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Propagation Kinetics of Acrylic and Methacrylic Acid in Water and Organic Solvents Studied by Pulsed-Laser Polymerization

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ABSTRACT: Pulsed laser-induced polymerization (PLP) in combination with analysis of formed polymer by size exclusion chromatography (SEC) has been successfully applied in determining propagation rate coefficient, k_p, of acrylic and methacrylic acid in organic solvents and water. For methacrylic acid solution polymerization in methanol and in dimethyl sulfoxide (DMSO), minor but not negligible variations of k_p with solvent have been observed. In contrast, k_p values for polymerizations in water are significantly influenced by the solvent *and* furthermore by monomer concentration. The k_p values obtained from polymerization experiments in water are significantly larger than the corresponding values obtained in methanol or DMSO. Weighted nonlinear least-squares fitting (NLLS) has been applied to calculate frequency factors, *A*, and activation energies, E_a, from the temperature dependence of k_p for methacrylic acid in methanol, DMSO, and water in order to underline the reliability of the data. For acrylic acid it turns out that optimized experimental conditions have to be chosen in order to determine reliable k_p values at ambient temperature. Laser pulse repetition rates of at least 90 Hz are necessary to ensure that “termination by the laser pulse” is the main chain stopping event. Smaller values of the laser pulse repetition rate will not yield reliable k_p data. Furthermore, evidence of at least one first overtone inflection point at $L_2 \approx 2L_1$ is not only recommended, it is necessary to ensure a reliable measure of k_p. This is the most important consistency criterion showing that experimental conditions are suitable.

Introduction

Pulsed laser polymerization (PLP) combined with molecular weight analysis of formed polymer preferably done by size exclusion chromatography (SEC) has been emerged as the method of choice for investigations into the field of free radical polymerization kinetics, i.e., to determine the rate coefficient of free radical propagation, k_p. The use of this method is strongly recommended by the IUPAC working party on *Modeling of reaction kinetics and processes*. For styrene and methyl methacrylate benchmark values based on the experimental results of different groups have been published.[1] Strong efforts have been taken to extend these investigations on k_p determination of acrylates and methacrylates,[2] respectively.

According to our knowledge, there is only one publication on the determination of k_p of methacrylic acid in organic solvents and one of acrylic acid in water using the PLP−SEC technique.[3] So far there is still a lack of reliable experimental data published on k_p of acrylic and methacrylic acid in organic solvents and water determined by different laboratories.

The aim of this publication is the accurate determination of k_p of acrylic acid (AA) and methacrylic acid (MAA) in organic solvents and water. As already mentioned previously, PLP−SEC is applied to do so. The features of the PLP−SEC technique are the following: (i) The polymerization is initiated by radicals instantaneously generated through irradiation of a photoinitiator/monomer mixture with an UV-laser pulse. (ii) The time between the laser pulses will be the time of growth of many of the polymer chains before they are terminated by newly formed radicals of the successive laser pulse. (iii) The molecular weight distribution (MWD) of the polymer produced at a fixed time between the laser pulses, t_d, has to be analyzed and the point of inflection, L_i, on the low molecular weight side of the SEC curve is the measure for k_p according to eq 1, where [M] is

$$L_i = ik_p[M]t_d \tag{1}$$

the monomer concentration at the reaction site and $i = 1, 2, 3, \ldots$, denotes higher order peaks which occur when growing chains survive termination by one or more subsequent pulses. The method has the major advantage that it is possible to carry out self-consistency checks to ascertain the reliability of the data obtained. (i) It is essential that there is at least one overtone inflection point located at $L_2 = 2L_1$, indicating that bimolecular radical termination is due to radicals from successive laser pulses. (ii) k_p has to be invariant due to changes in pulse repetition rate.[1]

The study of literature shows that usually the effect of the polarity of a medium on the chain propagation is neglected. This assumption seems to be true for low polarity monomers where the propagation rate coefficient changes only slightly (in most older reported cases within or close to the experimental error). In more recent publications, effects of solvent and monomer concentration are reported.[4−6,10] For polar monomers, especially those capable of forming hydrogen bonds such as carboxylic acids, however, the situation is very complex and the solvent effect turns out to be substantial.[7−9] AA and MAA are well-known to exist in different forms depending on the solvent: as a monomer, as a dimer (self-associate), and as a linear oligomer (self-association), associated with a solvent molecule or

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associated with the carboxylic group of a growing polymer chain. In this case, changing the solvent can change the equilibrium constants for the equilibrium between the different forms of the monomer. In combination with different reactivities of the monomer in different forms this can lead to a substantial solvent effect.

Chapiro[8] tried to explain the effect of solvent on overall reaction rate in AA and MAA polymerization by defining two groups of solvents: (i) The first group of solvents, i.e., water, methanol, and dioxane, are good polar solvents for the polymer. Because of hydrogen bonding between the monomers and between the solvent and the carboxyl groups within this group of solvents, the acid exhibits an associated structure forming oligomeric associates and monomer−solvent association complexes. Furthermore, at low conversions the reaction rate is extremely high in this group of solvents due to the formation of monomer−polymer associates. (ii) The second group, i.e., toluene and hexane, are nonsolvents for the polymer. In this group of solvents only self-association of the monomer (formation of cyclic dimers and linear oligomers) and association with the propagating chain is possible. Dilution of the system shifts the equilibrium from a linear oligomeric form to a cyclic dimer while increasing temperature favors the linear oligomer. The reaction rate turns out to be reduced for the cyclic dimer form.

Gromov et al.[9] applied the rotating sector technique to investigate into AA and MAA polymerization kinetics in various solvents. From their work they concluded that the effect of solvent on chain propagation and also on bimolecular termination seems to be due to variation of monomer and radical reactivity changing with solvation. Also monomer−solvent- and oligomer−solvent aggregates contribute to the observed solvent effect. Real separation of the solvent effects on propagation and termination was not possible.

