Macromolecules **2003,** *36,* 9355−9363

PLP−SEC Study into Free-Radical Propagation Rate of Nonionized Acrylic Acid in Aqueous Solution

Igor Lacík*

Polymer Institute of the Slovak Academy of Sciences, Dúbravská cesta 9,
842 36 Bratislava, Slovak Republic

Sabine Beuermann and Michael Buback

Institute of Physical Chemistry, Georg-August-University Göttingen, Tammannstrasse 6,
D-37077, Göttingen, Germany

Received June 30, 2003

ABSTRACT: Pulsed laser polymerization (PLP) in conjunction with size-exclusion chromatography (SEC), both being carried out in the aqueous phase, was used to determine propagation rate coefficients, k_p, of nonionized acrylic acid (AA) at temperatures between 2 and 25 °C and monomer concentrations, c_{AA}, from 1 to 10 wt %. The product $k_p c_{AA,local}$ is the primary experimental quantity deduced via the PLP−SEC technique. Assuming $c_{AA,local}$ to be identical to overall monomer concentration, c_{AA}, yields apparent k_p values, which, upon enhancing c_{AA}, first increase and, after passing through a maximum at around 3 wt % AA, significantly decrease. A k_p value as high as 180 000 $L \cdot mol^{-1} \cdot s^{-1}$ was determined for 3 wt % AA at 25 °C. The decrease observed toward higher AA concentration is fully consistent with what has been found in a preceding study into k_p of nonionized AA at monomer concentrations of 20 and 40 wt %. At constant temperature, variations in apparent k_p by about a factor of 3 are seen in the range up to 40 wt % AA. Discussion of the measured rate data suggests that it is primarily $c_{AA,local}$ that changes as a function of monomer concentration rather than k_p. As a consequence of strong hydrogen bonds between polymer segments, between polymer segments and AA monomer, and between both these species and water, the AA concentration at the radical site may significantly differ from overall c_{AA}. The assignment of the observed changes in apparent k_p to $c_{AA,local}$ is supported by PLP−SEC experiments in which appreciable amounts of propionic acid (PA) have been added to aqueous AA solutions. The addition of PA significantly reduces apparent k_p. Addition of NaCl to an aqueous solution of AA in its nonionized form, on the other hand, does not affect apparent k_p. Whether the observed changes in $k_p c_{AA,local}$ are entirely due to $c_{AA,local}$ differing from c_{AA} or whether also the “true” propagation rate coefficient varies cannot be safely decided on the basis of the presently available data.

Introduction

The advent of laser-assisted techniques has largely improved quantitative analysis of free-radical polymerization kinetics.[1] Investigations have been primarily carried out on homo- and copolymerization of the hydrophobic monomers.[2] Only limited information is available for water-soluble monomers,[2] although aqueous phase free-radical polymerizations are of eminent technical interest and accurate rate coefficients for such systems are badly needed. The current knowledge of acrylic acid (AA) polymerization kinetics in aqueous phase is essentially based on k_p values determined about 30 years ago by the rotating sector technique.[3] The lack of propagation rate coefficient, k_p, data from pulsed laser polymerization (PLP)−size-exclusion chromatography (SEC) experiments is due to difficulties associated with the SEC analysis of polymers from water-soluble monomers that may not be carried out under conventional SEC conditions with THF serving as the eluent. The problems may partly be circumvented by polymer modification of poly(acrylic acid) from PLP to yield poly(acrylic acid methyl ester) samples that may be analyzed via conventional SEC. This procedure may, however, be severely affected by changes in polymeric structure during polymer modification.[4,5] Within a recent study into free-radical propagation rate coefficients of nonionized acrylic acid in aqueous solution of 20 and 40 wt % AA, problems associated with SEC analysis of PLP-produced polymer were solved by measuring molecular weight distributions of poly(acrylic acid) via aqueous phase SEC.[6] The PLP−SEC-derived k_p values for 20 wt % AA were found to be 60% above the ones for 40 wt % AA. The purpose of the present study is to extend the PLP−SEC investigations on k_p of nonionized AA in aqueous solution to lower concentration with particular interest in examining whether the propagation rate is further enhanced upon dilution. Each monomer concentration was investigated between 2 and 25 °C. Toward lower temperatures, solidification occurs, and toward higher temperatures, the PLP structure of the polymeric samples is lost, both of which prevent reliable determination of propagation rate coefficients via PLP−SEC.

Although the PLP−SEC technique is the method of choice for k_p determination and as such constitutes the procedure recommended by the IUPAC Working Party “Modeling of polymerization kinetics and processes”,[7] an important limiting aspect needs to be noted: The product of propagation rate coefficient and local mono-

---

* Corresponding author. E-mail address: igor.lacik@savba.sk. Phone: +421 2 5477 2467. Fax: +421 2 5477 5923.

10.1021/ma030365e CCC: $25.00

Table 1. Temperature Dependence of k_p for 1 wt % Acrylic Acid in Water

c_{AA} (mol·L^{-1})	c_{AA} (wt %)	$10^4 c_{DMPA}$ (mol·L^{-1})	T (°C)	convn (%)	no. of pulses	$10^{-3}M_1$ (g·mol^{-1})	$10^{-3}M_2$ (g·mol^{-1})	M_1/M_2	$10^{-3}k_p$ (L·mol^{-1}·s^{-1})
0.139	1.02	0.5	2.9	4	100	9.4	18.2	0.52	73.0
0.139	1.02	0.5	2.9	10	100	9.8	20.4	0.48	78.7
0.150	1.07	1.0	2.5	1	30	10.4	27.1	0.38	74.2
0.150	1.07	1.0	2.5	1	60	10.4	25.5	0.41	74.3
0.139	1.02	0.5	6.3	9	100	10.5	22.8	0.46	84.1
0.139	1.02	0.5	6.3	1	100	10.6	21.8	0.49	81.3
0.150	1.07	1.0	6.4	1	30	11.7	30.6	0.38	83.5
0.150	1.07	1.0	6.4	1	60	12.0	27.9	0.43	85.7
0.139	1.02	0.5	10.0	12	100	11.5	24.5	0.47	93.2
0.139	1.02	0.5	10.0	8	100	11.6	24.4	0.48	92.4
0.150	1.07	1.0	9.9	1	30	13.3	34.2	0.39	95.0
0.150	1.07	1.0	9.9	1	60	13.6	34.9	0.39	97.1
0.139	1.02	0.5	14.9	7	100	13.5	30.1	0.45	106.7
0.139	1.02	0.5	14.9	15	100	13.4	33.2	0.40	110.6
0.150	1.07	1.0	14.3	1	30	15.0	39.8	0.38	107.2
0.150	1.07	1.0	14.3	1	60	15.2	40.2	0.38	108.6
0.149	1.07	1.0	19.5	4	30	18.2	52.5	0.35	131.8
0.149	1.07	1.0	19.5	5	60	16.9	49.2	0.34	123.3

mer concentration (at the free-radical site), $k_p c_{AA,local}$, is the primary experimental quantity obtained from the PLP−SEC experiment, as can be seen from

$$L_i = i k_p c_{M,local} t_0 \qquad i = 1, 2, 3, ... \tag{1}$$

where L_1 is the number of propagation steps between two successive laser pulses that is identified with the degree of polymerization at the point of inflection on the low molecular weight side of the MWD peak. t_0 is the time between two laser pulses. Higher order inflection points, L_2, L_3, ..., result from preferential termination of the propagating radicals generated at $t = 0$, by laser pulses applied at times $2t_0$, $3t_0$, ..., respectively.

