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Aqueous Phase Size-Exclusion-Chromatography Used for PLP−SEC Studies into Free-Radical Propagation Rate of Acrylic Acid in Aqueous Solution

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ABSTRACT: Pulsed laser polymerization (PLP) in conjunction with analysis of the resulting polymer by size-exclusion-chromatography (SEC) was used to measure propagation rate coefficients, k_p, of acrylic acid (AA) in aqueous solution at concentrations of 20 and 40 wt % and temperatures between 2.6 and 28.5 °C. Under these conditions, more than 99% of acrylic acid exists in the nonionized form. The molecular weight distribution (MWD) of poly(AA) is directly measured by aqueous SEC. The k_p values at 20 wt % are about 60% higher than at 40 wt %. The activation energy of k_p is close to 12.0 kJ·mol^{-1} at both concentrations. At 25 °C and 20 wt %, k_p of AA in aqueous solution exceeds 100 000 L·mol^{-1}·s^{-1} which is the highest k_p value determined by the PLP−SEC technique so far.

Introduction

Investigations into free-radical polymerization of water-soluble monomers such as (meth)acrylic acid and acrylamide(s) in aqueous phase are of both fundamental and application-oriented interest. For modeling polymerization kinetics and product properties, reliable rate coefficients are required. Pulsed-laser polymerization (PLP) in conjunction with analysis of the molecular weight distribution (MWD) of the resulting polymer by size-exclusion-chromatography (SEC) has emerged as the method of choice for accurately determining propagation rate coefficients, k_p. This so-called PLP−SEC technique, which was designed by Olaj et al.,[1] has been used to determine benchmark values of k_p of styrene and several alkyl methacrylates.[2−4] There are considerable ongoing efforts to benchmark k_p for a wide variety of other vinyl monomers. These studies include measurements up to high pressure in both bulk and solution. Moreover, the technique has been applied toward measuring copolymerization k_p.[5] The existing k_p values of monomers that are polymerized in aqueous phase have been determined almost exclusively by the rotating sector technique.[6−8] The k_p values obtained via PLP−SEC for polymerizations of acrylamide and its derivates in water[9] have not met the PLP consistency criteria.[3] Quite recently, the measurement of k_p for free-radical polymerizations of methacrylic acid,[10] acrylic acid,[10] and *N*-isopropylacrylamide[11,12] in aqueous solution has been re-addressed. These PLP−SEC studies have clearly outlined the specific aspects and problems of k_p analysis in water. There are strong solvent effects on k_p, and difficulties in identifying suitable PLP conditions and in accurately measuring molecular weight distribution (MWD). The MWD determination of the poly(acrylic acid) and poly(methacrylic acid) samples from PLP are generally determined by converting them to poly(methyl (meth)acrylates) and performing standard SEC analysis with tetrahydrofuran as the eluent and using universal calibration against polystyrene standards. This procedure has been applied in the preceding PLP−SEC study of (meth)acrylic acid k_p in aqueous solution[10] and of methacrylic acid in bulk and in organic solvents.[13] Nevertheless, this procedure is not well suited for analyzing k_p under a wide variety of polymerization conditions since several low conversion polymerizations must usually[13] be carried out under identical reaction conditions in order to provide sufficient material for the esterification reaction. In addition to the polymer modification (esterification) reaction, side reactions may take place which affect the polymer microstructure.[14,15]

The problems of PLP−SEC investigations of acrylic acid (AA) k_p might be overcome by direct SEC analysis of the poly(acrylic acid) PLP samples. The present paper uses aqueous-phase SEC calibrated with poly(sodium acrylate) standards. The propagation rate coefficient of AA dissolved in water will be studied at two concentrations and with some modest temperature variation carried out on solutions of 20 (pH = 1.8) and 40 wt % AA (pH = 1.7) in water. More than 99% of acrylic acid monomer and also of acrylic acid units contained in the polymer will be present in the nonionized form.

