Propagation Kinetics of Methacrylic Acid Studied by Pulsed-Laser Polymerization

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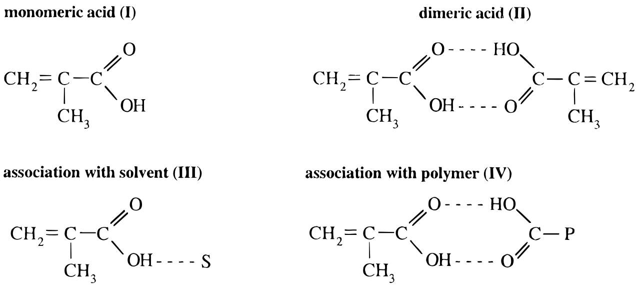
ABSTRACT: Propagation rate coefficients k_p have been determined for free radical polymerizations of methacrylic acid (MAA) using pulsed-laser polymerizations (PLP) combined with size exclusion chromatography (SEC). The temperature dependence of k_p has been studied for polymerizations of 33 vol % monomer in methanol in the temperature range from 20 to 60 °C. k_p is described by the following Arrhenius relation: $\ln[k_p/\mathrm{L{\cdot}mol^{-1}{\cdot}s^{-1}}] = (13.31 \pm 0.49) - (2132 \pm 133)K/T$. Variations in MAA concentration and the type of solvent do not influence k_p significantly. Any distinctions elicited in k_p by these variations are of the order of the experimental uncertainty and are much smaller than the relative changes in the MAA monomer−dimer equilibrium observed by FTIR spectroscopy. The magnitude of k_p and its variation with temperature are similar to results reported for methyl methacrylate and the rest of the methacrylate family.

Introduction

Pulsed-laser polymerizations (PLP) in combination with analysis of the corresponding molecular weight distributions (MWD) have been successfully applied to measure free radical rate coefficients for a number of different monomer systems, such as styrene,[1] acrylates,[2,3] methacrylates,[4,5] and vinyl acetate.[4] This technique reliably and directly provides individual propagation rate coefficients, k_p. So far, no PLP-generated data are reported on polar monomers like acrylic or methacrylic acid, although polymerizations and especially copolymerizations of these monomers have been the subject of numerous studies.[6−8] Generally, in these previous works, overall polymerization rates or copolymerization parameters have been determined and found to be greatly influenced by the choice of solvent. These apparent solvent effects may be explained by complexation arguments since, depending on the solvent, an acid molecule can exist in four different forms:[6] as a monomer, as a dimer, associated with a solvent molecule, or associated with the carboxylic group of a growing polymer chain. Chart 1 shows these four different forms for MAA. The apparent form of the acid depends on the nature of the solvent and its ability to complex the acid by formation of H-bonds to the carboxylic group. The exact nature of solvent effects in past MAA studies is difficult to identify, however, since the system often becomes multiphase during polymerization. Information on individual rate coefficients will improve the understanding of the complex behavior of this monomer.

Chart 1


monomeric acid (I)
dimeric acid (II)
association with solvent (III)
association with polymer (IV)

The propagation reaction involves two species, a monomer molecule and a radical. The propagation rate coefficient, therefore, depends on the stability and reactivity of both of these species, which are influenced by their tendency to associate. Plochocka[7] reports that the dimeric form of MAA is more reactive than the monomeric one. Generally, the reactivity of the different forms of methacrylic acid decreases in the following order:[7]

$$(\mathrm{acid})_2 > \mathrm{acid{\cdot}solvent} \sim \mathrm{acid}$$

The changes in reactivity of different forms of the acid suggest that k_p values for polymerizations in solvents which favor MAA dimerization should be higher than in polar solvents which support the formation of monomer−solvent complexes. This effect can best be studied by direct measurement of k_p in various solvents, now possible by the pulsed-laser technique.