In case that $c_{M,local}$ differs from overall c_M, no unambiguous assignment of observed changes to variations in k_p or $c_{M,local}$ can be made. In general, $c_{M,local}$ is expected to be identical to overall c_M. Strictly speaking, propagation rate coefficients deduced from PLP−SEC experiments under the assumption $c_{M,local} = c_M$ should be referred to as "apparent" k_p's. PLP−SEC experiments on a series of common monomers dissolved in fluid carbon dioxide provide a clear indication of "apparent" k_p being significantly, by up to 50% below bulk k_p with the extent of this deviation being larger in cases where carbon dioxide is of poor solvent quality for a particular polymer and where the polymer is composed of strongly interacting polar segments.[8] In the case of acrylic acid polymerizing in aqueous solution, hydrogen bonds are expected to give rise to significant interactions between polymeric AA segments, AA monomer molecules, and water.[9−12] It appears rewarding to investigate apparent k_p of AA in aqueous solution at widely differing AA concentration. To restrict complexity, the present study will be limited to AA occurring exclusively in the nonionized form. For an improved understanding of effects resulting from speciation in the aqueous medium, the PLP−SEC studies will be expanded to experiments where either up to 60 wt % propionic acid (PA) or up to 5.8 wt % (1.0 mol·L^{-1}) sodium chloride (NaCl) are added to the aqueous AA solutions subjected to PLP−SEC.

Experimental Part

Acrylic acid (Fluka, > 99.0%), photoinitiator DMPA (2,2-dimethoxy-2-phenylacetophenone, Aldrich, 99%), and propionic acid (Merck, >99.5%) were used as supplied. All other chemicals were of analytical grade. Demineralized water was used for preparation of monomer solutions and eluent for aqueous SEC. 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 details on pulsed laser polymerization setup and the conditions for the aqueous phase SEC were given in our previous paper.[6]

Results and Discussion

As the AA propagation rate coefficient is very high, PLP−SEC experiments, according to eq 1 require the maximum available pulse repetition rate of the setup (100 Hz) to be applied or AA concentration to be reduced. The lower limit of AA concentration in PLP−SEC experiments is determined by the minimum amount of polymer that is needed for reliable SEC analysis. One milligram of PLP-produced polymer turned out to be sufficient, which corresponds to a minimum AA concentration of 1 wt % to be studied via PLP−SEC.

k_p determination was carried out at 1, 2, 3, 5, and 10 wt % AA, at temperatures from 2 to 25 °C, at one to three different photoinitiator (DMPA) concentrations, and at varying numbers of pulses. The PLP structure is highly sensitive to the concentration of laser-generated free radicals, which quantity is determined by the DMPA concentration, c_{DMPA}, and by the laser pulse energy, which typically was around 10 mJ per pulse. For each AA concentration, optimum c_{DMPA} had to be identified by a series of PLP−SEC experiments. Beyond the optimum range, MWDs without PLP structure were obtained, which do not allow for estimating reliable k_p (see Figure 2 in ref 6).

The experimental conditions of the PLP experiments, such as initial AA and DMPA concentrations, polymerization temperature, and the monomer conversion reached by the indicated number of laser pulses are given in Tables 1−5, for studies on aqueous solutions of nonionized AA at initial c_{AA} of about 1, 2, 3, 5, and 10 wt %, respectively. Also given in these tables are the positions of the poly(acrylic acid) molecular weight at the positions of the first and second point of inflection of the MWD, M_1 and M_2, and the ratio of these two quantities, M_1/M_2. Listed in the final column are the "apparent" propagation rate coefficients, k_p, that were obtained, via eq 1, from the position of the first point of inflection, $L_1 = M_1/M_{AA}$, where M_{AA} is the molecular weight of monomeric AA. The estimate of apparent k_p

Table 2. Temperature Dependence of k_p for 2 wt % Acrylic Acid in Water

c_{AA} (mol·L^{-1})	c_{AA} (wt %)	$10^4 c_{DMPA}$ (mol·L^{-1})	T (°C)	convn (%)	no. of pulses	$10^{-3}M_1$ (g·mol^{-1})	$10^{-3}M_2$ (g·mol^{-1})	M_1/M_2	$10^{-3}k_p$ (L·mol^{-1}·s^{-1})
0.286	2.06	1.0	2.8	4	30	22.9	49.8	0.46	86.9[a]
0.286	2.06	1.0	2.8	4	30	21.5	47.0	0.46	81.6[a]
0.286	2.06	1.0	6.5	5	30	26.2	56.4	0.46	99.8[a]
0.286	2.06	1.0	6.5	5	30	24.8	55.2	0.45	94.5[a]
0.286	2.06	1.0	6.5	3	30	26.7	56.6	0.47	100.8[a]
0.286	2.06	1.0	6.5	3	30	24.9	54.3	0.46	94.0[a]
0.286	2.06	1.0	10.8	4	30	31.4	65.5	0.48	119.3[a]
0.286	2.06	1.0	10.8	4	30	31.1	65.2	0.48	118.2[a]
0.286	2.06	1.0	10.8	6	30	30.7	64.9	0.47	117.5[a]
0.286	2.06	1.0	10.8	6	30	29.2	62.7	0.47	111. 8[a]
0.285	2.06	1.0	15.3	4	30	35.5			135.2[a]
0.285	2.06	1.0	15.3	4	30	33.6	74.0	0.45	128.0[a]
0.285	2.06	1.0	15.3	4	30	34.4			130. 8
0.285	2.06	1.0	20.1	3	30	38.3	78.5	0.49	145.3

[a] Data from repeated SEC injections of the same PLP-prepared sample.

Table 3. Temperature Dependence of k_p for 3 wt % Acrylic Acid in Water

c_{AA} (mol·L^{-1})	c_{AA} (wt %)	$10^4 c_{DMPA}$ (mol·L^{-1})	T (°C)	convn (%)	no. of pulses	$10^{-3}M_1$ (g·mol^{-1})	$10^{-3}M_2$ (g·mol^{-1})	M_1/M_2	$10^{-3}k_p$ (L·mol^{-1}·s^{-1})
0.419	3.01	1.0	2.8	4	30	37.2	75.0	0.50	96.6[a]
0.419	3.01	1.0	2.8	4	30	35.5	72.3	0.49	92.2[a]
0.419	3.01	1.0	2.8	4	30	36.9	77.6	0.48	95.8[a]
0.419	3.01	1.0	2.8	5	30	38.5	77.8	0.49	100.1[a]
0.419	3.01	1.0	2.8	5	30	39.0	78.9	0.49	101.4[a]
0.419	3.01	1.0	6.5	5	30	42.7	84.7	0.50	111.4[a]
0.419	3.01	1.0	6.5	5	30	43.1	87.3	0.49	112.4[a]
0.419	3.01	1.0	6.5	5	30	43.8	86.1	0.51	113.9
0.418	3.01	1.0	10.8	5	30	49.1	94.8	0.52	128.1[a]
0.418	3.01	1.0	10.8	5	30	48.8	95.3	0.51	127.3[a]
0.418	3.01	1.0	10.8	5	30	48.9	94.8	0.52	127.2[a]
0.418	3.01	1.0	10.8	5	30	48.6	97.5	0.50	126.4[a]
0.418	3.01	1.0	15.3	5	30	52.8	100.0	0.53	137.7[a]
0.418	3.01	1.0	15.3	5	30	55.7	100.0	0.56	145.3[a]
0.418	3.01	1.0	20.1	3	30	62.5	114.3	0.55	163.0
0.418	3.01	1.0	20.1	3	30	61.4			158.5
0.417	3.01	1.0	24.7	3	30	65.4			169.2
0.417	3.01	1.0	24.7	5	30	69.5	164.4	0.42	179.8

[a] Data from repeated SEC injections of the same PLP-prepared sample.

thus is based on the assumption that $c_{AA,local}$ is identical to the known overall monomer concentration, c_{AA}.