Experimental Section

Acrylic acid (Fluka, > 99.0%) and the photoinitiator DMPA (2,2-dimethoxy-2-phenylacetophenone, Aldrich, 99%) were used as supplied. Demineralized water was used for preparation of monomer solutions and eluent for aqueous SEC. Tetrahydrofuran (p.a., Slavus, Slovak Republic) employed as eluent in organic SEC was dried over KOH and distilled from copper(I) chloride under nitrogen atmosphere before use. Pulsed laser polymerizations were performed using an excimer laser (LPX 210i, Lambda Physik) operated on the 351 nm (XeF) line at a pulse repetition rate of 100 Hz. The incident laser energy on the sample was always around10 mJ per pulse.

Due to the low solubility of DMPA in water, a stock solution of DMPA in acrylic acid was first prepared. Prior to polymerization, this solution was diluted with acrylic acid and water to yield the desired monomer and initiator concentrations. The polymerizations were carried out at initial DMPA concentrations between 10^{-3} and 10^{-4} mol·L^{-1}. Acrylic acid concentration, c_{AA}, was estimated for the experimental temperature range (2.6−28.5 °C) from the known densities of acrylic acid[10] r_{AA}/g·cm^{-3} = 1.0731 − 1.0826 × 10^{-3} (T/°C) − 7.2379 × 10^{-7} (T/°C)^2 and of water[16] (r_{water}/g·cm^{-3} = 0.9999 + 2.3109 × 10^{-5}

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$(T/°C) - 5.44807 \times 10^{-6} (T/°C)^2$. This procedure assumes ideal mixing of both materials. Density measurements at 25 °C demonstrate that the uncertainty of k_p determination associated with this assumption is negligible as compared to errors from other sources.

Approximately 1−1.5 mL of the solution was charged into an optical cell (Hellma-Worldwide) of 10 mm path length. The solution was purged with nitrogen for 2 min and closed with a PTFE stopper. Prior to polymerization, the cell was thermostated for 20 min. For laser pulsing, the cell was withdrawn from the thermostat and immediately irradiated with 30 laser pulses. The monomer conversion was typically in the range of 5%. Post-polymerization was prevented by adding around 0.1 mg of hydroquinone monomethyl ether to each sample. The polymer was isolated by freeze-drying and the conversion determined by gravimetry.

The polymer MWD was determined by aqueous phase SEC. The setup consisted of a Waters in-line degasser, a Waters pump 515 equipped with a plunger washing kit, a Rheodyne 7725i injector, a guard and three Suprema columns (Polymer Standards Service) with particle size 10 μm and pore sizes of 100, 1000, and 3000 Å (positioned in a Waters column heater module), and a differential refractometer Waters M2410. The analysis was performed at 80 °C using an aqueous eluent containing 0.1 mol·L^{-1} $LiNO_3$, 0.04 mol·L^{-1} phosphate buffer maintaining the pH at 8.0 (molar ratio NaH_2PO_4:Na_2HPO_4 = 5.3:94.7) and 200 ppm NaN_3. The eluent solution was permanently stirred to avoid concentration changes due to salt sedimentation. Ethylene glycol was used as the flow marker to control the eluent flow rate at 1 mL/min. Poly(acrylic acid) samples were dissolved in the eluent at concentrations between 0.3 and 0.5 mg/mL and filtered via a 0.45 μm filter prior to analysis. The injected volume was 200 mL. The poly(AA) samples were analyzed via calibration using poly(sodium acrylate) standards (Polymer Standards Service) of well-defined peak molecular weight ranging from 1250 to 1100000 g·mol^{-1}. Data acquisition and analysis were performed with WinGPC6 software (Polymer Standards Service), which was also used to identify the position of points of inflection on the MWD. The first-derivative curves of the MWD were smoothed by a Fourier fit program contained in the software package.

Aqueous SEC is frequently considered less straightforward than SEC in an organic phase. The operating conditions need to be optimized with respect to the analyzed solute and column packing material[17] in order to suppress nonsize exclusion phenomena resulting from hydrophobic or ionic interactions. We selected an eluent composition to control, by $LiNO_3$, both the polyelectrolyte effect and ionic interactions, and to provide, by the pH of 8.0, full ionization of the carboxylic groups of the polymer in order to eliminate hydrogen-bonded interactions between (a) carboxylic acid moieties of the polymer and (b) between polymer and column packing. Poly(AA) concentrations between 0.3 and 0.5 mg/mL are sufficiently low to exclude concentration effects[18] on the SEC analysis, but allow for an adequate sensitivity of detection.[19] The partitioning of the solute between stationary and mobile phases is also affected by eluent viscosity. At temperatures around 30 °C, the viscosity of the aqueous eluent is approximately twice that of a typical organic eluent.[16] Raising the temperature from 35 to 80 °C considerably improves the quality of SEC analysis of the PLP-prepared poly(AA) samples. The availability of poly(sodium acrylate) standards for direct calibration enormously enhances the accuracy by which the MWD may be determined from aqueous-phase SEC.

