obtained directly from eq 1 without any further assumptions. Because of effects such as stochastic broadening of chain length during propagation, the occurrence of transfer, and instrumental broadening in the SEC analysis, ν_p must be inferred from the SEC trace using the point of inflection, an assumption justified elsewhere.[4,7,8] That is, modeling of the kinetics of the PLP process shows that, essentially independent of assumptions as to the details of the termination kinetics, the value of ν_p can be identified as the first point of inflection on the weight molecular weight distribution (i.e., on the SEC trace), most easily located as that turning point at lowest molecular weights seen in the derivative of the SEC trace.

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To complement the k_p study, more direct evidence that AAm molecules undergo self-association in water was sought by FTIR spectroscopy. FTIR was used to determine the relative amounts of solvated and self-associated aqueous AAm by observing the carbonyl absorption as a function of AAm concentration. Two inherent difficulties in this experiment were, first, that water is a notoriously bad solvent in IR studies; and, second, that it is difficult to separate closely spaced overlapping bands. Fourier transformation largely overcomes these difficulties *inter alia* because the superior signal-to-noise and resolution allow the following: (i) narrow sample cell path lengths; (ii) accurate subtraction of the absorption of the symmetrical scissoring vibrational mode of the water molecule; and (iii) deconvolution, which assists identification of band structure.

The following is a brief review on AAm complexation in water. Addition of AAm to water is accompanied by a significant negative heat of dilution (where AAm is the diluent).[9] The overall process of AAm addition involves changes in amide–amide, amide–water, and water–water bonds. For primary amides, the observed enthalpy change reflecting this process is of the order -23 kJ mol^{-1}.[10] The reorganization to accommodate AAm in water is likely to be accompanied by a large change in the solvent entropy which may well include increased solvent order by enclosure of the solute, a so-called *clathrate* structure. Many studies show that dimers and higher order self-associations can occur between monomeric amide molecules.[10,11] While the driving force for self-association remains unclear, it is generally believed that H-bonding and hydrophobic interactions play a role. The hydrophobic free energy contribution is less than that of an H-bond, *e.g.*, about -2 to -3 kJ mol^{-1} between two methylene groups.[12] Calculations by Ben-Naim[12] indicate that the free energy gain for an indirect hydrophilic interaction through a one-water *bridge* (about -13 kJ mol^{-1}) is larger than that for a *direct* H-bond (about -6 to -8 kJ mol^{-1}). In some cases he expects these longer range forces to extend to two- and three-water bridges. This concept is important in considering the behavior of tertiary amides (which have no hydrogens available for H-bonding) as well as multimolecular self-association phenomena.

Chapiro and co-workers[13-17] have suggested that the polymerization of AAm (and other water-soluble monomers) in polar solvents, especially water, is controlled by multimolecular, self-associated aggregates. The evidence for such a phenomenon was based on solvent effects on, *e.g.*, viscosity, copolymerization kinetics, polymer tacticity, and the relative amounts of fully solvated and self-associated monomer. Chapiro invoked this model to explain, among other things, the relatively high values of k_p observed for certain aqueous systems, including AAm. It was claimed that the resultant high local monomer concentrations, possibly together with favorable monomer alignment, would enhance propagation. If such an alignment were specific, then one would expect stereoregularity in the polymer product, as observed for acrylic acid.[13,16-18] Indeed, there is evidence that P(AAm), produced in water, has a predominantly isotactic structure.[19]

Another possible model for AAm aggregation is the so-called *template* polymerization,[20] which Chapiro has also studied.[13,17] Here, the monomer molecules are postulated to undergo side-by-side H-bonding to the backbone of a preexisting polymer chain. This would essentially have the same effect on propagation as the self-association model described by Chapiro.

Table I. Mark–Houwink Parameters Used in the Universal MW Calibration for SEC

polymer	temp[a] (°C)	$K/10^{-3}$ (cm^3 g^{-1})	α	ref
poly(ethylene oxide)	25	7	0.75	23
poly(ethylene oxide)	30	11	0.78	23
poly(acrylamide)	25	4.9	0.80	24
poly(methacrylamide)	30	2.1	0.76	23
poly(*N*-methylacrylamide)	25	36.4	0.63	25
poly(*N*,*N*′-dimethylacrylamide)	25	2.32	0.81	26

[a] Calibration was performed with values of corresponding temperatures.