Molecular weight distributions together with the associated first derivative curves of poly(acrylic acid) samples produced by PLP at 2 °C and several initial AA concentrations are plotted in Figure 1A and 1B, respectively. The MWDs clearly show PLP structure with both primary and secondary points of inflection being easily identified from the first derivative curves. DMPA concentration was 1×10^{-4} mol·L^{-1} with all four PLP experiments. Increasing polymerization temperature results in reduced PLP structure of the MWDs with the consistency criteria, however, being fulfilled up to 25 °C. As has already been mentioned, the temperature range cannot be extended to subzero temperatures in aqueous phase, which has frequently been chosen for acrylate monomers in nonaqueous phase.[13-16] Thus, even at the high pulse repetition rate of 100 Hz, the temperature range for reliable PLP–SEC experiments is rather limited in aqueous phase polymerization and does not exceed 25 °C.

Inspection of the entries in Tables 1–5 shows that M_1/M_2 is close to 0.5. Moreover, differences in c_{DMPA} and in the number of applied laser pulses do not significantly affect k_p. Both observations demonstrate that the consistency criteria for reliable PLP–SEC experiments, as put forward by the IUPAC Working Party,[17] are fulfilled.

Plotted in Figure 2 are the apparent k_p values measured at five concentrations of nonionized AA in water. Changing AA concentration leads to variations in apparent k_p by up to 30%. Closer inspection of the data for lower AA concentration (Figure 2A) and for higher concentration (Figure 2B) indicates that the highest values for k_p are observed at an intermediate AA concentration around 3 wt %. This surprising result is illustrated in Figure 3 where apparent k_p is plotted vs c_{AA} for 2, 10, and 20 °C. Included in Figure 3 are the k_p data for 20 and 40 wt % from the preceding paper into k_p of nonionized AA in aqueous solution.[6] It is gratifying to note that the data from the present study nicely fit this literature data. The k_p values at the lowest experimental AA concentration, close to 1 wt %, are about 20–30% below the maximum k_p for the same temperature. k_p at the highest c_{AA} under investigation, 40 wt %,[6] is about a factor of 3 below the associated maximum k_p value. Whereas a lowering in k_p toward increasing monomer concentration has already been seen for aqueous phase polymerization of methacrylic acid (MAA)[18] and *N*-isopropylacrylamide,[19] an intermediate maximum in k_p as a function of c_{AA} has not been reported so far. This unexpected maximum and thus the changes of k_p in the entire experimental concentration range of nonionized AA most likely are not, at least not entirely, due to “true” kinetics, i.e., to variations in k_p resulting from changes in either the preexponential

Table 4. Temperature Dependence of k_p for 5 wt % Acrylic Acid in Water

c_{AA} (mol·L^{-1})	c_{AA} (wt %)	$10^4 c_{DMPA}$ (mol·L^{-1})	T (°C)	convn (%)	no. of pulses	$10^{-3} M_1$ (g·mol^{-1})	$10^{-3} M_2$ (g·mol^{-1})	M_1/M_2	$10^{-3} k_p$ (L·mol^{-1}·s^{-1})
0.699	5.02	0.5	2.7	9	50	60.0	114.3	0.52	95.6
0.699	5.02	0.5	2.7	6	50	63.0	117.2	0.54	98.7
0.701	5.04	1.0	2.7	3	30	66.3	125.6	0.53	101.9
0.701	5.04	1.0	2.7	3	30	67.6	123.6	0.55	104.2
0.696	5.00	5.0	2.7	5	30	65.6	133.4	0.49	102.5
0.696	5.00	5.0	2.7	5	30	61.5	127.1	0.48	96.2
0.698	5.02	0.5	6.4	7	50	68.1	125.9	0.54	107.6
0.701	5.04	1.0	6.5	5	30	74.8	138.7	0.48	116.1
0.701	5.04	1.0	6.5	5	30	71.8	123.3	0.46	111.4
0.696	5.00	5.0	6.5	5	30	70.1	145.2	0.48	109.9
0.696	5.00	5.0	6.5	5	30	70.1	151.0	0.46	109.7
0.698	5.02	0.5	10.1	3	50	75.7	139.6	0.54	117.1
0.698	5.02	0.5	10.1	5	50	74.1	132.7	0.56	115.6
0.701	5.04	1.0	10.8	6	30	79.4	158.5	0.50	124.0
0.701	5.04	1.0	10.8	3	30	83.6	159.6	0.52	128.7
0.695	5.00	5.0	10.8	7	30	75.5	184.1	0.41	119.5
0.695	5.00	5.0	10.8	7	30	74.8	144.5	0.52	118.3
0.698	5.02	0.5	15.1	5	50	82.6	136.0	0.61	129.0
0.698	5.02	0.5	15.1	6	50	83.0	150.0	0.55	130.4
0.700	5.04	1.0	15.3	5	30	92.9	184.9	0.50	145.1
0.700	5.04	1.0	15.3	5	30	90.4	184.5	0.49	141.1
0.700	5.04	5.0	15.3	5	30	81.8	197.7	0.41	128.6[a]
0.695	5.00	5.0	15.3	5	30	84.3	224.0	0.38	132.6[a]
0.695	5.00	5.0	15.3	7	30	87.1	184.9	0.47	137.7[a]
0.695	5.00	5.0	15.3	7	30	84.3	177.8	0.47	133.5[a]
0.697	5.02	0.5	20.1	6	50	92.5	161.8	0.57	145.8
0.697	5.02	0.5	20.1	7	50	90.6	160.3	0.57	143.0
0.699	5.04	1.0	20.1	5	30	105.6	184.5	0.57	166.2

[a] Data from repeated SEC injections of the same PLP-prepared sample.

Table 5. Temperature Dependence of k_p for 10 wt % Acrylic Acid in Water

c_{AA} (mol·L^{-1})	c_{AA} (wt %)	$10^4 c_{DMPA}$ (mol·L^{-1})	T (°C)	convn (%)	no. of pulses	$10^{-3} M_1$ (g·mol^{-1})	$10^{-3} M_2$ (g·mol^{-1})	M_1/M_2	$10^{-3} k_p$ (L·mol^{-1}·s^{-1})
1.43	10.3	5.0	2.6	8	30	106.9	198.2	0.54	82.5
1.43	10.3	5.0	2.6	5	30	102.6	191.2	0.54	77.9
1.54	11.0	5.0	2.1	10	30	111.7	217.3	0.51	81.6
1.54	11.0	5.0	2.1	10	30	114.8	239.9	0.48	83.6
1.43	10.3	5.0	6.3	5	30	112.2	217.3	0.52	84.8
1.43	10.3	1.0	6.3	4	30	119.7	227.5	0.53	88.5
1.54	11.0	5.0	6.1	8	30	125.6	235.5	0.53	90.8
1.54	11.0	5.0	6.1	10	30	127.4	228.0	0.56	92.7
1.43	10.3	6.0	10.3	7	30	119.7	215.3	0.56	92.0
1.43	10.3	5.0	10.0	10	30	125.3	243.8	0.51	98.1
1.53	11.0	5.0	10.0	9	30	138.0	274.0	0.50	100.2
1.53	11.0	5.0	10.0	10	30	137.4	255.3	0.54	100.0
1.43	10.3	5.0	15.7	5	30	139.0	276.7	0.50	106.1
1.43	10.3	1.0	15.7	5	30	155.3	274.8	0.57	116.2
1.53	11.0	5.0	15.0	10	30	151.0	319.2	0.47	110.3
1.53	11.0	5.0	15.0	7	30	157.8	297.7	0.53	113.7
1.43	10.3	5.0	20.1	6	30	158.9	298.5	0.53	121.8
1.43	10.3	1.0	20.1	4	30	162.5	296.5	0.55	120.7
1.53	11.0	5.0	19.9	9	30	165.6	320.6	0.52	120.7

factor and/or in activation energy. It is assumed that solvent effects that modify local monomer concentration at the site of the propagating radical are responsible for the remarkable effects seen for apparent k_p. It comes as no surprise that effects which cause $c_{AA,local}$ to be different from overall c_{AA} are particularly pronounced in systems where different types of strong hydrogen-bonded interactions occur, such as in aqueous solution of AA,[9,10,20] where monomers coexist with dimers and higher aggregates of AA and where water molecules may participate in aggregate formation.[9]