However, PLP−SEC studies into the influence of solvents on propagation kinetics for styrene (ethanol, methanol, toluene, ethylbenzene), methacrylic acid (methanol, tetrahydrofuran, 2-propanol, toluene, acetic acid), methyl methacrylate (methanol, ethyl acetate, ethanol, toluene, 2-butanone), and butyl acrylate (toluene, tetrahydrofuran) showed, so far, that k_p is invariant with monomer concentration.[3,10] Recently O'Driscoll et al.[11] (benzyl alcohol) and Zammit et al.[4] (diethyl malonate, diethyl phthalate, bromobenzene, chlorobenzene, dimethyl sulfoxide, *N*-methyl pyrrolidinone, benzonitrile, benzyl alcohol), however, reported a pronounced solvent effect on k_p for MMA and styrene homopolymerizations in dimethyl sulfoxide and benzyl alcohol. For the other solvents listed only small effects are observed. These authors determined an increase in k_p compared to bulk k_p values with increasing solvent concentration. This effect is interpreted as being due to complex formation between radical chain ends and solvent molecules. The determination of k_p values for methyl methacrylate and butyl acrylate homopolymerizations in fluid carbon dioxide yield up to 40% smaller k_p values than corresponding bulk data.[5]

The k_p data obtained for AA and MAA polymerizations in the various solvents used within this investigation are discussed with respect to the broad body of literature available on free radical propagation in organic solvents and water.

Experimental Section

Acrylic and methacrylic acid (AA and MAA, Aldrich) were distilled under reduced pressure. To avoid polymerization during the distillation copper powder and wires were added to the monomers. 2,2-Dimethoxy-2-phenylacetophenone (DMPA, Ciba Geigy), was used as a photoinitiator without further purification. The solvents (methanol, dimethyl sulfoxide (DMSO), and acetic acid, all from Merck) were used as received. Polymerizations in aqueous phase were performed in water of SuperQwater (doubly demineralized) quality. The experiments were carried out in a temperature range from 18 to 90 °C with DMPA concentrations between 1 and 2 mmol/L. The mixture of monomer, photoinitiator, and solvent was purged with argon for 20 min in order to remove oxygen. Within the polymerization experiments no precipitation of polymer was observed.

The pulsed laser experiments were performed by applying a Lambda Physics LPX 110 iMC excimer laser operating at the XeF line at 351 nm with a pulse width of 20 ns. Laser pulse repetition rates between 20 and 100 Hz were chosen. The energy per laser pulse directly measured at the laser exit was set at 50 or 55 mJ. Taking the quartz glass of the optical cell into account, the energy per pulse applied on the sample is 20% less. The monomer concentration is calculated according to the weight of acid added to one kilogram of solvent, assuming ideal mixing. The density data for AA, MAA, and the solvents are taken from literature.[12]

After the PLP experiment, hydroquinone was added as inhibitor to avoid postpolymerization. Residual monomer and solvent were evaporated in a vacuum oven at 50 °C, and the monomer conversion was determined by gravimetry. Prior to molecular weight analyses, the polymers formed in PLP experiments were derivatized to poly(methyl acrylate) (pMA) and poly(methyl methacrylate) (pMMA), respectively. This was achieved by methylation of the acids using diazomethane. The diazomethane was generated by using *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide (Diazald) as the reagent. To generate diazomethane the reaction of Diazald dissolved in diethyl ether with potassium hydroxide in ethanol was carried out according to the standard procedure recommended by Aldrich[13] using the special glassware Diazald Kit. At the end of this procedure one obtains a yellow solution of diazomethane in diethyl ether. The polymer obtained in the PLP experiment is swollen for at least 12 h in a tetrahydrofuran/methanol (1:1−1:3) mixture. An excess of a freshly prepared yellow solution of diazomethane in ether is added dropwise to the swollen polymer sample until no further nitrogen generation is observed and the solution remains yellow. White pMMA is seen to be precipitating if one adds methanol to the mixture. After 2−6 h of reaction time, additional diazomethane has been added to achieve quantitative esterification. Furthermore, some of the polymer samples are usually stored overnight in a fume hood in order to ensure that the decomposition of remaining diazomethane is completed before IR spectroscopy and/or titration were used to check for complete methylation. In general, acetic acid is added to all polymer samples that are not to be analyzed in this fashion in order to destroy the remaining diazomethane.

The molecular weight distribution of the polymer formed in PLP experiments and after methylation was analyzed by SEC. The SEC setup consists of a Waters 510 pump, Waters autosampler (WISP 712), four columns PLgel MIXED-B (Polymer Laboratories), and a Waters 410 differential refractometer. For SEC analyses Tetrahydrofuran (THF) was used as eluent at 40 °C with a flow rate of 1 mL/min. Polymer concentrations of 1−3 mg/mL were analyzed. Narrow molecular weight standards of polystyrene (pS) and pMMA were used for SEC calibration. Mark−Houwink parameters[14] for pS ($K = 1.14 \times 10^{-4}$ dL/g, $\alpha = 0.716$) and pMA[23] ($K = 1.95 \times 10^{-4}$, $\alpha = 0.660$) were applied for the transformation of the molecular weight distribution (MWD) as pS into the MWD of pMA.

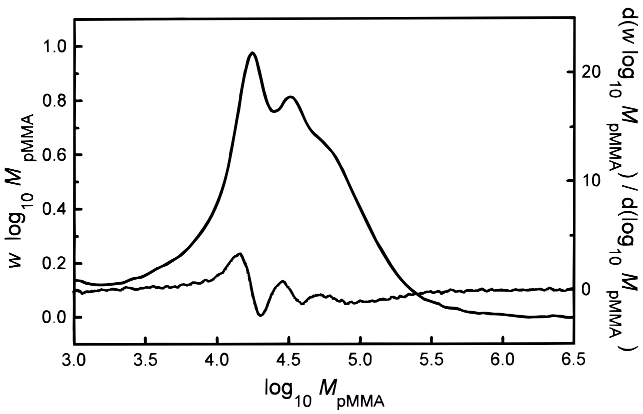

Figure 1. Molecular weight distribution (MWD) and corresponding derivative of polymer formed in a pulsed-laser polymerization of MAA in methanol at 60 °C after derivatization to pMMA. The laser pulse repetition rate is 20 Hz, the initiator concentration is 1.0 mmol/kg, the laser pulse energy is 55 mJ, and the average monomer concentration in methanol is 2.80 mol/L.