The PLP/MWD technique involves the irradiation of a monomer sample containing a photoinitiator by repeated laser pulses. The number of growth steps DP_0 in the time interval t_0 between two successive laser pulses is given by the following equation

$$\mathrm{DP}_0 = k_p[M]t_0 \qquad (1)$$

with the monomer concentration [M]. Olaj and coworkers[9,10] have shown that DP_0 is best represented by the inflection point on the low molecular weight side of the MWD. The PLP/MWD method is recommended as the method of choice for the evaluation of k_p by the IUPAC working party on “modeling of kinetics and processes of polymerization”.[1] It has been applied to bulk, solution, and microemulsion polymerizations of various monomers. The majority of solvents examined has no effect on k_p, although it has been reported recently that benzyl alcohol has a significant effect on styrene and MMA k_p values.[11]

The aim of this work is to expand the use of the PLP/MWD technique to MAA as a new monomer system, and to obtain individual propagation rate coefficients. Be-

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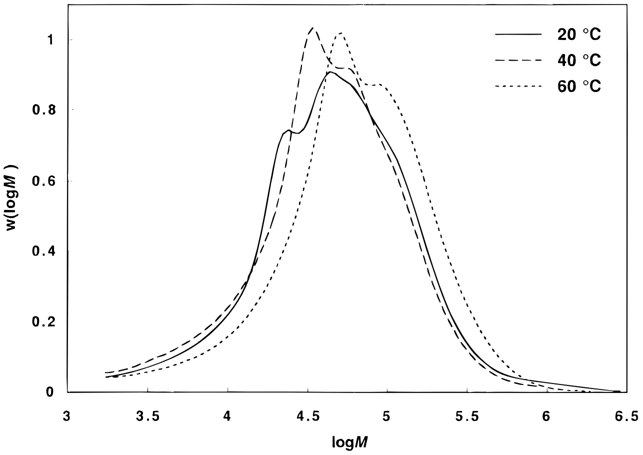

Figure 1. Molecular weight distributions for polymer samples generated by pulsed-laser polymerization after derivatization to pMMA. The laser pulse repetition rate is 10 Hz, initiator concentration 5 mmol/L, laser pulse energy 16 mJ, and MAA monomer concentration 33 vol % in methanol.

cause of the dimerization equilibrium, it is of special interest to study solvent effects on the propagation rate, such as variation of monomer concentration or type of solvent. FTIR spectroscopy is also used to qualitatively examine monomer–solvent interactions. It has proven to be a valuable tool for studying the monomer–dimer equilibrium for methacrylic acid,[12] since distinct peaks assigned to monomeric and dimeric species are well separated in the spectral range of the C=O– stretching fundamental.

Experimental Section

The experimental pulsed-laser setup has been described previously.[4] A Quanta-Ray Nd:YAG GCR-190-100 laser with a harmonic generator is operated at a wavelength of 355 nm. In this study a laser pulse repetition rate of 10 Hz, resulting in laser pulse energies of 20–50 mJ, was chosen. The monomer (Aldrich), the photoinitiator benzoin (Aldrich), and the solvents (methanol, 2-propanol, tetrahydrofuran (THF), toluene, and acetic acid, all from Aldrich) were used as received. Polymerizations are carried out in a temperature range from 20 to 60 °C with initiator concentrations between 2 and 5 mmol/L. In most cases the reaction mixture turned milky during the course of the reaction, indicating that polymer has precipitated. Small amounts of *p*-methoxyphenol (Kodak) were added to the reaction mixture after irradiation to prevent further polymerization.

The MWDs were obtained by size exclusion chromatography. The SEC instrument consists of a Waters pump (Model 590), Waters autosampler (WISP 712), two SHODEX columns (KF80M), and a Waters differential refractometer (Model 410). Prior to SEC analyses, the polymer was isolated by evaporation of residual monomer and solvent and derivatized to poly(methyl methacrylate); IR spectroscopy was used to check for complete methylation. Because of the need for greater amounts of polymer for the methylation reaction, up to three samples prepared under identical conditions were combined. The SEC analyses are performed at 30 °C on solutions of pMMA in THF, with polymer concentrations of 1–3 mg/mL. Calibration is based upon a calibration curve obtained from narrow polydispersity pMMA standards. Inflection points are obtained from the w(log *M*) distribution. [M] is calculated according to the volume of acid added to the solvent, assuming ideal mixing. The densities for MAA and the solvents at the polymerization temperature are taken from the DIPPR database.[13]

FTIR spectra were recorded at room temperature on a Bruker IFS 88 spectrometer using a globar source, a silicon-coated CaF_2 beam splitter, and a DTGS detector. Film spectra were obtained in order to stay within the linear operating regime of the detector.