The decrease in PLP-determined k_p by about 1 order of magnitude, from around 4000 to 500 L·mol^{-1}·s^{-1} observed for MAA in aqueous solution between 14 wt % MAA up to pure MAA at 25 °C has been assigned to solvent effects.[18] The drop in k_p by a factor of 2 in going from 14 to 40 wt % MAA in aqueous solution[18] is close to the change seen with AA under corresponding conditions (Figure 3). A monotonic decrease of apparent k_p from 70 000 to 10 000 L·mol^{-1}·s^{-1} was reported to occur in the narrow monomer concentration range from 0.7 to 7 wt % for *N*-isopropylacrylamide polymerized in aqueous phase at temperatures between 8 and 10 °C with initiation by uranyl nitrate.[19] As part of the work in ref 19, the concentration of dimers was determined by osmometry. A kinetic model that takes dimerization explicitly into account, however, was not capable of describing the experimentally observed dependence of k_p on monomer concentration. The local concentration being different from bulk monomer concentration was one of the explanations put forward.[19]

The discussion of the unusual behavior k_p vs c_{AA} will be split into two parts: (i) region 1 for $c_{AA} > 3$ wt %, where apparent k_p decreases with monomer concentration, and (ii) region 2 for $c_{AA} < 3$ wt %, where k_p increases with monomer concentration.

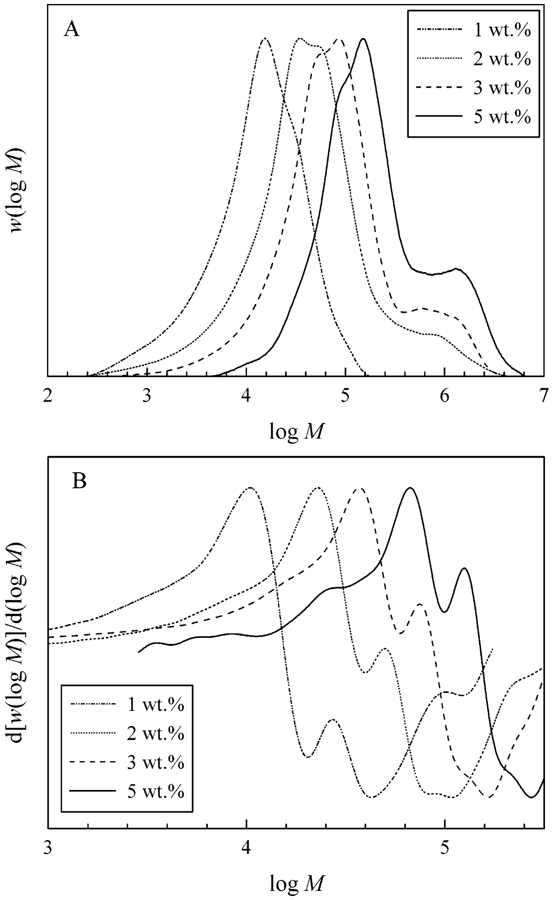

Figure 1. Molecular weight distributions (A) and associated derivative curves (B) obtained in PLP−SEC experiments on acrylic acid in an aqueous solution at overall monomer concentrations of 1, 2, 3, and 5 wt % and 2 °C. The laser repetition rate was 100 Hz and the initial photoinitiator concentration was $c_{\mathrm{DMPA}} = 1 \times 10^{-4}$ mol·L^{-1}.

(i) Region 1: $c_{\mathrm{AA}} > 3$ wt %. Applying the dimerization model put forward by Ganachaud et al.,[19] with the concentration of AA dimer species being adopted from the Raman spectroscopic data on propionic acid in aqueous solution,[21] provides results that, as with the study into k_p of *N*-isopropylacrylamide,[19] indicate that the dimerization model is insufficient to account for the experimentally observed decrease of k_p with c_{AA} due to enhanced AA dimerization upon increasing AA concentration.

Adopting the "local" monomer concentration argument basically says that a decrease of "apparent" k_p is indicative of a lowering in monomer concentration at the site of the free-radical chain end rather than to a decrease in "true kinetic" k_p. What may be the reason for a decrease in $c_{\mathrm{AA,local}}$ at AA concentrations above 3 wt %? Increasing AA concentration corresponds to a gradual replacement of water molecules by AA molecules. As water is known to be a better solvent for poly(acrylic acid) than is AA, solvent quality is reduced toward increasing c_{AA}. As a consequence, poly(acrylic acid) and also AA macroradicals may be swollen by a water−monomer solution that is lower in AA content than overall AA concentration. In addition, the reduction in solvent quality for poly(acrylic acid) molecules and radicals toward higher AA monomer content gives rise to a larger extent of intrasegmental interactions that further lowers $c_{\mathrm{AA,local}}$ and that may also enhance the barrier for monomer diffusion to free-radical sites on the AA macroradicals.

Whether solvent effects are responsible for the observed changes in apparent k_p may be studied by adding to an aqueous AA solution another acid that, however, does not polymerize. Propionic acid (PA) appears to be a suitable candidate for this kind of investigation. The solvent properties of PA in aqueous solution containing poly(acrylic acid) species should be very close to the ones brought upon by AA itself. Thus PA should be able to substitute AA at any site within the polymerization system, including the site of propagation as well as dimers and other associated structures. A similar approach has been applied within studies into k_p of acrylamide in aqueous solution where propionamide has been added as a saturated analogue.[22]

Aqueous solutions have been prepared which, in addition to 10 wt % AA contain 30 and 60 wt % propionic acid, respectively. Listed in Table 6 are the k_p values obtained in PLP−SEC experiments with an initial photoinitiator concentration of $c_{\mathrm{DMPA}} = 5 \times 10^{-4}$ mol·L^{-1} and with 30 pulses being applied at a pulse repetition rate of 100 Hz. Primary and secondary points of inflection were obtained with the entire set of experiments. In contrast to the experiments without addition of PA, a high-molecular-weight fraction of background polymer was observed. This background polymer gives rise to the relatively high degrees of monomer conversion (Table 6) which, however, do not markedly affect k_p and will not invalidate the conclusions to be drawn from this set of experiments.

Shown in Figure 4 are Arrhenius plots of apparent k_p for 10 wt % aqueous solutions of AA with 30 and 60 wt % PA, respectively, being added. Also given in Figure 4 is the apparent k_p for aqueous solutions of 10 and 40 wt % AA (without PA being present). Addition of PA lowers the apparent k_p to a similar extent, as does increasing AA concentration. The values of k_p determined for 10 wt % AA in the presence of 30 wt % PA are slightly above and the numbers measured for 10 wt % AA in the presence of 60 wt % PA are below the apparent k_p determined for a 40 wt % AA aqueous solution (Figure 4). The results suggest that it is primarily carboxylic acid concentration that affects k_p. The effects of AA and of PA on solvent quality in the aqueous phase of poly(acrylic acid) appear to be rather similar.