Results and Discussion

The Dependence of k_p on Temperature and Solvent in Methacrylic Acid Polymerizations. To check the reliability of k_p data obtained according to our methylation procedure k_p values of MAA in methanol (30 wt %) were determined at different temperatures and compared with literature data obtained by Beuermann et al.[3]

Figure 1 shows the molecular weight distribution (MWD) of MAA polymerized in methanol (30 wt %) at 60 °C after derivatization to pMMA. The laser was operating at a pulse repetition rate of 20 Hz. Inflection points occurring in the molecular weight distribution are visualized as maxima in the derivative plots. For all temperatures well-defined primary, secondary, and even ternary inflection points are observed in MAA polymerizations performed in methanol. This observation clearly indicates that radicals newly formed in successive laser pulses terminate the propagating chain. The consistency check further indicates that reliable k_p data can be obtained from this experiments. The degree of polymerization at the inflection point, L_i, is calculated by dividing the molecular weight at the inflection point, depict from the molecular weight distribution, by the molecular weight of the pMMA calibration standard (100.12).

The comparison of our k_p data (full circles) with the data obtained by Beuermann et al.[3] (open circles) are plotted in Figure 2. The data are in good agreement and only minor deviations at the lowest temperature are observed, thus indicating that the methylation procedure followed in this work also yields reliable k_p data. The activation energies, E_a, and frequency factors, A, obtained by a linear Arrhenius fit of the individual data sets (full and dashed line in Figure 2) and the combined data set (not shown in Figure 2) are listed in Table 2. These data will be discussed later in detail.

The influence of temperature and solvent on k_p were further studied in polymerizations of MAA in water (15 wt %) at temperatures ranging from 18 to 90 °C and in DMSO (30 wt %) at temperatures ranging from 25 to 90 °C. DMSO was chosen because of it its polar aprotic solvent character and its high boiling point (188 °C).

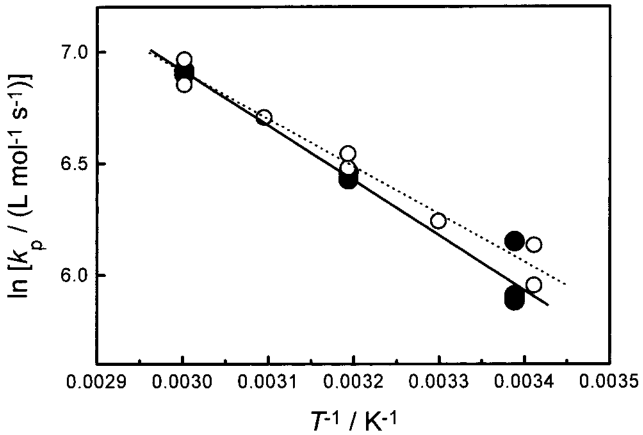

Figure 2. Arrhenius plot of the propagation rate coefficient k_p for MAA in methanol. Full circles and full line represent the data of this work; open circles and dashed line are independently measured data by Beuermann et al.[3] (see text).

Table 1. Experimental Results Obtained for the Temperature Dependence of k_p for Methacrylic Acid Polymerizations in Various Solvents

solvent	ϑ (°C)	ν (Hz)	[MAA] (mol/L)	monomer convn	L_1	L_2	L_3	k_p (L mol^{-1} s^{-1})
water	18	20	1.68	0.018	237	473	770	2824
water	18	20	1.66	0.030	245	470	734	2955
water	25	20	1.72	0.020	341	673		3961
water	25	20	1.72	0.020	340	647		3941
water	25	20	1.71	0.022	335	639		3922
water	30	20	1.65	0.032	308	593		3733
water	30	20	1.67	0.024	312	625		3737
water	40	20	1.66	0.022	393	754	1228	4739
water	40	20	1.65	0.028	410	785	1228	4970
water	50	20	1.66	0.015	467	900		5627
water	50	20	1.63	0.037	469	903		5755
water	60	20	1.65	0.016	587	1080		7096
water	60	20	1.63	0.038	587	1124	1832	7180
water	69	20	1.62	0.029	638	1230		7877
water	70	20	1.59	0.050	650	1252		8176
water	89	20	1.61	0.022	839	1680		10422
water	89	20	1.59	0.033	845	1692		10629
MeOH	22	10	2.92	0.010	105	213	352	361
MeOH	22	10	2.93	0.010	105	213	364	359
MeOH	22	20	2.93	0.010	69	130		469
MeOH	22	20	2.93	0.010	54	109		368
MeOH	40	20	2.87	0.014	89	180	288	619
MeOH	40	20	2.87	0.014	92	186		641
MeOH	60	20	2.80	0.016	141	286	525	1009
MeOH	60	20	2.80	0.016	139	285		993
DMSO	23	20	3.67	0.015	87	181	313	473
DMSO	25	20	3.60	0.034	111	219	337	619
DMSO	25	20	3.60	0.034	110	217	346	613
DMSO	39	20	3.54	0.037	170	323	513	960
DMSO	40	20	3.53	0.038	175	332	529	990
DMSO	50	20	3.48	0.043	217	397	655	1244
DMSO	50	20	3.48	0.043	217	412	655	1244
DMSO	60	20	3.43	0.048	281	534	790	1636
DMSO	60	20	3.50	0.048	227	491		1298
DMSO	60	20	3.55	0.028	229	459		1291
DMSO	61	20	3.41	0.055	277	527	808	1626
DMSO	71	20	3.50	0.021	332	679		1899
DMSO	71	20	3.42	0.048	338	641	1020	1976
DMSO	88	20	3.42	0.028	476	871	1434	2780
DMSO	90	20	3.41	0.030	449	853	1356	2632

Figure 3 shows molecular weight distributions of MAA polymerized at 18, 40, and 60 °C in water (15 wt %) after derivatization to pMMA. The laser was operating at a pulse repetition rate of 20 Hz with a laser pulse energy of 50 mJ. All molecular weight distributions show a distinct primary and secondary peak. With