The methyl esterification procedure of a few poly(AA) samples was carried out following the procedure of Kuchta et al.[10] The completeness of the esterification reaction was checked by FTIR. Absorption by carboxylic groups was not seen in these spectra.

The organic-phase SEC of methyl-esterified samples in tetrahydrofuran was carried out by using the SEC setup, operated as a parallel setup to the aqueous SEC, consisting of a Waters system (pump 515, DRI detector Model 410) with guard column and three 8 × 300 μm PSS SDV 5 mm columns (Polymer Standards Service) of pore sizes 10^2, 10^3, and 10^5 Å contained in a Waters column heater module set to 30 °C. Poly(methyl acrylate) solutions were prepared at concentrations of 3 mg/mL. The sample injection volume was 100 mL. The eluent flow rate 1.0 mL/min was controlled by toluene as a flow marker. Molecular-weight calibration was established via narrow polydispersity polystyrene standards (Polymer Standards Service), which was transformed into the calibration via poly(methyl acrylate) using the universal calibration procedure.[20] Mark−Houwink constants for polystyrene, $K = 11.4 \times 10^{-5}$ dL·g^{-1} and $a = 0.716$, and for poly(methyl acrylate), $K = 1.95 \times 10^{-4}$ dL·g^{-1} and $a = 0.660$, were applied.[21]

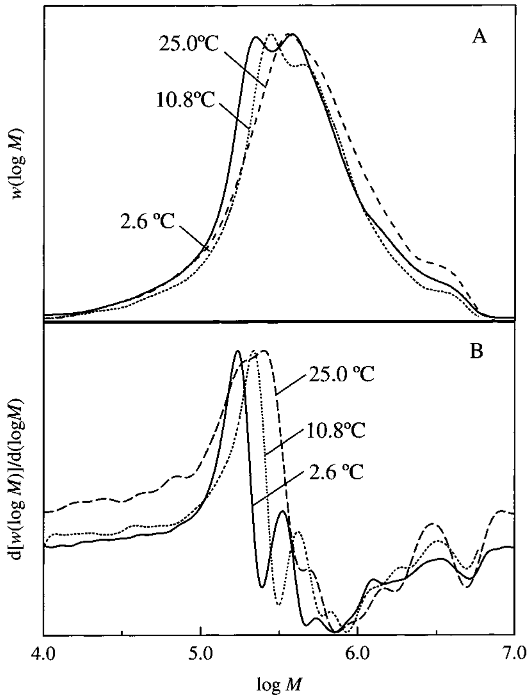

Figure 1. Temperature dependence of peak-normalized MWDs (A) and of the associated derivative curves (B) for 20 wt % acrylic acid polymerized in water at a laser pulse repetition rate of 100 Hz and DMPA concentration of 5×10^{-4} mol·L^{-1}.

Results and Discussion

According to eq 1, the propagation rate coefficient, k_p, is obtained from the degree of polymerization, L_1, which is the primary point of inflection on the first derivative curve of the MWD.[1]

$$k_p = \frac{L_1}{c_M t_0} = \frac{M_1}{m_0 c_M t_0} \qquad (1)$$

M_1 is the molecular weight at the primary point of inflection, and m_0 is the molecular weight of sodium acrylate (94.05 g·mol^{-1}), which is the monomeric unit for both standards and poly(acrylic acid) samples at pH 8.0 of the eluent in the aqueous SEC, c_M is the (molar) monomer concentration and t_0 is the time between two successive laser pulses.