To further investigate the reasons for the significant changes in apparent k_p as a function of solvent quality, it appeared interesting to see whether the addition of NaCl to aqueous AA solutions will have an influence on k_p. The addition of salt should be accompanied by a decrease in solvent quality, which in turn may affect k_p. Popov et al.,[23] however, observed that the polymerization rate of nonionized AA in aqueous solution is not changed by the presence of 1,1-salts. At 25 °C, the limiting NaCl concentration to be dissolved in an aqueous solution containing 0.5 wt % polyAA is about 6.4 wt % (1.1 mol·L^{-1}).[24] PLP−SEC experiments were carried out on aqueous solutions containing 20 wt % AA with 2.9 wt % NaCl, corresponding to 0.5 mol·L^{-1}, being added. The apparent k_p data measured with and without NaCl (for 20 wt % AA) are listed in Table 7 and are plotted in Figure 5. No clear difference between the numbers determined with and without NaCl can be detected within the limits of accuracy. As can be seen from Table 8, the same result is obtained from experi-

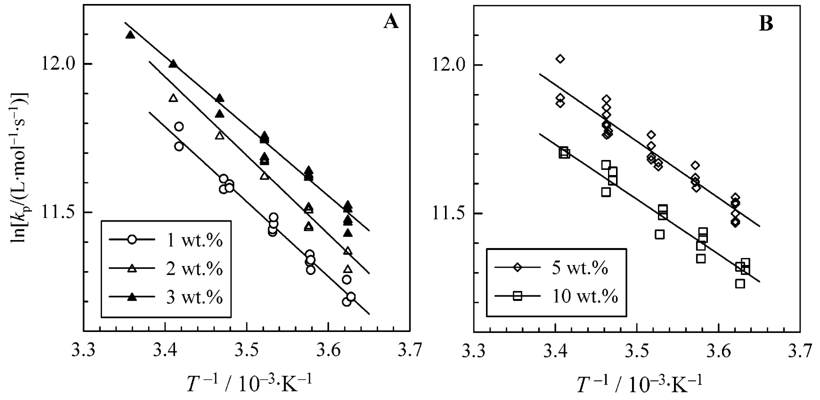

Figure 2. Arrhenius plots for apparent k_p of acrylic acid in aqueous solution at overall acrylic acid concentrations of 1, 2, 3, 5, and 10 wt %.

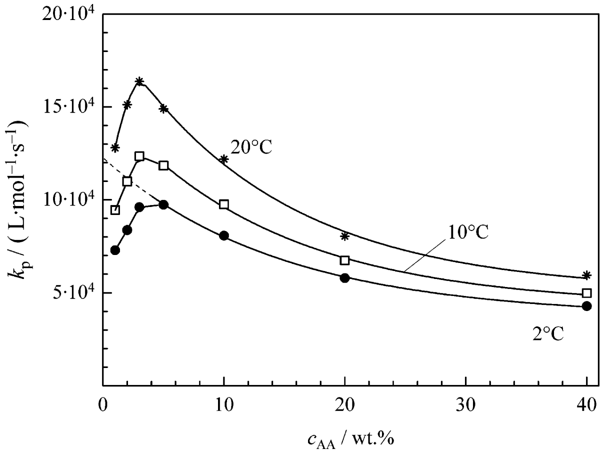

Figure 3. Dependence of apparent k_p on acrylic acid concentration at 2, 10, and 20 °C. The data for precisely these temperatures are calculated from the Arrhenius-type expressions given in the text (eqs 2−6) and, for acrylic acid concentration above 10 wt %, in ref 6. For 2 °C, a third-order polynomial (dashed line) is fitted to the data at acrylic acid concentration concentrations above 3 wt % (see later in the text).

Table 6. Temperature Dependence of k_p for 10 wt % Acrylic Acid in Water after Addition of 30 and 60 wt % of PA ($c_{DMPA} = 5 \times 10^{-4}$ mol·L^{-1}, 30 Pulses)

c_{PA} (wt %)	T (°C)	convn (%)	$10^{-3}M_1$ (g·mol^{-1})	$10^{-3}M_2$ (g·mol^{-1})	M_1/M_2	$10^{-3}k_p$ (L·mol^{-1}·s^{-1})
30	2.5	17	63.5	117.2	0.54	52.9
	2.5	11	64.7	120.8	0.54	52.1
	6.2	14	68.5	136.5	0.50	56.1
	6.2	13	70.0	141.3	0.50	56.8
	6.3	15	71.4	127.1	0.56	59.0
	6.3	15	66.7	125.6	0.53	55.2
	10.6	10	76.0	141.3	0.54	60.9
	10.6	17	75.7	145.5	0.52	63.1
	15.2	12	83.4	163.7	0.51	67.5
	15.2	11	83.6	161.1	0.52	67.4
	20.1	16	89.9	201.4	0.45	74.6
60	6.2	10	44.6	75.2	0.59	36.1
	10.6	10	48.5	80.2	0.60	39.2
	10.6	10	48.5	78.5	0.62	39.4
	15.2	13	52.1	98.2	0.53	42.8
	20.1	5	58.3	113.5	0.51	46.0
	25.0	8	61.1	116.4	0.52	48.9

ments carried out at two additional NaCl concentrations, 0.1 and 1.0 mol·L^{-1}. The observations are thus consistent with literature data[23] reporting the polymerization rate of nonionized AA in aqueous solution to be independent of salt content. The changes in solvent quality that are relevant for apparent k_p thus appear to be primarily the ones that are induced by the action of hydrogen bonds. It is the close similarity of effects associated with either increasing AA or PA concentration that provides convincing evidence for the importance of hydrogen-bonded interactions of carboxylic acid groups on solvent quality and thereby on apparent k_p. On the other hand, it needs to be admitted that, at present, it is by no means clear which type of interactions, segment−segment or solvent−segment interactions, play the dominant role.

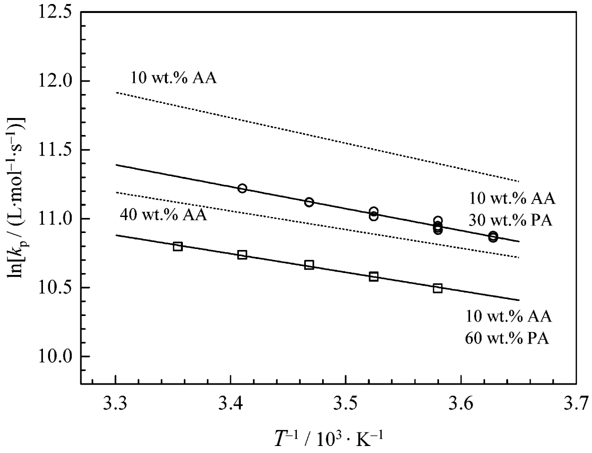

Figure 4. Arrhenius-type plots of apparent k_p for 10 wt % acrylic acid polymerized in the presence of different amounts of propionic acid (solid lines with data points). The dashed lines refer to the apparent k_p of acrylic acid solutions containing no propionic acid.