Table 2. Activation Energies, E_a, and Frequency Factors, A, Obtained for Various Solvents from Linear Arrhenius Plots and NLLS Fitting

solvent	$10^{-6}A$ (L mol^{-1} s^{-1})	E_a (kJ/mol)	$10^{-6}A$ NLLS (L mol^{-1} s^{-1})	E_a NLLS (kJ/mol)	$10^{-6}A^{\text{lit.}}$ (L mol^{-1} s^{-1})	$E_a^{\text{lit.}}$ (kJ/mol)
water	1.72	15.3 ± 1.0	1.55	15.0	6.7	18.0 ± 0.4[8]
MeOH	1.63	20.5 ± 1.7	1.52	20.3	0.6	17.7 ± 1.1[3]
MeOH[a]	1.11	19.4 ± 1.1	1.02	19.2	0.6	17.7 ± 1.1[3]
DMSO	3.4	21.4 ± 1.0	2.49	20.5	4.1	30.5 ± 0.8[8]

[a] Data obtained by fitting the combined k_p data sets of Beuermann et al.[3] together with the data of this work (see Figure 2).

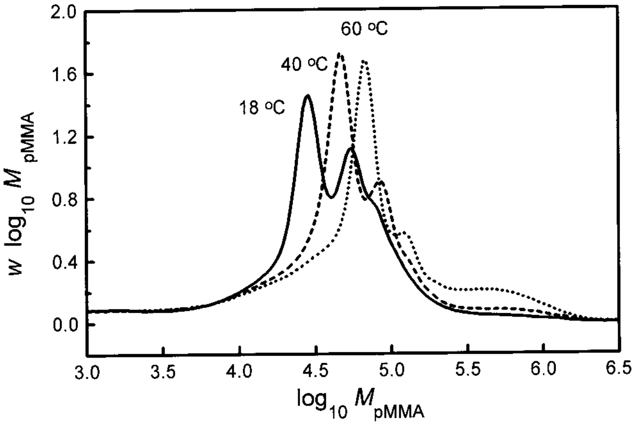

Figure 3. MWD of polymer samples prepared by PLP of MAA in water at different temperatures. Prior to molecular weight analysis by SEC, the polymer is derivatized to pMMA. The pulse repetition rate is 20 Hz, the photoinitiator concentration is 1 mmol/kg, and the laser pulse energy is 50 mJ.

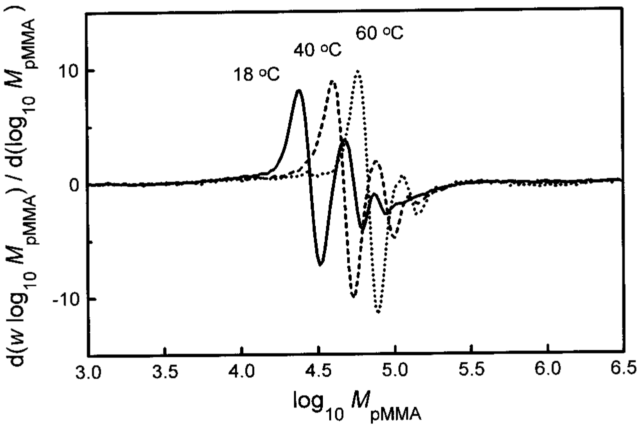

Figure 4. Derivatives of the MWDs shown in Figure 3. The points of inflection L_i can clearly be identified as maxima in the derivative of the MWD.

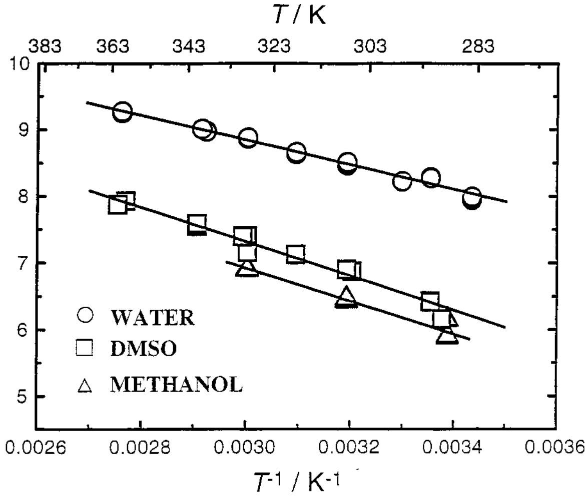

Figure 5. Values of the MAA propagation rate coefficient k_p from Table 1 in different solvents as a function of temperature. The solid lines represent the best individual Arrhenius fit to the points (see text). The corresponding frequency factors A and activation energies E_a are listed in Table 2.

increasing temperature peak positions are shifted toward higher molecular weight and the intensity of the secondary peak is decreased.

In Figure 4 the corresponding derivative plots of the molecular weight distributions (Figure 3) are presented. Again, inflection points occurring in the molecular weight distribution are visualized as maxima in the derivative plots. For all temperatures well-defined primary, secondary, and even ternary inflection points are observed in MAA polymerizations performed in water. This observation clearly indicates that the propagating chain is terminated by radicals newly formed in successive laser pulses, and reliable k_p data can be obtained from these experiments.

Table 1 contains the polymerization temperature ϑ, laser pulse repetition rate ν, arithmetic mean of the monomer concentration [M], and the monomer conversion over the course of the experiment. Although the degree of polymerization at the first, second and third inflection point is tabulated, only the intense first inflection point, L_1, has been used to calculate the propagation rate coefficient. The k_p data, calculated according to eq 1 for the various solvents, are given in the last column of Table 1.

The variation of k_p with temperature is illustrated in Figure 5 for various solvents used in this investigation.

The experimental k_p values of MAA polymerization in water (15 wt %) (open circles)

$$\ln k_p = (14.36 \pm 0.47) - (1839 \pm 145)\ \text{K}/T \quad (2)$$

DMSO (30 wt %) (open squares)

$$\ln k_p = (15.03 \pm 0.39) - (2575 \pm 127)\ \text{K}/T \quad (3)$$

and methanol (30 wt %) (open triangles)

$$\ln k_p = (14.31 \pm 0.65) - (2464 \pm 199)\ \text{K}/T \quad (4)$$

are adequately represented by the Arrhenius equations eqs 2, 3, and 4. By fitting the combined data sets (not shown in the Figures 2 and 5) of Beuermann et al.[3] and this work for MAA polymerizations in methanol, one obtains the following Arrhenius equation, eq 5. The

$$\ln k_p = (13.92 \pm 0.44) - (2334 \pm 138)\ \text{K}/T \quad (5)$$

corresponding (eqs 2–5) activation energies, E_a, frequency factors, A, and literature data are listed in Table 2.