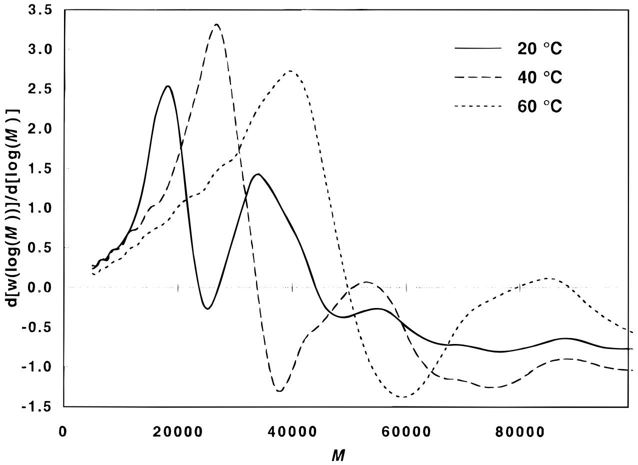

Figure 2. Derivative curves for MWDs shown in Figure 1.

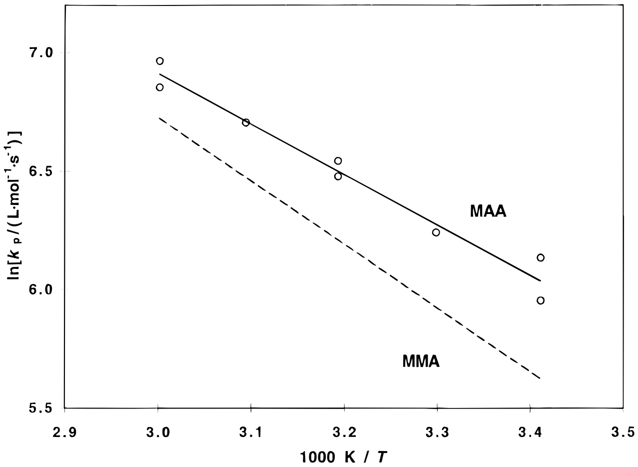

Figure 3. Arrhenius diagram for MAA. k_p obtained for polymerizations in methanol at a laser pulse repetition rate of 10 Hz. Monomer concentration: 33 vol %. The dashed line represents the temperature variation of k_p for bulk methyl methacrylate (MMA) polymerizations.[5]

Results and Discussion

Temperature Dependence of k_p. To study the temperature dependence of k_p, polymerizations of 33 vol % MAA in methanol were performed from 20 to 60 °C. Figure 1 depicts MWDs for 20, 40, and 60 °C. All MWDs show a distinct primary and secondary peak. The MWDs are shifted to higher molecular weights with temperature, and the intensity of the primary peak increases. The corresponding derivative plots are given in Figure 2. For all temperatures sharp, well-defined primary inflection points and secondary inflection points at twice the molecular weight are observable. Inflection points are indicated by the maxima in the derivative curves. These values are divided by 100 (molecular weight of pMMA) to obtain DP_0. The variation of the obtained k_p values with temperature is presented in Figure 3. All experimental data are listed in Table 1. They are nicely described by the following Arrhenius equation:

$$\ln[k_p/\mathrm{L\cdot mol^{-1}\cdot s^{-1}}] = (13.31 \pm 0.49) - (2132 \pm 133)K/T \quad (2)$$

resulting in a frequency factor *A* of 0.60×10^6 L·mol^{-1}·s^{-1} and an activation energy E_A of 17.7 kJ/mol. This activation energy is slightly smaller than the values reported for a number of methacrylates (methyl meth-

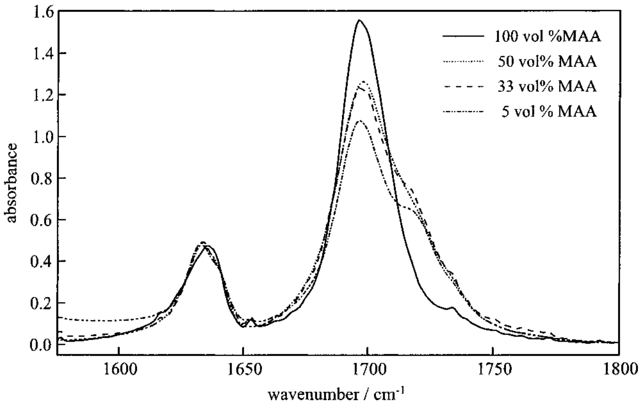

Figure 4. Absorbance spectra for MAA in methanol in the C=C− and C=O− stretching fundamental regions at room temperature.