Table 7. Temperature Dependence of k_p for 20 wt % Acrylic Acid in 0.5 mol·L^{-1} NaCl Solution in Water ($c_{DMPA} = 5 \times 10^{-4}$ mol·L^{-1}, 30 Pulses)

c_{AA} (mol·L^{-1})	c_{AA} (wt %)	T (°C)	convn (%)	$10^{-3}M_1$ (g·mol^{-1})	$10^{-3}M_2$ (g·mol^{-1})	M_1/M_2	$10^{-3}k_p$ (L·mol^{-1}·s^{-1})
2.82	20.0	2.7	2	172.6	338.8	0.51	65.9
2.82	20.0	2.7	1	176.6	337.3	0.52	66.7
2.82	20.0	6.3	1	177.8	354.0	0.50	67.4
2.82	20.0	6.3	1	183.7	365.6	0.50	69.7
2.81	20.0	10.6	2	204.6	394.5	0.52	78.1
2.81	20.0	10.6	1	212.3	411.1	0.52	80.6
2.81	20.0	15.1	1	225.4	447.7	0.50	85.5
2.81	20.0	15.1	1	211.8	427.6	0.50	80.6
2.80	20.0	20.2	2	225.4	468.8	0.48	86.4
2.80	20.0	20.2	1	230.6	501.0	0.46	87.9
2.80	20.0	25.0	3	244.3	538.3	0.45	94.2
2.80	20.0	25.0	1	238.8	504.7	0.47	91.1

(ii) Region: $c_{AA} < 3$ wt % AA. The arguments presented so far refer to situations where k_p decreases

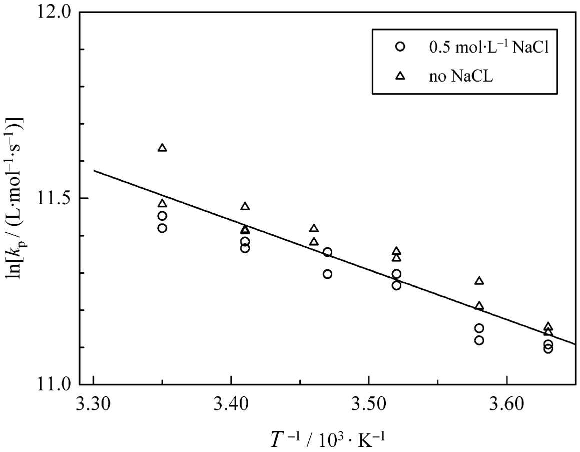

Figure 5. Temperature dependence of apparent k_p for 10 wt % of acrylic acid in water and in 0.5 mol·L^{-1} NaCl in water.

Table 8. Effect of NaCl Concentration in Water on Apparent k_p at 6.3 °C for Different AA Concentrations

	$10^{-3}k_p$ (L·mol^{-1}·s^{-1})			
c_{AA} (wt %)	0 wt % NaCl	0.58 wt % NaCl	2.9 wt % NaCl	5.8 wt % NaCl
5	107.3[a]	96.9	115.6	111.6
20	70.1[a]	71.6	68.6	78.1
40	46.5[a]	51.3	43.7	48.0

[a] From Arrhenius equations.

with increasing AA concentration. Thus they are not capable of providing an explanation for the maximum in k_p vs c_{AA} at around 3 wt % AA and the lowering in k_p upon further dilution of the aqueous AA solution (Figure 3). This maximum behavior of k_p is interesting on its own. Moreover, k_p of AA at low concentration should be known, for example, to achieve a better understanding of aqueous phase kinetics in emulsion polymerization, where particles are electrosterically stabilized by a copolymer of AA and a hydrophobic monomer formed in situ in the aqueous phase.[25]

One explanation for the drop in k_p toward very low AA concentrations could be that, according to the Ostwald dilution law, the degree of dissociation, α, of the weak electrolyte AA is enhanced at low AA concentrations. Propagation reactions of negatively charged molecules and radicals are known to be associated with a lower k_p.[26] Ionization according to Ostwald dilution law, however, does not come into play until c_{AA} approaches K_a^{-1}, where $K_a = 4.25 \times 10^{-5}$ mol·L^{-1} is the acidity constant of acrylic acid.[27] Pronounced dissociation of acrylic acid thus occurs only at AA concentrations below 1×10^{-3} mol·L^{-1}. The dissociation of polymeric carboxylic acid groups occurs at even lower concentrations due to the lower acidity strength of these groups as compared to acrylic acid, which makes reaction between ionized species even less probable. Accordingly, dissociation may be ruled out as the reason for the lowering in k_p observed upon decreasing c_{AA} from 3 to 1 wt %.

Kratochvil et al.[28] suggested that pronounced differences between local and overall monomer concentration in solution resulting from preferential solvation are to be expected at low monomer concentrations. Such effects should be detectable in systems characterized by strong specific interactions. Both these conditions are met in aqueous-phase AA polymerization below 3 wt %. A lowering in local monomer concentration at the free-radical site and thus a reduction in apparent k_p may result from AA monomer molecules being associated to AA segments on the polymeric backbone. Such a chemically adsorbed layer of monomer molecules may lead to a detectable difference between $c_{AA,local}$ and overall c_{AA} only at low AA concentrations.

To test the hypothesis of monomer being adsorbed, via strong hydrogen bonds, on poly(acrylic acid) molecules and radicals, the dependence on c_{AA} of apparent k_p measured for AA in aqueous solution at 2 °C was extrapolated by using the k_p data measured at c_{AA} above 3 wt %. Fitting these data with a third-order polynomial yields the dashed line shown in Figure 3. A *local* monomer concentration $c_{AA,local}$ may be estimated as the concentration that turns apparent k_p deduced from overall c_{AA} into $k_{p,extrapolated}$, as given by the dashed line. The $c_{AA,local}$ data are found from the simple relation $c_{AA}k_p = c_{AA,local}k_{p,extrapolated}$ to be 0.64, 1.54 ,and 2.73 wt % at the overall concentrations c_{AA} of 1, 2, and 3 wt %, respectively. The difference between $c_{AA,local}$ and c_{AA} turns out to be approximately the same for the three AA concentrations. The "missing" amount of about 0.3–0.5 wt % AA may be considered to be the amount of AA chemically adsorbed to polymeric molecules or radicals. At overall AA concentrations of 5 wt % or more, such a small quantity of absorbed monomer will have a negligible effect on the analysis of PLP–SEC experiments.

Another explanation for the maximum in apparent k_p vs c_{AA} may be self-assembling of AA monomer. Chapiro suggested that the formation of linear plurimolecular aggregates via hydrogen bonds results in a favorable orientation of monomer molecules, allowing for very fast AA propagation.[9] Acrylic acid concentrations around $c_{AA} = 3$ wt % may represent the limiting concentration at which effective self-assemblies of monomer promoting fast propagation can be formed. Below this concentration self-assembling may be insufficient. Without further experiments no clear decision can be made whether and to what extent the two interpretations both assuming preferential or even specific adsorption of AA monomer to the polymeric molecules and radicals apply. The first of the two mechanism considers adsorbed AA as being inefficient for propagation whereas the second mechanism assumes particularly strong contributions to propagation by adsorbed AA molecules.

In concluding this section, the k_p values measured as a function of c_{AA} exhibit an interesting phenomenon in that they pass through a maximum at about 3 wt % AA. Various mechanisms responsible for this behavior can be operative and have been discussed. In view of the current understanding of solvent effects we tend to believe that the local monomer concentration at the locus of propagation plays the dominant role in the case of AA polymerization in water.