It is apparent from Figure 5 that k_p data obtained in DMSO are slightly larger than the data obtained in methanol within the same temperature range. For

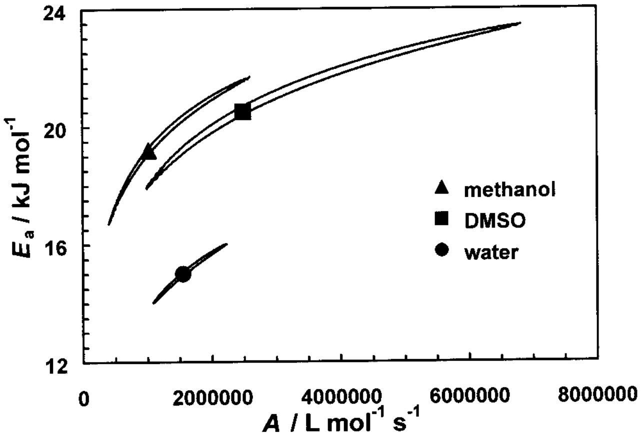

Figure 6. The 95% joint confidence ellipsoids for the frequency factors A and the activation energies E_a from weighted linear least-squares fitting (NLLS) of propagation rate coefficient data for MAA in methanol (30 wt %), DMSO (30 wt %), and water (15 wt %) (see text). The full triangle, square, and circle are the values with least residuals. The corresponding frequency factors A_{NLLS} and activation energies E_a^{NLLS} are listed in Table 2.

polymerizations of MAA in DMSO at 25 °C a 36% larger k_p is calculated from eq 5 compared to the value calculated in methanol by applying eq 4. This relative difference in k_p is slightly greater than the relative uncertainty of $\pm$25% assumed for the determination of k_p from PLP−SEC experiments in such a system. Thus, the increase in k_p is suggested to show evidence for a solvent effect by changing the solvent from methanol to DMSO. Furthermore, a substantial increase in k_p is observed by changing from an organic solvent to water. It is important to point out at this early stage of the discussion that the significant difference between k_p data obtained in water and in organic solvents is *not* due to the fact that slightly different monomer concentrations have been applied in order to determine k_p as a function of temperature.

To support the evidence of the solvent effect that occurs in polymerizations of MAA in various solvents a more sophisticated data analysis has been performed on the k_p data obtained (see Tables 1 and 2). It recently has been pointed out that data can be analyzed by nonlinear fitting to the Arrhenius equation itself. A good method for carrying out such fitting is the weighted nonlinear least-squares fitting (NLLS) method.[15] NLLS fits on the data listed in Table 1 are therefore performed. An absolute uncertainty of $\pm$ 0.5 K in temperature and a relative uncertainty of $\pm$ 25% for the determination of a k_p value is assumed for all k_p data. It turned out that the error in temperature can be neglected compared to the overall error assumed for the individual k_p determination.

The 95% joint confidence interval[15] is given in Figure 6 for the data obtained in methanol, DMSO and water. It is stressed that values of activation energy, A_{NLLS}, and frequency factor, E_a^{NLLS}, listed in Table 2 are highly correlated. Therefore, it is incorrect to assign individual uncertainties to these parameter values as would be common for an individual linear Arrhenius fit of the k_p data.

Figure 6 exhibits the 95% joint confidence ellipsoids for the frequency factors, A_{NLLS}, and the activation energies, E_a^{NLLS}, from NLLS fitting of propagation rate coefficient data for MAA in methanol (30 wt %), DMSO (30 wt %), and water (15 wt %). The 95% joint confidence ellipsoids for MAA polymerizations in methanol and DMSO are clearly separated, indicating differences in the data. The authors suggest that these observed differences in the k_p data are due to slightly different interactions of the acid with the solvent.

The comparison of activation energies, E_a, and frequency factors, A, calculated from linear Arrhenius plots on k_p data obtained in organic solvents and water (see Table 2) is indicating that the activation energies show only minor differences in the organic solvents. These differences seem to be well within the experimental uncertainties. In water the activation energy for the propagation reaction is 4−6 kJ/mol less than in the organic solvents used. Furthermore, a two times larger frequency factor is calculated from the k_p data obtained in DMSO whereas in methanol it is slightly smaller than the value obtained in water. The same tendencies are also qualitatively reflected in the Arrhenius parameters calculated by applying the NLLS fitting procedure to the experimental k_p data obtained in the various solvents (see Table 1).

The drop in activation energy for MAA polymerizations observed by changing the solvent from organic to water is believed to be due to the well-known tendency of carboxylic acids to exhibit associated structure forming oligomeric associates and monomer−solvent association complexes. This last association is particular pronounced in water.

MAA is forming self-associates in bulk (cyclic dimers). In solvents such as methanol and DMSO the self-association of the acid has to compete with the formation of monomer−solvent complexes. MAA is always self-associated to some extent in methanol and DMSO but to a larger extent compared with the self-association in water.[8] This more pronounced self-association in methanol and DMSO should result in increased activation energies for propagation and thus a reduced rate coefficient of this reaction compared with the reaction in water.[9] Both dependencies of the kinetic parameters are indeed observed in the present investigation. This observation can be explained as follows: As “individual” monomers take part in the propagation reaction, additional energy is needed for the breaking of the intramolecular hydrogen bonds of the self-associate. Thus, the activation energy of propagation is increased and consequently the activation energy in water where the degree of self-association is less pronounced must have its least value.

The observed increase in frequency factor A by changing the solvent from methanol to DMSO can be explained by a mass effect originated from complex formation with the solvent.[16] It seems to be reasonable to assume that the predominant factor responsible for the observed differences in frequency factor observed in DMSO thus can be attributed to monomer−solvent complex formation.