Table 1. Experimental Results Obtained for the Temperature Dependence of k_p for Polymerizations at a Laser Pulse Repetition Rate of 10 Hz

T (°C)	vol % MAA	solvent	[MAA] (mol/L)	k_p ($L\cdot mol^{-1}\cdot s^{-1}$)
20	33	MeOH	3.93	385
20	33	MeOH	3.93	461
30	33	MeOH	3.88	513
40	33	MeOH	3.84	651
40	33	MeOH	3.84	695
50	33	MeOH	3.79	817
60	33	MeOH	3.74	1059
60	33	MeOH	3.75	947

acrylate (MMA) to dodecyl methacrylate),[4] which cover a range from 21 to 23 kJ/mol. Comparison with the k_p value for MMA at 60 °C as recommended by the IUPAC working party[5] shows that k_p for the acid is of the same order as for the corresponding methyl ester: 830 $L\cdot mol^{-1}\cdot s^{-1}$ for MMA and 1003 $L\cdot mol^{-1}\cdot s^{-1}$ for methacrylic acid, calculated according to eq 2.

Influence of Monomer Concentration. FTIR spectra of pure MAA and of MAA concentrations of 10, 33, and 50 vol % in methanol were recorded at room temperature. The spectra are shown in Figure 4 in the spectral range of the C=C− and C=O− stretching fundamentals. The absorbance from 1600 to 1650 cm^{-1} is assigned to the C=C olefin stretching vibration, which is not significantly influenced by the monomer concentration. The peaks in the spectral range from 1650 to 1750 cm^{-1} are due to the carbonyl vibration. All spectra are baseline corrected in the range from 1825 to 1850 cm^{-1}, where no absorbances occur, and are normalized to comparable peak intensities of the C=C vibration around 1634 cm^{-1}. This peak shows only very little variation in shape and position with acid concentration. The intense absorbances in the region of the C=O stretching vibration show some trends: For the pure acid a single peak is obtained. With increasing MeOH concentration a shoulder at a higher wavenumber occurs. This shoulder is best developed for the smallest MAA concentration. According to the literature the peak at 1696 cm^{-1} is assigned to the vibrations of dimeric acid molecules and the higher wavenumbers are related to monomeric acid molecules. Bouderska and Todorova[6] report an increase in the carbonyl stretching vibration of 31 cm^{-1} when the solvent changes from chloroform to acetonitrile. Supported by NMR data, they assign this change to the presence of dimeric acid molecules in chloroform and monomeric acid molecules in acetonitrile. The spectra in Figure 4 indicate the presence of mainly dimeric acid molecules in MeOH for all concentrations. But the significant decrease in absorbance of the peak at 1696 cm^{-1} and the appearance of a shoulder at higher wavenumbers qualitatively indicate the presence of higher monomeric acid concentrations with increasing MeOH concentration. These qualitative results should still hold at polymerization conditions, which are only 40 °C higher than the temperatures at which spectra were recorded.

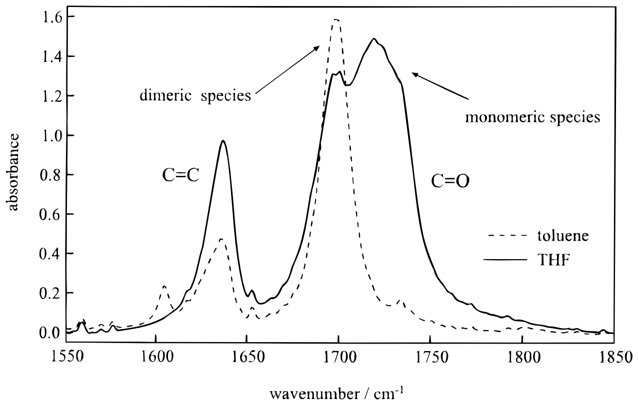

Figure 5. Absorbance spectra for MAA in THF and toluene in the C=C− and C=O− stretching fundamental regions at room temperature. Film spectra were recorded for MAA concentrations of 33 vol % in the solvents.

Table 2. Experimental Results Obtained for Polymerizations at 60 °C, a Laser Pulse Repetition Rate of 10 Hz and Various Monomer Concentrations in Methanol

T (°C)	vol % MAA	solvent	[MAA] (mol/L)	k_p ($L\cdot mol^{-1}\cdot s^{-1}$)
60	33	MeOH	3.75	947
60	33	MeOH	3.74	1059
60	50	MeOH	5.63	1037
60	50	MeOH	5.63	1111
60	50	MeOH	5.63	980
60	50	MeOH	5.63	1022
60	50	MeOH	5.63	955
60	100		11.35	1190
60	100		11.35	1167

In order to study whether these variations influence k_p, polymerizations at 60 °C in methanol were performed with varying amounts of monomer (33−100 vol %). The experimental conditions and k_p values are summarized in Table 2. There is, perhaps, a weak trend in k_p to increase as the monomer concentration rises; however, it is not significant beyond the experimental scatter in these determinations. An average value of (1052 ± 100) $L\cdot mol^{-1}\cdot s^{-1}$ is obtained for all polymerizations in methanol and in bulk. The small variations in fractions of monomeric and dimeric acid observed by FTIR at the different monomer concentrations do not result in substantial variations in k_p.