The preceding discussion provides strong evidence for significant contributions to apparent k_p from solvent quality and from association both resulting from strong hydrogen-bonded interactions in aqueous AA solution. As a consequence, Arrhenius fitting of the temperature dependence of k_p will not result in meaningful Arrhenius parameters, although the underlying data for limited temperature ranges as, for example, plotted in Figure 2 closely fit to straight Arrhenius lines. Moreover, these lines may not be useful for extrapolation beyond the temperature range of the underlying experiments. With these caveats being kept in mind, the Arrhenius expres-

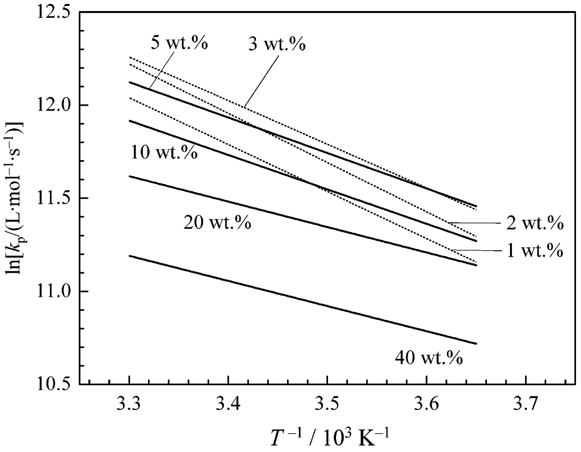

Figure 6. Arrhenius fits of apparent k_p for acrylic acid in aqueous solution at concentrations from 1 to 10 wt % (this work) and at 20 and 40 wt % (ref 6). At low concentrations, up to 3 wt %, the apparent k_p values are fitted by dotted lines to indicate that the Arrhenius parameters associated with these lines are untypical for acrylate-type monomers (see text).

sions for apparent k_p deduced from PLP–SEC experiments at about 1, 2, 3, 5, and 10 wt % nonionized AA in aqueous solution (see Figure 2 and Tables 1–5) will now be presented as

1 wt % AA:

$$\ln[k_p/(\mathrm{L\cdot mol^{-1}\cdot s^{-1}})] = (20.4 \pm 0.60) - (2523 \pm 171)(T^{-1}/\mathrm{K^{-1}}) \quad (2.5 \le T/^\circ\mathrm{C} \le 19.5) \quad (2)$$

2 wt % AA:

$$\ln[k_p/(\mathrm{L\cdot mol^{-1}\cdot s^{-1}})] = (21.0 \pm 1.38) - (2648 \pm 389)(T^{-1}/\mathrm{K^{-1}}) \quad (2.8 \le T/^\circ\mathrm{C} \le 20.1) \quad (3)$$

3 wt % AA:

$$\ln[k_p/(\mathrm{L\cdot mol^{-1}\cdot s^{-1}})] = (20.0 \pm 0.64) - (2343 \pm 179)(T^{-1}/\mathrm{K^{-1}}) \quad (2.8 \le T/^\circ\mathrm{C} \le 24.7) \quad (4)$$

5 wt.% AA:

$$\ln[k_p/(\mathrm{L\cdot mol^{-1}\cdot s^{-1}})] = (18.4 \pm 0.78) - (1905 \pm 218)(T^{-1}/\mathrm{K^{-1}}) \quad (2.7 \le T/^\circ\mathrm{C} \le 20.1) \quad (5)$$

10 wt % AA:

$$\ln[k_p/(\mathrm{L\cdot mol^{-1}\cdot s^{-1}})] = (18.0 \pm 0.74) - (1848 \pm 209)(T^{-1}/\mathrm{K^{-1}}) \quad (2.1 \le T/^\circ\mathrm{C} \le 20.1) \quad (6)$$

In Figure 6, the Arrhenius-type expressions (2)–(6) are plotted together with the corresponding equations for the higher AA concentrations, 20 and 40 wt %, from ref 6. The associated Arrhenius-type parameters are listed in Table 9. The activation energies and preexponential factors for the low-concentration "apparent" k_p data (Figure 6 and Table 9) are significantly above the corresponding data deduced from the experiments on AA solutions containing between 5 and 40 wt % AA. The Arrhenius correlations for 1–3 wt % AA are given as dotted lines. The activation energies at the higher AA contents are closer to numbers of 14 ± 2 kJ·mol^{-1}, which are considered as being characteristic for free-radical polymerization of monomers belonging to the acrylate family.[13–16,29] Activation energies of this size are also derived from studies into the addition reaction of acrylate monomers to small acrylate-like free radicals.[30,31] The apparent activation energies obtained for $c_{AA} \le 3$ wt % are obviously atypical for acrylate monomers and are closer to what is considered to be an activation energy for propagation of methacrylate-type monomers.[32] That the Arrhenius parameters for low AA concentration are not reasonable kinetic quantities is also suggested by the unrealistically high preexponential factors that, for the 2 wt % AA solution, even exceed 10^9 L·mol^{-1}·s^{-1}. The kinetic parameters for very low AA contents thus clearly support the view that effects other than purely kinetic ones significantly contribute to apparent k_p.

Table 9. Arrhenius Parameters E_A and A for Different Acrylic Acid Concentrations in Water

c_{AA} (wt %)	E_A (kJ·mol^{-1})	$10^{-8}A$ (L·mol^{-1}·s^{-1})	temp interval (°C)
1	21.0	7.2	2.5–20.0
2	22.0	13.2	2.8–20.0
3	19.5	4.9	2.8–24.7
5	15.8	0.98	2.7–20.1
10	15.4	0.66	2.1–20.1
20[a]	11.9	0.11	2.6–25.0
40[a]	12.2	0.09	2.6–28.5

[a] Determined in ref 6.

The apparent k_p values deduced for AA concentrations at and above 5 wt % AA appear to be of reasonable size, as indicated by a comparison with rate coefficients deduced by the Fischer group for the addition of acrylate molecules to small radicals of acrylate type.[30] Rate coefficients for small AA species have not yet been measured but are assumed to be similar to numbers reported for acrylonitrile being added to a small species that mimics an acrylate-type radical.[30] The addition rate coefficient in acetonitrile solution between these two species is 5.4×10^5 L·mol^{-1}·s^{-1} with $E_A = 15.4$ kJ·mol^{-1} and $A = 3.2 \times 10^8$ L·mol^{-1}·s^{-1}. As the preexponential for addition of a monomer molecule to a macroradical is typically by about 1 order of magnitude below the preexponential for the reaction to an associated small radical, the agreement between the literature value for small species and the apparent k_p determined within the PLP–SEC experiments carried out on aqueous AA solutions at and above 5 wt % AA is rather satisfactory.

The Arrhenius fits of apparent k_p for polymerization of 10 wt % AA in the presence of different amounts of propionic acid (eqs 7 and 8) are close to the ones observed for apparent k_p in concentrated aqueous AA solutions containing no added PA. The expressions referring to the data in Figure 4 and to the numbers in Table 6 read:

30 wt % PA added:

$$\ln[k_p/(\mathrm{L\cdot mol^{-1}\cdot s^{-1}})] = (16.6 \pm 0.61) - (1591 \pm 173)(T^{-1}/\mathrm{K^{-1}}) \quad (2.5 \le T/^\circ\mathrm{C} \le 25.0) \quad (7)$$

60 wt % PA added:

$$\ln[k_p/(\mathrm{L\cdot mol^{-1}\cdot s^{-1}})] = (15.3 \pm 0.32) - (1351 \pm 92)(T^{-1}/\mathrm{K^{-1}}) \quad (6.2 \le T/^\circ\mathrm{C} \le 25.0) \quad (8)$$

The associated Arrhenius parameters are $E_A = 13.2$ kJ·mol^{-1} (30 wt % PA) and 11.2 kJ·mol^{-1} (60 wt % PA) and $A = 1.6 \times 10^7$ L·mol^{-1}·s^{-1} (30 wt % PA) and 0.4×10^7 L·mol^{-1}·s^{-1} (60 wt % PA). As is to be expected from

Figure 5, the Arrhenius expression for apparent k_p of an aqueous solution of 20 wt % AA with 2.9 wt % NaCl(eq 9) is close to the expression for k_p of a solution containing the same amount of AA, without any NaCl.

$$\ln[k_p/(\mathrm{L{\cdot}mol^{-1}{\cdot}s^{-1}})] = (15.7 \pm 0.72) - (1260 \pm 206)(T^{-1}/\mathrm{K}^{-1}) \quad (2.7 \le T/°\mathrm{C} \le 25.0) \quad (9)$$

The discussion may be summarized: The variations seen with apparent k_p for aqueous AA solutions at moderate and high AA concentrations appear to be due to solvent quality effects that reduce local monomer concentration at the site of the macroradical functionality. The maximum in k_p as a function of AA concentration, which occurs at around 3 wt %, and the apparent k_p values being decreased toward even lower AA concentration are assigned to preferential adsorption of monomeric AA on poly(acrylic acid) molecules and radicals. Because of significant contributions of monomer association and solvent quality to the PLP−SEC-derived apparent k_p values, extrapolation of rate data to conditions beyond the range of the underlying experiments is risky. This is particularly true for the lowest experimental AA concentrations, where the observed “apparent” activation energies differ from what is considered to be typical for an acrylate-type monomer. As the PLP−SEC experiments are not easily extended to the technically relevant higher temperatures, other types of experiments are required such as chemically initiated polymerization, which, however, needs to be accompanied by additional experimental information on initiator decomposition rate, initiator efficiency, and termination rate. Also EPR-assisted techniques may be considered for determination of AA k_p at higher polymerization temperatures.