Influence of Monomer Concentration on k_p in Aqueous Phase Polymerization. Beuermann et al.[3] showed, in a recent publication, that k_p of MAA in methanol is invariant with monomer concentration. Furthermore, these authors determined the average bulk value of the propagation rate coefficient at 60 °C to be 1179 L mol^{-1} s^{-1}. Within the present work it should be investigated whether the observation of a concentration independent k_p value also holds for MAA polymerizations in water where less self-association is observed.

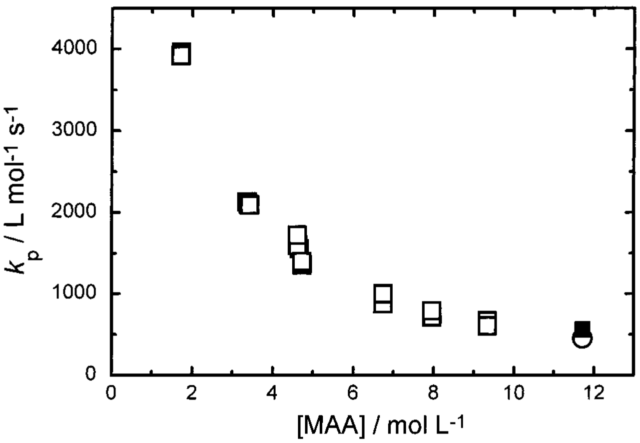

Figure 7. Propagation rate coefficient of MAA in water at 25 °C determined at various monomer concentrations. The full square represents the calculated bulk value and the open circle the calculated literature value (see text).

Table 3. Experimental Results Obtained at 25 °C for Methacrylic Acid Polymerizations in Water at Different Monomer Concentrations

[MAA] (mol/L)	ν (Hz)	L_1	k_p (L mol^{-1} s^{-1})	[MAA] (mol/L)	ν (Hz)	L_1	k_p (L mol^{-1} s^{-1})
1.71	20	335	3922	4.73	20	320	1353
1.72	20	340	3941	6.74	20	296	878
1.72	20	341	3961	6.74	30	224	999
3.36	20	358	2127	7.95	30	209	790
3.39	20	356	2099	7.96	20	284	714
3.42	20	358	2092	9.34	30	208	667
4.61	40	198	1722	9.34	20	283	605
4.62	20	367	1589	11.72			*455* (calcd)[3]
4.66	20	362	1555	11.72			*605* (calcd)[a]
4.72	30	219	1392				

[a] This work.

Figure 7 shows the propagation rate coefficient of MAA for polymerizations in water at various monomer concentrations. The full square represents a bulk value that has been calculated from a nonlinear fit of the experimental data. The open circle represents the bulk value calculated with $k_p = 1179$ L mol^{-1} s^{-1} at 60 °C assuming an activation energy[3] of 18 kJ mol^{-1}.

It is apparent from Figure 7 that k_p values of MAA polymerizations in water are decreasing with increasing monomer concentration. Starting at bulk conditions the addition of water to the reaction system yields only minor changes in k_p up to ~8 mol/L. On further dilution the k_p values are increasing. Table 3 contains the arithmetic mean of the monomer concentration [M], laser pulse repetition rate ν, the first inflection point, L_1, and the corresponding k_p values calculated from eq 1. The overall monomer conversion in the individual experiments has been kept below 5%.

On higher dilution an increase of polymerization rate has been observed that is interpreted as an indication for a higher propagation-to-termination ratio.[8] The present data on individual propagation rate coefficients support this interpretation, pointing at an increase in polymerization rate caused by an increase in k_p.

The origin of the increased k_p values at lowest monomer concentration is not easily interpreted on the basis of the well-known features of MAA polymerization rate depending on degree of self-association. From MAA pulsed laser polymerizations in methanol,[3] it is known that k_p is invariant with monomer concentration. Thus, additional effects are suggested to contribute to the enhanced k_p values determined in the present investigation using different acid concentrations in water. It should be addressed that Kamachi[17] discusses arguments for solvent effects on propagation rate coefficients in free-radical polymerizations due to polarity of the propagating radical, transfer reactions, interaction between monomer–solvent and polymer–solvent, and formation of complexes between the propagating radical and the solvent. Most of these issues are already tackled within the existing literature on carboxylic acid polymerization in various reaction media. Nevertheless the present work exhibits that there is still a lack of complete understanding of the solvent effect in free-radical polymerizations, especially in water. Furthermore, the interpretation of solvent effects on activation parameters is not straightforward and more considerations have to be taken into account to do so.

Table 4. Experimental Results Obtained for the Dependence of k_p^{apparent} on Pulse Repetition Rate (ν), Solvent, and Monomer Concentration for Acrylic Acid Polymerizations

solvent	T (°C)	ν (Hz)	[AA] (mol/L)	monomer convn	L_1	L_2	k_p^{apparent} (L mol^{-1} s^{-1})
water	20	20	0.90	0.040	1393		30956
water	20	20	0.90	0.040	1475		32778
water	20	20	0.86	0.079	1515		35233
water	20	20	0.90	0.040	1506		33467
water	20	20	0.83	0.114	1581		38096
water	20	50	0.89	0.050	841		47247
water	20	50	0.85	0.092	914		53765
water	20	50	0.83	0.114	988		59518
water	20	50	0.88	0.060	1061		60284
water	20	50	0.85	0.090	937		55118
water	25	50	0.93	0.111	762		40968
water	25	50	0.95	0.095	760		40000
water	25	60	0.93	0.110	733		47290
water	25	60	0.93	0.110	737		47548
water	25	70	0.93	0.108	733		55172
water	25	70	0.91	0.129	680		52308
water	25	80	0.93	0.115	684		58839
water	25	80	0.90	0.136	741		65867
water	25	90	0.91	0.128	703		69527
water	25	90	0.91	0.128	676		66857
water	25	90	1.37	0.060	723	1537	47496
water	25	90	1.32	0.094	915	1721	62386
water	25	90	1.33	0.090	912	1778	61714
water	25	100	1.36	0.068	717	1531	52721
water	25	100	1.34	0.088	849	1659	63358
water	25	100	1.35	0.074	862	1647	63852
water	20	100	0.88	0.060	807	1648	91705
water	20	100	0.85	0.092	784	1660	92235
water	20	100	0.83	0.114	785	1559	94578
water	25	100	0.89	0.050	716	1594	80449
water	25	100	0.91	0.129	709	1546	77912
MeOH	25	100	1.24	0.065	179	333	14400
MeOH	25	100	1.34	0.031	158	324	11791
MeOH	25	100	1.97	0.025	276		14010
MeOH	25	100	1.98	0.022	259		13081
acetic acid	25	100	1.82	0.008	333	604	18130
acetic acid	25	100	1.83	0.006	334	657	18251