Experimental Section

FTIR Spectroscopy. All measurements were performed with a Bio-Rad FTS-20/80 (Digilab Division) instrument at about 20 °C under dried N_2. The sample cell consisted of two calcium fluoride plates separated with Mylar film of 12-mm thickness. The spectrum of water was subtracted from each spectrum of aqueous AAm, assuming the sample cell path length to be equivalent for both spectra. For a given sample, this subtraction procedure was consistently reproducible, and therefore considered adequate. For deconvolution, the simple triangular apodization function was selected for the truncation of the interferogram.[21] By differentiating the spectrum, the resultant energy bands at 1678, 1664, and 1653 cm^{-1} were identified as various carbonyl stretches ($\nu_{C=O}$/*amide I* band), which without Fourier transform techniques have previously been assigned as a single $\nu_{C=O}$ Raman band at 1673 cm^{-1}.[22] The identified bands were fitted by an overdetermined linear least-squares procedure using analytical derivatives. The residuals between the calculated and observed experimental curves at each datum were minimized by adjusting the half-bandwidth and peak heights. It was found that convergence could be obtained, with the sum of the residuals being within the uncertainty in reading the experimental data points. There are several factors associated with condensed phases which can contribute to the shape of an absorption curve (*e.g.*, polarity of the solvent, H-bond interactions, *etc.*). A functional form found appropriate for fitting to the absorption data obtained in this study was 90% Gaussian and 10% Lorentzian.

Pulsed Laser Polymerization. Descriptions of the reagents, photopolymerization, and the SEC procedure have for the most part been outlined previously.[2] Additional reagents used here include the following: *N*-methylacrylamide (Polysciences, distilled), *N*,*N*′-dimethylacrylamide (Aldrich, 99%), and propionamide (Aldrich, 97%). All monomers for PLP were prepared as 0.5 mol dm^{-3} aqueous solutions, except methacrylamide, which was 1 mol dm^{-3}. For each monomer it was important that the absorption coefficient per 1 cm of solution was kept below *ca.* 0.3 so that a sufficient intensity of light was able to pass through the entire sample. The pH of the AAm solutions (pH = 4) was not adjusted for the temperature and propionamide studies. For the comparison of k_p values between AAm and its derivatives, however, the pH was decreased by adding perchloric acid (0.1 mol dm^{-3}). The pH of all these experiments before and after polymerization did not change noticeably. The value of t_f, kept constant for a given experiment, was varied between 0.1–0.2, 0.5–1, 0.5–1, and 0.1–0.2 s for AAm, methacrylamide, *N*-methylacrylamide, and *N*,*N*′-dimethylacrylamide, respectively. Each result reported here represents an average of at least five polymerizations. The Mark–Houwink parameters used in the universal molecular weight (MW) calibration for SEC are given in Table I.[23-26] Illustrated in Figure 1 are typical SEC traces of P(AAm) obtained from a pulsed laser experiment. Due to technical limitations (described previously)[2] the concentration of monomer adopted in these experiments was low. Consequently, monomer consumption during polymerization was so significant that values of [M], used to calculate k_p (eq 1), were treated as an average over the initial and final values (justified by Schnöll-Bitai and Olaj,[27] *viz.*, 0.94, 0.98, 0.95_5, and 0.94 of the initial values for AAm, methacrylamide, *N*-methylacrylamide, and *N*,*N*′-dimethylacrylamide, respectively).

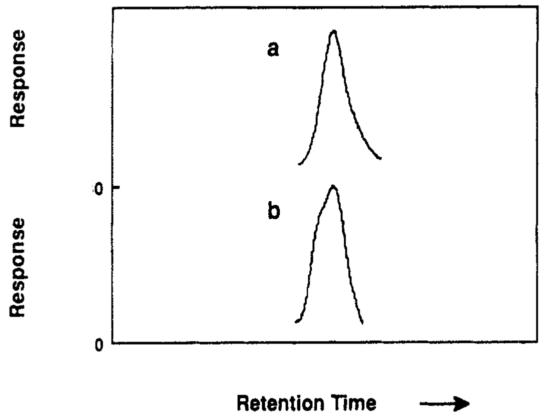

Figure 1. Examples of SEC traces of P(AAm) obtained from pulsed laser polymerizations: (a) mostly of chain-length ν_p and (b) showing a shoulder on the high-MW side which represents a contribution of chain-length $2\nu_p$.