Conclusions

Suitable PLP conditions have been identified for reliable PLP−SEC experiments on k_p of nonionized AA in aqueous solution. The PLP−SEC data are analyzed under the assumption that local monomer concentration at the free-radical site is identical to overall AA concentration. The resulting k_p’s are referred to as “apparent” propagation rate coefficients. These k_p’s are significantly affected by the strong hydrogen-bonded interactions in aqueous AA solution. The observed decrease of k_p toward high monomer concentrations appears to be characteristic for water-soluble monomers polymerized in the aqueous phase. AA shows a special type of behavior in that a maximum in k_p occurs at rather small AA concentrations around 3 wt %. The changes in apparent k_p are assigned to solvent quality effects and to association of monomeric AA to the poly(acrylic acid) molecules and radicals. Because of the significant effects of the solvent environment on k_p, information on the polymerization conditions, in particular on monomer concentration, needs to accompany the presentation of results on k_p. Studies into k_p of partially and of fully ionized AA in aqueous solution will be the subject of a forthcoming paper, as will be investigations into the termination rate coefficient of nonionized, partially ionized and fully ionized AA in aqueous solution.

Acknowledgment. We thank BASF AG (Ludwigshafen) for funding this project and to Drs. B. G. Manders, I. Rau, and K.-H. Hungenberg, all from BASF AG, for helpful discussions.

References and Notes

(1) Olaj, O. F.; Schnöll-Bitai, I.; Hinkelmann, F. *Makromol. Chem.* **1987**, *188*, 1689−1702.
(2) Beuermann, S.; Buback, M. *Prog. Polym. Sci.* **2002**, *27*, 191−254.
(3) *Polymer Handbook*, 4th ed.; Brandrup, J., Immergut, E. H., Grulke, E. A., Eds.; John Wiley & Sons: New York, 1999; Section II, p 80.
(4) Brüssau, R.; Goetz, N.; Mächtle, W.; Stölting, J. *Tenside Surf. Det.* **1991**, *28* (6), 396−406.
(5) Kilz, P. Polymer Standards Service GmbH, Mainz, Germany, private communication.
(6) Lacík, I.; Beuermann, S.; Buback, M. *Macromolecules* **2001**, *34*, 6224−6228.
(7) Buback, M.; Gilbert, R. G.; Russell, G. T.; Hill, D. J.; O'Driscoll, K. F.; Shen, J.; Winnik, M. A. *J. Polym. Sci., Polym. Chem. Ed.* **1992**, *30*, 851−863.
(8) Beuermann, S.; Buback, M.; El Rezzi, V.; Jürgens, M.; Nelke, D. Manuscript in preparation.
(9) Chapiro, A. *Eur. Polym. J.* **1973**, *9*, 417−427.
(10) Plochodzka, K. *J. Macromol. Sci.-Rev. Macromol. Chem.* **1981**, *C20*, 67−148.
(11) Gromov, V. F.; Galperina, N. I.; Osmanov, T. O.; Khomikovskij, P. M.; Abkin, A. D. *Eur. Polym. J.* **1980**, *16*, 529−535.
(12) Gromov, V. F.; Bune, E. V.; Teleshov, E. N. *Russ. Chem. Rev.* **1994**, *63*, 507−517.
(13) Lyons, R. A.; Hutovic, J.; Piton, M. C.; Christie, D. I.; Clay, P. A.; Manders, B. G.; Kable, S. H.; Gilbert, R. G. *Macromolecules* **1996**, *29*, 1918−1927.
(14) Manders, B. Ph.D. Thesis, TUE Eindhoven, 1997.
(15) Couvreur, L.; Piteau, G.; Castignolles, P.; Tonge, M.; Coutin, B.; Charleux, B.; Vairon, J.-P. *Macromol. Symp.* **2001**, *174*, 197−207.
(16) Plessis, C.; Arzamendi, G.; Alberdi, J. M.; van Herk, A. M.; Leiza, J. R.; Asua, J. M. *Macromol. Rapid Commun.* **2003**, *24*, 173−177.
(17) Beuermann; S.; Buback, M.; Davis, T. P.; Gilbert, R. G.; Hutchinson, R. A.; Olaj, O. F.; Russell, G. T.; Schweer, J.; van Herk, A. M. *Macromol. Chem. Phys.* **1997**, *198*, 1545−1560.
(18) Kuchta, F.-D.; van Herk, A. M.; German, A. L. *Macromolecules* **2000**, *33*, 3641−3649.
(19) Ganachaud, F.; Balic, R.; Monteiro, M. J.; Gilbert, R. G. *Macromolecules* **2000**, *33*, 8589−8596.
(20) Ng, J. B.; Shurvell, H. F. *J. Phys. Chem.* **1987**, *91*, 496−500.
(21) Tanaka, N.; Kitano, H.; Ise, N. *J. Phys. Chem.* **1990**, *94*, 6290−6292.
(22) Pascal, P.; Winnik, M. A.; Napper, D. H.; Gilbert, R. G. *Macromolecules* **1993**, *26*, 4572−4576.
(23) Popov, V. G.; Topchiev, D. A.; Kabanov, V. A.; Kargin, V. A. *Vysokomol. Soedin.* **1972**, *A14*, 131−146.
(24) *Encyclopedia of Polymer Science and Technology*, 1st ed..; Mark, H. F.; Gaylord, N. G.; Bikales, N. M., Eds.; John Wiley & Sons: New York, London, Sydney, 1964; Vol 1, p 197.
(25) Vorwerg, L.; Gilbert, R. G. *Macromolecules* **2000**, *33*, 6693−6703.
(26) Kabanov, V. A.; Topchiev, D. A.; Karaputadze, T. M.; Mkrtchian, L. A. *Eur. Polym. J.* **1975**, *11*, 153−159.
(27) Kilpatrick, M.; Morse, J. G. *J. Am. Chem. Soc.* **1953**, *75*, 1854−1856.
(28) Kratochvil, P.; Straková, D.; Stejskal, J.; Tuzar, Z. *Macromolecules* **1983**, *16*, 1136−1143.
(29) Beuermann, S.; Paquet, D. A.; Jr.; McMinn, J. H.; Hutchinson, R. A. *Macromolecules* **1996**, *29*, 4206−4215.
(30) Fisher, H.; Radom, L. *Angew. Chem., Int. Ed.* **2001**, *40*, 1340−1371.
(31) Fisher, H.; Radom, L. *Macromol. Symp.* **2002**, *182*, 1−14.
(32) Beuermann, S.; Buback, M.; Davis, T. P.; Gilbert, R. G.; Hutchinson, R. A.; Kajiwara, A.; Klumperman, B.; Russell, G. T. *Macromol. Chem. Phys.* **2000**, *201*, 1355−1364.

MA030365E