The suitability of aqueous SEC for the analysis of the PLP-generated MWDs of poly(acrylic acid) samples is demonstrated in Figure 1. Both the SEC traces (A) and the associated first derivative (B) curves are shown for samples from PLP experiments carried out on solutions of 20 wt % acrylic acid in water at temperatures between 2.6 and 25.0 °C. The logarithmic weight distributions obtained directly from SEC clearly exhibit primary and secondary points of inflection, which appear as pro-

Table 1. Temperature Dependence of k_p for 20 wt % Acrylic Acid in Water[a]

c_{AA} (mol·L^{-1})	c_{AA} (wt %)	$c_{DMPA} \times 10^4$ (mol·L^{-1})	T (°C)	convn (%)	$M_1 \times 10^{-3}$ (g·mol^{-1})	$M_2 \times 10^{-3}$ (g·mol^{-1})	M_1/M_2	$k_p \times 10^{-3}$ (L·mol^{-1}·s^{-1})
2.86	20.3	5	2.6	6.3	176	345	0.51	67.1
2.86	20.3	5	2.6	6.0	171	334	0.51	65.7
2.86	20.3	5	6.3	6.9	193	378	0.51	74.4
2.85	20.2	10	6.3	7.0	191	377	0.50	73.8
2.86	20.3	5	10.8	6.3	216	418	0.52	83.1
2.84	20.2	10	10.8	6.2	206	416	0.50	79.6
2.85	20.3	5	15.7	4.5	228	442	0.52	87.1
2.84	20.2	10	15.7	6.9	218	437	0.50	84.7
2.85	20.3	5	20.1	5.6	237	476	0.50	91.2
2.84	20.2	10	20.1	5.7	248	465	0.53	95.9
2.85	20.3	5	25.0	7.0	251	485	0.52	97.5
2.87	20.5	1.25	25.0	6.4	267	494	0.54	102.5

[a] M_1 and M_2 represent primary and secondary points of inflection.

Table 2. Temperature Dependence of k_p for 40 wt % Acrylic Acid in Water[a]

c_{AA} (mol·L^{-1})	c_{AA} (wt %)	$c_{DMPA} \times 10^4$ (mol·L^{-1})	T (°C)	convn (%)	$M_1 \times 10^{-3}$ (g·mol^{-1})	$M_2 \times 10^{-3}$ (g·mol^{-1})	M_1/M_2	$k_p \times 10^{-3}$ (L·mol^{-1}·s^{-1})
5.70	40.0	6	2.6	6.8	223	435	0.51	43.1
5.58	39.2	12	2.6	4.6	217	420	0.52	42.3
5.69	40.0	6	6.3	5.1	240	461	0.51	45.3
5.58	39.2	12	6.3	4.6	230	454	0.51	45.0
5.57	39.2	12	10.8	5.1	260	527	0.49	50.9
5.67	40.0	6	15.7	5.6	282	558	0.51	54.4
5.56	39.2	12	15.7	7.6	289	537	0.54	57.6
5.66	40.0	6	20.1	4.8	290	548	0.53	55.9
5.55	39.2	12	20.1	5.9	319	575	0.55	63.2
5.54	39.2	12	25.0	7.1	311	647	0.48	60.6
5.65	40.2	12	28.5	6.9	333	631	0.53	65.0
5.65	40.2	12	28.5	6.6	363	645	0.56	70.6

[a] M_1 and M_2 represent primary and secondary points of inflection.

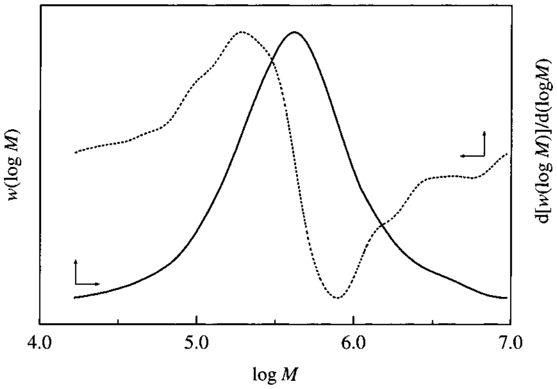

Figure 2. MWD and the derivative curves for 20 wt % acrylic acid polymerized in water at 28.5 °C, laser pulse repetition rate of 100 Hz, and DMPA concentration of 5·10^{-4} mol·L^{-1}.

nounced maxima in the first derivative curves (B). The curves at 2.6 and 10.8 °C even have a third inflection point. The MWDs from PLP experiments at temperatures above 25 °C do not exhibit the PLP features (Figure 2). The same trend has been seen in PLP–SEC work on acrylates.[22,23] The MWDs determined from PLP experiments on solutions containing 40 wt % AA (Figure 3) are of the same quality as those for 20 wt % AA.