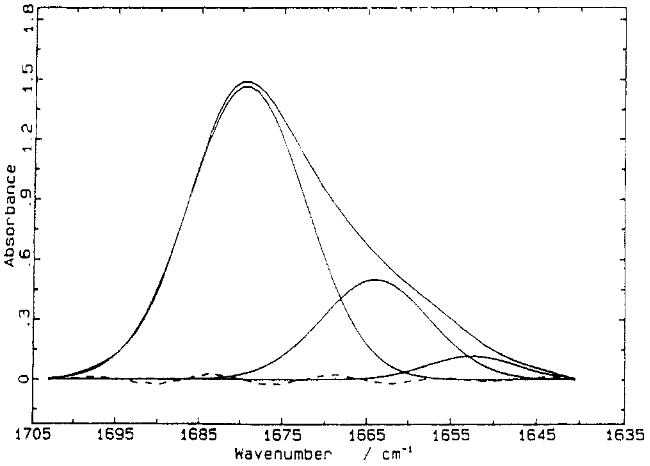

Figure 2. Deconvoluted FTIR spectrum for $\nu_{C=O}$ of AAm in water. This spectrum is fitted with three curves, representing fully solvated AAm (1678 cm^{-1}) and two variations of self-associated AAm (1664 and 1653 cm^{-1}). The dashed line shows the difference between the real spectrum and the fitted curves.

Results and Discussion

Self-Association of AAm in Water. Figure 2 presents a typical carbonyl-stretch ($\nu_{C=O}$, or *amide I* band) peak of AAm in water obtained by FTIR. The broad, lopsided nature of this peak represents an envelope of a number of individual $\nu_{C=O}$ peaks corresponding to particular H-bond arrangements. The highest energy peak was interpreted as representing the fully solvated ("free") carbonyl; and the two lower energy peaks were interpreted as representing the self-association of amides.[11] The difference in energy of these two lower energy peaks is usually attributed to varying degrees of self-association, *e.g.*, dimeric and multimolecular. Quantitative analysis of the $\nu_{C=O}$ peaks as a function of concentration was restricted to comparison of the ratio between the areas of the highest (fully solvated) and middle (self-associated) energy peaks (Table II). These ratios, which can be regarded as a crude measure of the relative equilibrium constants, do not appear to differ drastically between 0.3 and 3 mol dm^{-3} AAm. The values corresponding to the largest and smallest AAm concentrations cannot be taken with a great degree of confidence as these concentrations represent the limits of sensitivity of the FTIR instrument. These data hence support the claim that AAm undergoes self-association in water, at least within the concentration range used here for the PLP experiments.

Table II. Results for FTIR Analysis of the $\nu_{C=O}$ Peaks Corresponding to Fully Solvated and Self-Associated AAm in Water as a Function of [AAm]

[AAm] (mol dm^{-3})	fully solvated (1678 cm^{-1}) pk abs[a]	fully solvated (1678 cm^{-1}) area	self-associated (1664 cm^{-1}) area	ratio of areas
0.3	0.2	4.0	0.87	4.4
0.5	0.4	6.0	1.7	3.5
1.7	1.3	21.5	5.4	4.0
2.5	2.1	35.4	10.7	3.3
3.0	2.5	41.0	15.2	2.7

[a] Pk abs = maximum peak absorbance.

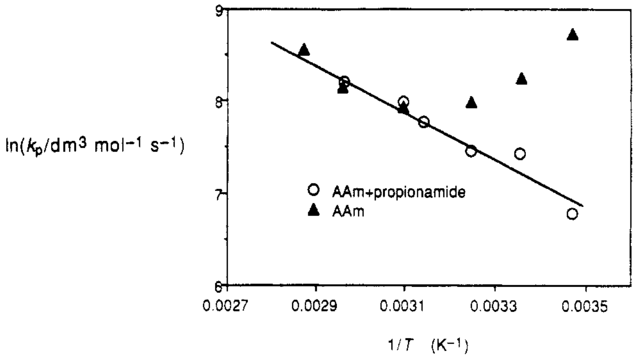

Figure 3. Arrhenius plot of k_p for 0.5 mol dm^{-3} AAm (pH 4) in the presence (○) and absence (▲) of 3 mol dm^{-3} propionamide.

Table III. Activation Entropies and Enthalpies for k_p at 25 °C Calculated for AAm and Some Well-Characterized Monomer Systems[a]

monomer	$\Delta S^{\ddagger}$ (J K^{-1} mol^{-1})	$\Delta H^{\ddagger}$ (kJ mol^{-1})	ref
acrylamide	−122	18.6	present work
methacrylamide	−128	17.3	2
tert-butyl methacrylate	−111	25.2	30
methyl methacrylate	−144	15.7	28
styrene	−118	27.3	28
ethyl methacrylate	−135	18.0	31
butyl methacrylate	−128	20.8	31
dodecyl methacrylate	−146	13.7	31

[a] Value for acrylamide is $k_{p,norm}$.