Influence of Pulse Repetition Rate in Acrylic Acid Polymerizations. Pulsed laser-induced polymerizations of AA in water (7 wt %) have been performed at different pulse repetition rates between 20 and 100 Hz in order to determine k_p data. The corresponding values are listed in Table 4. Figure 8 shows the molecular weight distribution of poly(acrylic acid) (after derivatization to pMA) polymerized in water (7 wt %) at 20 °C, operating the laser with a pulse repetition rate of 100 Hz. To determine k_p from the degree of polym-

Table 5. Table of Density Data Obtained from the DSM Solvent and Monomer Data Base

T (°C)	ρ(AA) (g cm^{-3})	ρ(MAA (g cm^{-3})	ρ(water) (g cm^{-3})	ρ(CH$_3$OH) (g cm^{-3})	ρ(acetic acid) (g cm^{-3})	ρ(DMSO) (g cm^{-3})
0	1.0731	1.0288	1.0002	0.8100		
10	1.0622	1.0222	1.0003	0.8008		
20	1.0511	1.0140	1.0018	0.7915	1.0491	1.0992
30	1.0399	1.0048	1.0044	0.7825	1.0392	1.0900
40	1.0286	0.9951	1.0078	0.7740	1.0284	1.0809
50	1.0171	0.9857	1.0121	0.7650	1.0175	1.0720
60	1.0055	0.9770	1.0171	0.7555	1.006	1.0632
70	0.9938	0.9697	1.0227		0.9948	1.0546
80	0.9819	0.9644	1.0290		0.9835	1.0461
90	0.9698	0.9617	1.0359		0.9718	1.0377
100	0.9575	0.9622	1.0434		0.9599	1.0295

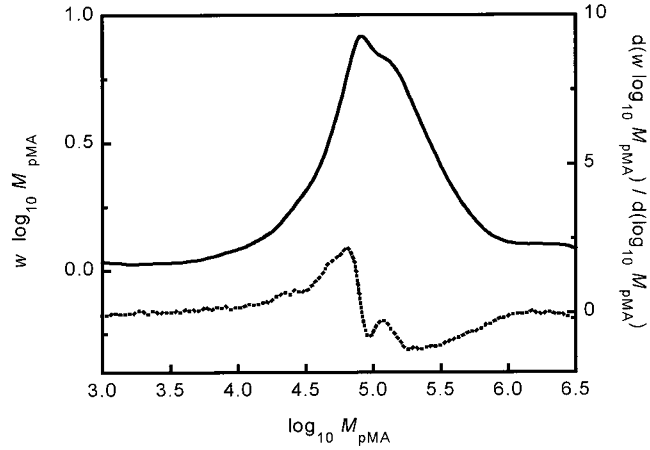

Figure 8. MWD and corresponding derivative plot of polymer formed in a pulsed-laser polymerization of AA in water at 20 °C after derivatization to pMA. The laser pulse repetition rate is 100 Hz, the initiator concentration is 1.0 mmol/kg, the laser pulse energy is 55 mJ, and the average monomer concentration in water is 0.88 mol/L.

erization, the molecular weight distribution measured on the basis of pS was transformed by applying Mark–Houwink parameters[14] into the molecular weight distribution of pMA. A shoulder observed at the high molecular weight side of the distribution indicates that in this case free radical termination is controlled by the successive laser pulses. Under these experimental conditions, the consistency criteria[1] of the IUPAC working party are fulfilled for the reliable determination of k_p data. Only the experiments with a high pulse repetition rate (>90 Hz) fulfill these criteria. Nevertheless, we feel that it is appropriate to consider the obtained k_p values of AA being apparent k_p values as long as the sources of the problems are not clear. At pulse repetition rates lower than 90 Hz, a featureless molecular weight distribution without any distinct higher order peak is obtained at ambient temperature; thus, such a molecular weight distribution is not suitable to determine reliable k_p data because termination due to successive laser pulses is not the main chain-stopping event. In this case, values calculated according to eq 1 yield only apparent k_p values due to the fact that the consistency criteria are not fulfilled.

A closer look on the entities in Table 4 shows that k_p values for AA obtained from polymerizations in water exhibit an decrease in k_p with increasing monomer concentration by changing the acid concentration from 0.9 to 1.35 mol/L. The same effect has been observed in MAA polymerizations in water.

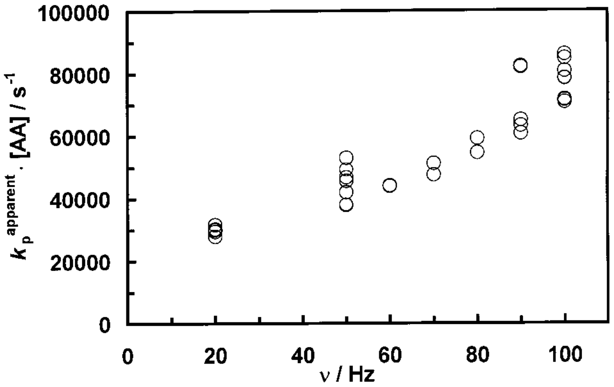

Figure 9. k_p^{apparent}[AA] data determined from pulsed-laser polymerization of AA in water (7 wt %) as a function of laser pulse repetition rate ν.

In Figure 9 the product of an apparent k_p (k_p^{apparent}) times [AA] is plotted vs the pulse repetition rate ν in order to visualize the problem of choosing appropriate pulse repetition rates to get a distinguished PLP structure in the resulting molecular weight distribution. Up to pulse repetition rates of 90 Hz, no PLP structure has been observed, and the molecular weight distributions are not affected by applying different pulse repetition rates.