Influence of Different Solvents on k_p. In order to demonstrate the large influence of solvent on the dimerization equilibrium, Figure 5 shows FTIR spectra of 33 vol % MAA in THF and in toluene. These two solvents are of special interest since their interactions with MAA are completely different: THF has the ability to form H-bonds with the acid molecule, whereas toluene does not. Thus, in toluene, only self-association of the acid and association with propagating chains is possible, while solvent−monomer complexes can compete with self-association in hydrogen-bonding solvents like THF, methanol, 2-propanol, and acetic acid. The spectra in

Table 3. Experimental Results Obtained for Polymerizations at 60 °C and a Laser Pulse Repetition Rate of 10 Hz in Various Solvents

T (°C)	vol % MAA	solvent	[MAA] (mol/L)	k_p (L·mol^{-1}·s^{-1})
60	33	MeOH	3.75	1059
60	33	MeOH	3.74	947
60	33	THF	3.75	880
60	33	THF	3.75	844
60	33	acetic acid	3.77	1023
60	33	acetic acid	3.77	1057
60	33	2-propanol	3.75	981
60	33	2-propanol	3.75	973
60	33	toluene	3.77	1187
60	33	toluene	3.77	1264

Figure 5 reflect this difference: In THF mainly monomeric species (monomer−solvent complexes) are observed, indicated by the large peak around 1718 cm^{-1}. Only a small fraction of the acid undergoes dimerization, indicated by the absorbance around 1696 cm^{-1}. Conversely, the spectrum in toluene shows almost no monomeric species and is dominated by the absorbance of the dimeric species. This spectrum is nearly identical with the spectrum of pure MAA. The other solvents examined had spectra intermediate to the THF and toluene extremes; contributions from both monomeric and dimeric acid species were seen, with the absorbances due to dimeric species larger.

The spectra of Figure 5 suggest that if MAA monomer and dimer have different propagation kinetics, results in THF should significantly differ from the other solvents. The MAA k_p values obtained in the different solvents are listed in Table 3 but do not show large variations. With THF, k_p is slightly smaller (862 L·mol^{-1}·s^{-1}) than with the alcohols and acetic acid (1007 L·mol^{-1}·s^{-1}), whereas for toluene values of 1187 and 1264 L·mol^{-1}·s^{-1} were obtained. Interestingly, the latter values are very close to the k_p data obtained for bulk polymerizations (1167 and 1190 L·mol^{-1}·s^{-1}). This might be explained by considering MAA as a nonpolar solvent, similar to toluene, which only allows self-association of the monomer. This is supported by the nearly identical FTIR spectra for MAA in bulk and in toluene. As described in the introduction, MAA dimers are believed to be more reactive. Therefore, a higher k_p value is expected for solvents in which dimerization is favored. The fact that THF is the solvent with the highest fraction of less reactive monomeric species is consistent with the reported small value of k_p relative to other solvents. However, the magnitude of the variations in k_p with solvent type is small compared to the differences observed in the FTIR spectra. The differences in k_p with solvent are only of the order of the uncertainty of the data points.

Conclusions

PLP experiments were performed on MAA in a variety of solvents. Despite differences in MAA monomer−dimer equilibrium seen by FTIR spectroscopy, only minor variations of k_p with solvent type are observed. MAA concentration does not show a significant influence on k_p. This leads to the conclusion that the dimerization equilibrium and the association of the acid with solvent molecules have only, at most, a small effect on MAA propagation kinetics. In addition, the variation of k_p with temperature and the actual k_p values are very close to results obtained for MMA. In terms of propagation kinetics, methacrylic acid lies well within the group of methacrylates.

Previously published results on the homopolymerization of MAA in various solvents show a significant influence of concentration and the nature of the solvent on overall reaction rates, molecular weights, and viscosities;[14] the overall rates reported in toluene are much smaller than those in methanol or dioxane. Our work indicates that these findings cannot be attributed to varying propagation rates in the solvents but must be due to other considerations.

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