Propagation of AAm. The values of k_p for AAm in the absence and presence of propionamide are plotted in Arrhenius form in Figure 3. The effect of 3 mol dm^{-3} urea at 25 °C was similar to that of propionamide: with urea, $k_p = 1.89 \times 10^3$ dm^3 mol^{-1} s^{-1}; and with propionamide, $k_p = 1.66 \times 10^3$ dm^3 mol^{-1} s^{-1}. As observed in our previous communication,[2] the results for AAm in the absence of propionamide below 50 °C are extraordinry. They show a positive slope, indicating that k_p *increases* as the temperature *decreases*. In the presence of 3 mol dm^{-3} propionamide, however, the values of k_p appear to behave normally, giving a positive activation energy of 21 ± 2 kJ mol^{-1}. These propionamide data are in line with the values of k_p determined in the absence of propionamide above 50 °C.

By assuming that the propionamide k_p data reflect propagation of AAm in the absence of intermediate complexes, such as those described above, the standard activation enthalpy ($\Delta H^{\ddagger}$) and entropy ($\Delta S^{\ddagger}$) were calculated from the observed Arrhenius parameters A and E_a ($\Delta H^{\ddagger} = E_a - RT$, $\Delta S^{\ddagger} = R \ln[Ah/ek_BT]$, where h is Planck's constant, e the base of natural logarithms, and k_B Boltzmann's constant). The results are given in Table III, along with values from the literature[2,28-31] for other monomer systems. These results show that the activation parameters for k_p of AAm are comparable to those obtained for other well-characterized monomer systems.

The activation parameters associated with the k_p data for pure aqueous AAm above *ca.* 50 °C do not appear

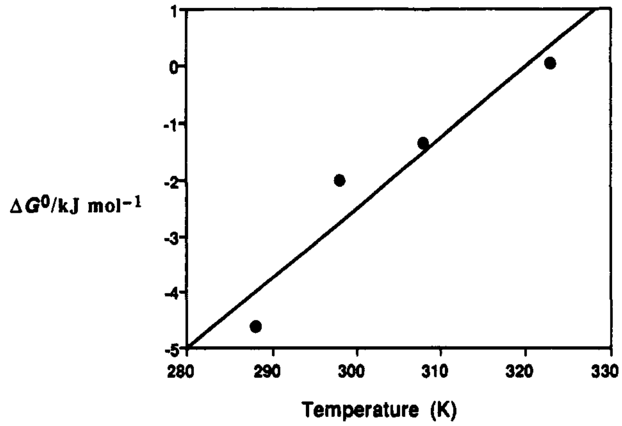

Figure 4. ΔG° versus temperature for the proposed equilibrium process occurring during the propagation of aqueous AAm below 50 °C.

unusual. The k_p data obtained for aqueous AAm with propionamide additive above and below 50 °C also appear normal and indeed are in line with the aforementioned data obtained above 50 °C. It is thus expected that these data represent the rate coefficients for "normal" reactive encounters between free radicals of degree of polymerization i, $P_i^\bullet$, and monomer:

$$P_i^\bullet + \text{AAm} \xrightarrow{k_{p,norm}} P_{i+1}^\bullet \qquad (2)$$

In order to explain the unusual temperature dependence of k_p below 50 °C, at least one other mechanism needs to be invoked in addition to that depicted in eq 2. Assuming that a temperature-sensitive intermediate bound complex exists along the propagation pathway, the simplest reaction scheme may be envisaged as

$$P_i^\bullet + \text{AAm} \overset{K_{eq}}{\rightleftarrows} (P_i^\bullet\cdots\text{AAm}) \xrightarrow{k_{p,comp}} P_{i+1}^\bullet \qquad (3)$$

where K_{eq} is an equilibrium constant and the subscript "comp" refers to propagation via the intermediate complex. The apparent k_p is then

$$k_{p,app} = K_{eq}k_{p,comp} \propto \exp(-\Delta H^\circ/RT)\exp(-\Delta H^\ddagger/RT) \qquad (4)$$