The experimental conditions of the PLP experiments are summarized for AA concentrations of 20 and 40 wt % in Tables 1 and 2, respectively. The molar AA concentration varies slightly within each group of experiments (Tables 1 and 2) as a consequence of the minor variations in the initial concentration of components and in the temperature dependence of the density.

Tables 1 and 2 show that the ratio of the primary and secondary inflection point positions, M_1/M_2, is always close to 0.5 and k_p is independent of initiator concentration. The k_p data thus meet the consistency criteria of reliable PLP–SEC analysis of k_p established by the IUPAC working party "Modeling of polymerization kinetics and processes".[3] The procedure of using aqueous-phase SEC for k_p measurement of AA dissolved in water thus is a valid one.

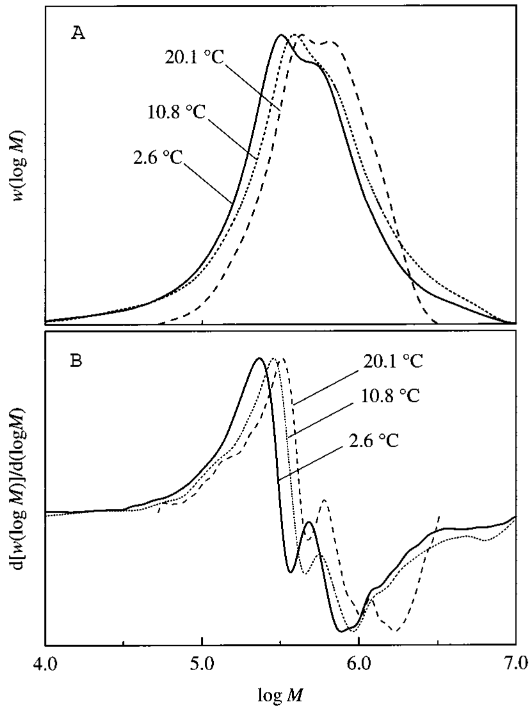

Figure 3. Temperature dependence of peak-normalized MWDs (A) and of the associated derivative curves (B) for 40 wt % acrylic acid polymerized in water at a laser pulse repetition rate of 100 Hz and DMPA concentration of 12 × 10^{-4} mol·L^{-1}.

The k_p data in Tables 1 and 2 are several times higher than k_p values for nonionized AA obtained by Galperina et al.[24] via the rotating sector method (see also Refs.[6,7]). In the temperature range 0−30 °C, these literature k_p values are between 18 000 and 31 900 $L\cdot mol^{-1}\cdot s^{-1}$. It is not clear to which extent the discrepancies are due to uncertainties originating from application of the rotating sector method or to the difference in AA concentration, which was between 0.4 and 0.5 $mol\cdot L^{-1}$ in the literature study. The recent PLP−SEC data for AA polymerization in aqueous phase reported by Kuchta et al.[10] support the view that the Galperina et al.[24] k_p values are much too small. For 10 wt % AA in water, Kuchta et al.[10] report k_p values in the range 53 000−64 000 $L\cdot mol^{-1}\cdot s^{-1}$ at 25 °C. Even these higher numbers are, however, clearly below the k_p values of the present study. The mean value of k_p at 25 °C and 20 wt % AA from Table 1 is 100 000 $L\cdot mol^{-1}\cdot s^{-1}$, and considering the decrease in k_p with AA concentration (see Table 2), it should be even higher at 10 wt % AA in water. Some preliminary studies currently underway in our laboratories indicate that k_p indeed increases upon going from 20 to 10 wt % AA. According to these measurements, k_p at 10 wt % AA and 25 °C should be close to 130 000 $L\cdot mol^{-1}\cdot s^{-1}$. Thus the data of Kuchta et al.[10] are lower than our k_p values by about a factor of 2.