By increasing the pulse repetition rate to 90 or 100 Hz, one is able to determine a second overtone inflection point. The molecular weight distribution is also shifted toward lower molecular weights according to the factor of 0.9 that is due to the differences in pulse repetition rate. This external check gives a further indication that the molecular weight distributions obtained from such PLP experiments determined at pulse repetition rates of at least 90 Hz (and higher) are suitable for reliable k_p determination.

Thus, PLP experiments have been performed under such optimized experimental conditions at 25 °C to determine k_p^{apparent} of AA in acetic acid (13 wt %) and methanol (13 wt %). Acetic acid was chosen because of its acidic potential (pk_a = 4.76) which is comparable to that of AA (pK_a = 4.20) and the low dielectric constant (DC = 6) compared to water (DC = 78) and methanol (DC = 33). A pulse repetition rate of 100 Hz was applied to ensure that a distinct molecular weight distribution is generated in the experiments that fulfill all criteria to ascertain a reliable k_p determination. From the molecular weight distribution in Figure 10, k_p can be calculated to be 18130 L mol^{-1} s^{-1} in acetic acid.

From the molecular weight distribution of the polymer formed in a pulsed-laser polymerization of AA in methanol at 25 °C and its corresponding derivative plot (both not shown here) k_p^{apparent} is calculated to be 14400 L mol^{-1} s^{-1} (average monomer concentration of AA in methanol of 1.24 mol/L).

As a consequence of the limited amount of data, the deviation between both values is suggested to be due to experimental uncertainties rather than to a solvent effect.

It should be noted that a laser operating at laser pulse repetition rates much higher than 100 Hz is recommended to determine k_p data of AA over an extended temperature range, especially up to higher temperatures which are of technical importance.

The PLP experiments of acrylic acid show similar problems as the acrylates in general.[2,10,18] For the

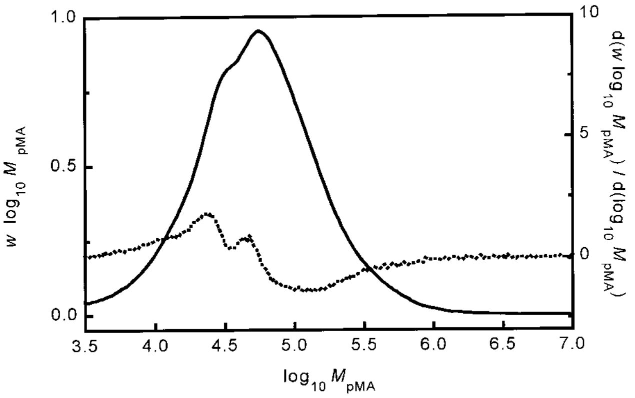

Figure 10. MWD and corresponding derivative plot of polymer formed in a pulsed-laser polymerization of AA in acetic acid at 25 °C after derivatization to pMA. The laser pulse repetition rate is 100 Hz, the initiator concentration is 1.0 mmol/kg, the laser pulse energy is 55 mJ, and the average monomer concentration in water is 1.82 mol/L.

acrylates the authors see a strong frequency dependence, broad molecular weight distributions and nonlinear Arrhenius plots. Only at relatively low temperatures and high frequencies can the typical PLP features be found. Speculations about the origin of these problems include transfer to monomer[19] and transfer to polymer.[20] In a forthcoming publication,[21] an extensive study on methyl acrylate and butyl acrylate is reported which shows that initiator concentration and the laser pulse energy also affect the molecular weight distribution. Besides the presence of transfer to monomer, recently extensive transfer to polymer for the acrylates has been reported.[20] At low conversions and high monomer concentrations the main cause of branching is intramolecular transfer to polymer and proton abstraction by initiator-derived radicals (which explains the laser energy and initiator concentration dependence). If the monomer is diluted with solvent, the intramolecular transfer process will be enhanced;[20] it was observed that PLP features completely disappeared when diluting the monomer[21] with several solvents. Transfer to polymer will have two effects on the molecular weight distribution.

(i) A growing polymer chain will be terminated and a dead chain will be reinitiated with a net broadening of the molecular weight distribution. Because branched polymer chains are more compact than linear chains, the branching will also give an apparent shift to lower molecular weights and thus lower k_p values. After transfer to polymer, there is also a chance of β-scission which would further decrease the value of the apparent k_p.

(ii) A second and even larger effect will be the slow reinitiation constant of the transfer-derived polymeric radical; the radical has changed from a very reactive secondary radical to a very nonreactive tertiary radical (e.g., compare the decrease of reactivity of 3 orders of magnitude in going from acrylates to alkacrylates). Although the number of branch points in the polymer will probably be no more than 1%, this still could have a distinct effect on the resulting propagation rate coefficient.

The ratio of polymeric radicals vs reactive radicals can be much higher than 1%. The situation is comparable to a copolymerization of an acrylate with styrene, already a few percent of styrene will decrease the overall k_p tremendously.[10] A similar explanation needed to be invoked to explain the kinetics and gel content of butyl acrylate emulsion polymerization.[22]

Conclusions

By application of the PLP–SEC technique, the problem of determining reliable kinetic parameter for free-radical propagation of AA and MAA in organic solvents and water is attacked. The problem of molecular weight determination of carboxylic polymer formed in the experiments is solved by esterification. Because of this procedure calibration by pMMA standards is possible which yield k_p data of high accuracy for MAA. Unfortunately the determination of pMA molecular weight distribution is not straightforward and Mark–Houwink[14] constants from literature needed to be applied. Several conclusions can be drawn from the present investigation: (i) For MAA a minor but not negligible variation of k_p with organic solvent has been found. (ii) The experimental observation that k_p values for MAA and AA are decreasing with increasing monomer concentration is not easily understood and has to be further investigated. (iii) For AA, it should be stressed that high laser pulse repetition rates, such as at least 100 Hz, are necessary for reliable k_p determination.

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(23) In the original paper a typing error occurred for the Mark–Houwink parameters of PMA; the correct numbers are used here.

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