where ΔH° is the standard enthalpy change for complexation and $\Delta H^\ddagger$ is the activation enthalpy of the transition state for the second (propagation) step. The apparent activation energy ($E_a \approx \Delta H^\circ + \Delta H^\ddagger$) will be negative whenever ΔH° is negative and $|\Delta H^\circ| > \Delta H^\ddagger$. The overall apparent k_p observed over the entire temperature range sampled here is then the sum of the rate coefficients for these competing reactions and is given by

$$k_{p,app} = k_{p,norm} + K_{eq}k_{p,comp} \qquad (5)$$

The term $K_{eq}k_{p,comp}$ would predominate below *ca.* 50 °C, and $k_{p,norm}$ would predominate above *ca.* 50 °C. Note that $k_{p,app}$ is a second-order rate coefficient while $k_{p,comp}$ is first-order.

As pointed out earlier, the propionamide k_p data above and below 50 °C give normal activation parameters and are in line with the k_p data for pure aqueous AAm above 50 °C. This implies that $k_{p,app}$ obtained in the presence of propionamide approximately equals $k_{p,norm}$. Given this observation, the following is a method of estimating the enthalpy of formation of the complex. According to eq 4, if $k_{p,comp}$ and $k_{p,norm}$ have the same transition state, one may estimate the enthalpy of complex formation from the temperature dependence of the quantity obtained by taking the k_p values determined for pure aqueous AAm below 50 °C and dividing by the corresponding propionamide k_p data. The results are expressed in Figure 4 as ΔG° versus temperature. The corresponding ΔH° value is -40 kJ mol^{-1}. Given the large error associated with the value of ΔH° ($\pm$*ca.* 30%), this value seems quite reasonable for H-bonding phenomena observed in water.[10]

Although eq 5 implies only binary complexes, there is no reason to exclude multimolecular aggregates of the sort proposed by Chapiro. In light of this, an alternative way of viewing K_{eq} is to recognize that these aggregates can present high local monomer concentrations in the vicinity of the propagating radicals. Thus, a kinetically equivalent expression for $k_{p,app}$ (*cf.* eq 4) is

$$k_{p,app} = k_{p,comp}\frac{[\text{M}]_{local}}{[\text{M}]_{overall}} \qquad (6)$$

and the corresponding K_{eq} will now refer to aggregate formation ($k_{p,comp}$ in eq 6 is a bimolecular rate coefficient, whereas that in eq 3 is unimolecular). One could use eq 6 to calculate ΔS° and ΔH° if $k_{p,comp} \approx k_{p,norm}$ above 50 °C. This assumption may not strictly be correct, since the possible prealignment of the proposed aggregated AAm molecules could affect the transition state and hence manifest itself in the value of $\Delta S^\ddagger$. This could cause $k_{p,comp}$ to be greater than $k_{p,norm}$ (as Chapiro has effectively already suggested).[13-17] Given $[\text{M}]_{local}$ as a function of temperature, the values of $\Delta H^\ddagger$ and $\Delta S^\ddagger$ for $k_{p,comp}$ could be calculated via eq 6. Comparing the magnitude of these values to those in Table III would be useful for testing the validity of the assumption in question. The quantity $[\text{M}]_{local}$ would lie somewhere between the concentration of pure AAm (15.8 mol dm^{-3}) and $[\text{M}]_{overall}$. However, because the size and number concentration of AAm aggregates remain unknown, it is difficult to ascertain the actual value of $[\text{M}]_{local}$. One piece of evidence implying that the proposed prealigned monomer aggregates do not significantly change $k_{p,norm}$ would be if a reasonable value of ΔH° could be calculated on the assumption that $k_{p,comp} \approx k_{p,norm}$. Unfortunately, the noise in the data prevents a more accurate estimate of the significance of prealigned AAm molecules with respect to their apparent propagation rate coefficient.

Propagation of AAm Derivatives. The values of k_p for AAm, methacrylamide, *N*-methylacrylamide, and *N,N'*-dimethylacrylamide at 25 °C are gathered in Table IV. It is difficult to ascribe a precision to these values; however, the error could be as high as ±30%. Even with such an error, it is striking that the k_p value for methacrylamide is an order of magnitude lower than those for AAm and its *N*-methyl-substituted derivatives; from Table III, the difference resides in the lower activation enthalpy for propagation of methacrylamide, not an activation entropy difference. Moreover, Otsu and co-workers have found that methacrylamides with a bulky N-substituent do not homopolymerize[32] and that certain N-monosubstituted methacrylamides have ceiling temperatures of only *ca.* 125 °C.[33] These data imply a distinct association of low k_p values with α-methyl-substituted AAm derivatives. One likely contribution to their relatively low reactivity is that the α-carbon, being tertiary for the polymethacrylamidic radical, creates a more stable site for the free-radical electron, presumably due to hyperconjugation and increased steric strain; however, such an explanation assumes that the suggested effect is applicable to reactant but not to the transition state, an assumption which may or may not be justified. Another possible contribution, already suggested for methacrylamide,[2] is that the α-substituent imposes steric and hydrophobic constraints on complex formation and/or the transition state. Supporting this claim are infrared studies which have shown that bulky substituents (*e.g.*, a chlorine atom) at the α-carbon position