As identical pulse repetition rates have been used in both PLP−SEC studies, the only reason for this discrepancy is the characterization of the polymer MWD, which was indirect in the Kuchta et al.[10] study, via methyl esterification and subsequent analysis of the poly(methyl acrylate), and was direct in the present study. To focus on this issue, we applied both procedures to a limited number of PLP samples. The resulting MWDs for samples from a PLP experiment on a 40 wt % sample produced at 2.6 °C are presented in Figure 4. Both MWDs clearly exhibit a PLP structure which, however, is more pronounced for the sample subjected to aqueous SEC. The methyl-esterified products were also incompletely soluble in tetrahydrofuran. The SEC curve only shows the MWD of the THF soluble fraction in which high-molecular-weight fractions were seen that are absent in the aqueous phase SEC of the parent poly(AA) polymers. These observations demonstrate that the esterification of poly(acrylic acid) polymer does not take place as a true polymer modification reaction without any change in the degree of polymerization.

The primary and secondary inflection points of the esterified sample yield $M_1/M_2 = 0.42$. The points of inflection for the parent sample subjected to aqueous SEC analysis yield $M_1/M_2 = 0.52$. Corresponding analysis of other samples by the two SEC techniques shows that the M_1/M_2 ratio for esterified samples exhibits a large scatter (numbers between 0.39 and 0.78). In contrast, the M_1/M_2 ratios for the samples from aqueous SEC are consistently close to 0.5 (Tables 1 and 2). Also, degrees of polymerization at the points of inflection and thus the resulting k_p values deduced via the two SEC strategies are markedly different. Analysis of the SEC of the esterified sample yields $k_p = 22\,800$ $L\cdot mol^{-1}\cdot s^{-1}$, which is about half of the corresponding value (42 300 $L\cdot mol^{-1}\cdot s^{-1}$) obtained from aqueous-phase SEC. As noted above, our data for 10 wt % AA differ by the same factor from the Kuchta et al.[10] value, which was deduced from conventional SEC on esterified samples. These observations suggest that esterification of poly(acrylic acid) samples results in major structural changes. A similar conclusion was derived by Brüssau et al.[14] and by Kilz.[15] There is no indication that esterification of poly(methacrylic acid) affects polymer structure[15] and one does not need to be concerned about the k_p values of methacrylic acid that have been deduced via the esterification route.[10,13] On the other hand, it cannot be ruled out that very small amount of COOH moieties, which have survived the esterification process, may affect the SEC analysis, e.g., via some additional retention due to enthalpic interactions with the hydrophobic column.[15] As this effect may occur with esterified poly(AA), this potential source of error provides an additional argument for carrying out the molecular weight analysis of poly(AA) via aqueous SEC. The k_p values derived by this method will now be briefly discussed.

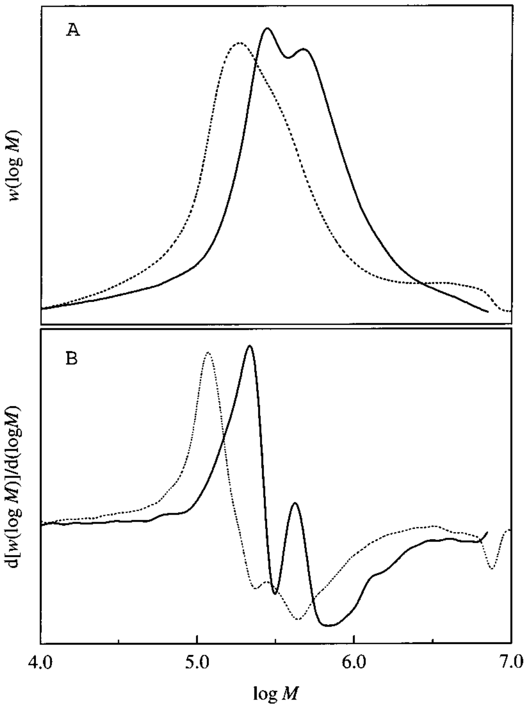

Figure 4. MWDs (A) and associated derivative curves (B) of a poly(acrylic acid) sample determined by aqueous-phase SEC (full line) and by organic-phase SEC in tetrahydrofuran after methyl-esterification (dotted line). The corresponding points of inflection are $M_1 = 216\,700$ $g\cdot mol^{-1}$, $M_2 = 419\,800$ $g\cdot mol^{-1}$ (aqueous-phase SEC) and $M_1 = 116\,800$ $g\cdot mol^{-1}$, $M_2 = 276\,400$ $g\cdot mol^{-1}$ (organic-phase SEC). To compare both MWDs in one plot, the measured M values of the methylated sample were multiplied by a factor of 1.093, which is the ratio of the molar mass of monomer units of sodium acrylate (94 $g\cdot mol^{-1}$) and methyl acrylate (86 $g\cdot mol^{-1}$).