Table IV. Average Values of k_p for AAm and Its Derivatives at 25 °C

monomer	pH	k_p (10^3 dm^3 mol^{-1} s^{-1})	monomer	pH	k_p (10^3 dm^3 mol^{-1} s^{-1})
$CH_2{=}CHC(O)NH_2$	1.3	15.8	$CH_2{=}CHC(O)NHMe$	1.9	9.9
$CH_2{=}CHC(O)NH_2$	1.8	14.3	$CH_2{=}CHC(O)NMe_2$	1.4	15
$CH_2{=}CHMeC(O)NH_2$	1	1.1			

of amides can reduce their degree of self-association considerably.[34,35] This model would also be consistent with Chapiro's suggestion that high k_p values in these kinds of monomer systems are associated with complexation phenomena.

Although N-substitution of methacrylamides drastically suppresses their polymerization, *N*-methylacrylamide and *N*,*N*′-dimethylacrylamide propagate almost as rapidly as AAm. This observation does not support the idea of aggregate formation via *direct* H-bonding between their amide moieties, if one believes that rapid propagation is due to intermediate H-bonded complexes. Instead, the concept of solvent *bridging* proposed by Ben Naim[12] would provide a more adequate model for the complexation of aqueous AAm and its derivatives.

Conclusions

The major result of this k_p study for aqueous AAm is the temperature dependence. Above 50 °C, estimates of $\Delta S^\ddagger$ and $\Delta H^\ddagger$ gave values (−122 J mol^{-1} K^{-1} and 18.6 kJ mol^{-1}) that are normal for free-radical propagation. Below 50 °C, however, k_p displayed a negative temperature dependence. On the basis of the Arrhenius parameters, it is proposed that propagation of aqueous AAm proceeds via a bound complex, which enhances the reaction at low temperatures, but which dissociates at elevated temperatures and therefore slows the reaction. Results for k_p studies of AAm solutions containing propionamide or urea strongly suggest that H-bonding interactions are the driving force responsible for the intermediate complexation. Chapiro has suggested that this complex consists of H-bonded multimolecular aggregates of AAm which polymerize extraordinarily rapidly upon encounter with a radical. The $\Delta H°$ value estimated here appears reasonable for the equilibrium process associated with such aggregates (*ca.* −40 kJ mol^{-1}) and is consistent with the assumption made in this estimate that $k_{p,norm}$ and $k_{p,comp}$ have similar transition states. The equivalence between these two quantities gives reason to believe that the unusually rapid propagation originates from the resultant high local AAm concentrations produced by aggregation, rather than favorable alignment of the AAm molecules which could otherwise have enhanced k_p (*i.e.*, caused $K_{eq}k_{p,comp}$ to be greater than $k_{p,norm}$).

The actual architecture of the H-bonding in the proposed intermediate reaction complex remains unclear. Our k_p study for *N*-methylacrylamide and *N*,*N*′-dimethylacrylamide, together with recent calculations made by Ben-Aim, suggests that solvent *bridging* facilitates in stabilizing the H-bonded complexes rather than *direct* H-bond links between two (or more) amide moieties. Both *N*-methyl substitution and α-methyl substitution tend to suppress the rapid propagation reaction of AAm, although the latter appears to be more severe. Infrared studies by other workers and our k_p studies indicate that bulky α-substituents, such as the methyl group, could impose steric and hydrophobic constraints on complex formation (and/or the transition state). It is also likely that α-substitution lowers the reactivity of the polymeric radical by providing a relatively stable site for the free-radical electron at the α-carbon, although this postulate is only valid if this did not lead to the same change in the transition state (since it is $\Delta G^\ddagger$, not the free energy of formation of the macroradical, that determines the rate coefficient). Future k_p temperature studies on these AAm derivatives would lend further information on this subject.

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