The k_p of AA in aqueous phase is very high. The numbers determined in the present study are the highest k_p values that have been measured so far via PLP−SEC. Arrhenius plots of k_p for the two AA concentrations are shown in Figure 5. The two lines are parallel, which demonstrates that the activation energy is insensitive to AA concentration, at least at the concentrations under investigation. Linear regression yields the Arrhenius expressions in eqs 2 and 3.

$$\text{20 wt \% AA: } \ln [k_p/(L\cdot mol^{-1}\cdot s^{-1})] = (16.3 \pm 0.29) - (1437 \pm 83)\,(T^{-1}/K^{-1}) \quad (2.3 \le T/°C \le 25.0) \quad (2)$$

$$\text{40 wt \% AA: } \ln [k_p/(L\cdot mol^{-1}\cdot s^{-1})] = (16.0 \pm 0.39) - (1468 \pm 112)\,(T^{-1}/K^{-1}) \quad (2.3 \le T/°C \le 28.5) \quad (3)$$

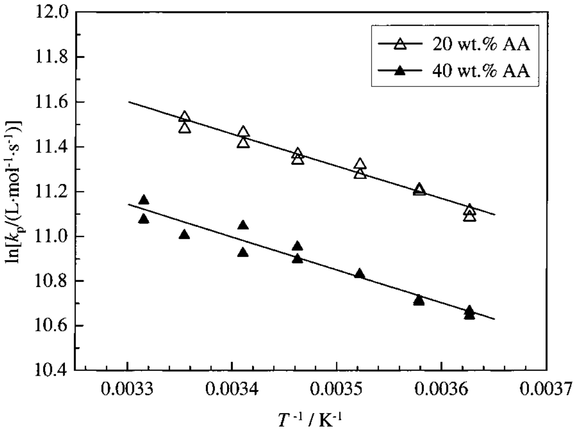

Figure 5. Arrhenius plots for 20 wt % and 40 wt % acrylic acid in water based on the data from Tables 1 and 2, respectively.

The k_p values given by eqs 2 and 3 are significantly different and 95% joint confidence intervals calculated according to van Herk[25] do not overlap. The activation energy is close to 12 kJ·mol^{-1} for both concentrations. The k_p values at 20 wt % monomer are about 60% higher than those at 40 wt % monomer. The trend is similar in polymerizations of other monomers in aqueous solution studied by PLP−SEC, e.g. methacrylic acid[10] and *N*-isopropylacrylamide.[12] We do not yet fully understand this increase in k_p toward lower monomer concentration and will examine it within a wider range of monomer concentrations in a subsequent paper. Comparison with k_p of methacrylic acid polymerization in aqueous phase under otherwise similar conditions shows that acrylic acid propagation is by about 1 order of magnitude faster. The difference between the k_p of acrylates and methacrylates polymerized in organic phase is similar.[4,22]

The aqueous-phase method will now be applied to acrylic acid k_p studies at other monomer concentrations and at quite different pH where AA also or even predominantly occurs in the ionized form. Part of this work is currently underway in our laboratories.

Conclusion

Aqueous SEC is well suited for analyzing the MWD of poly(acrylic acid) samples and, in conjunction with pulsed laser polymerization, allows accurate measurement of acrylic acid k_p. The propagation rate coefficients determined for aqueous solutions with 20 and with 40 wt % AA at temperatures between 2.6 and 28.5 °C show a decrease of k_p toward higher AA concentration whereas the activation energy of k_p does not depend on AA concentration. Direct aqueous SEC obviously is better suited for poly(AA) analysis than the previously applied indirect method via methyl esterification and subsequent conventional SEC of the produced poly(methyl acrylate).

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