Impact of Hydrogen Bonding on Propagation Kinetics in Butyl Methacrylate Radical Polymerizations

Sabine Beuermann

Institut für Physikalische Chemie, Georg-August-Universität Göttingen, Tammannstrasse 6, 37077 Göttingen

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ABSTRACT: Pulsed laser initiated polymerizations of butyl methacrylate in butanol show a significant enhancement of the propagation rate coefficient k_p compared to polymerizations in bulk. The activation energy E_A of k_p is reduced due to the presence of butanol: at a monomer concentration of 0.8 mol·L^{-1} k_p for polymerizations in butanol at 0°C is about 85% higher than in bulk, the difference reduces to 44% at 80°C. These findings are associated with a reduction in E_A of k_p from 23.0 kJ·mol^{-1} for bulk systems to 20.5 kJ·mol^{-1} for polymerizations in butanol. The increase of k_p in the presence of an alcohol is explained by the formation of hydrogen bonds between the OH group of the solvent and the carbonyl group of the monomer.

Introduction

The solvent influence on the propagation reaction has been recognized since long.[1,2] However, the origin of the solvent induced changes in the propagation rate coefficients, k_p, were not clearly identified. With the advent of the so-called PLP−SEC technique,[3] which combines pulsed-laser initiated polymerizations (PLP) and polymer analysis via size-exclusion chromatography (SEC), additional studies were carried out. For several systems under investigation only small variations in the propagation rate were observed.[4] For example, from styrene polymerizations in acetonitrile and dimethylformamide a decrease in k_p by 15 and 25%, respectively, was derived.[5] Similar solvent effects for MMA and styrene homopolymerizations in a wide variety of solvents were reported.[6] For polymerizations in supercritical CO_2 (scCO_2) a reduction in k_p up to 40% was seen, which was explained by changes in the local environment of the free-radical chain end and thus by the occurrence of a local monomer concentrations, $c_{M,loc}$, at the site of the propagation reaction.[7] While the propagation rate is changed due to the presence of scCO_2, the activation energy, E_A, and the activation volume, $\Delta V^{\#}$, are not influenced. Similar findings with respect to E_A and $\Delta V^{\#}$ are reported for polymerizations in organic solvents, when large differences in molar volumes of the monomer and the solvent occur.[8] Contrary, for systems involving either monomers or solvents carrying an OH group, changes in k_p and in the activation energy are reported. The groups of Davis[9] and O'Driscoll[10] first reported about a strong increase of k_p by up to 80% for methyl methacrylate (MMA) polymerizations in benzyl alcohol. In addition, Morrison and Davis observed an even stronger solvent influence on k_p for ethyl α-hydroxymethacrylate, which was related to the polarity of the solvent.[11] Recently, we demonstrated for 2-hydroxypropyl methacrylate that hydrogen bonding involving the carbonyl group has a strong impact on the propagation rate and on the activation energy.[12]

To get a better understanding of the solvent influence on k_p for methacrylate systems involving hydrogen bonding, butyl methacrylate polymerizations in butanol were carried out. The system was chosen because it is anticipated that solvation effects are rather small, because both the monomer and the solvent carry a butyl group.

Experimental Section

Materials. All materials are used as received: the monomer butyl methacrylate (BMA; Fluka AG, stabilized with 0.02% hydroquinone monomethyl ether), the photoinitiator 2,2-dimethoxy-2-phenylacetophenone (DMPA, Aldrich-Chemie, 99%) used to initiate the polymerization, and the solvent *n*-butanol (Merck, uvasol). THF (Rotipuran ≥99.5%, p.a, stabilized with 2,6 di-*tert* butyl 4-methylphenol) used for size-exclusion chromatography is obtained from Carl Roth.

Pulsed Laser Initiated Polymerizations. The polymerizations were carried out in an internal cell consisting of a Teflon tube closed by two quartz windows on each side. This internal cell is placed in an optical high-pressure cell, which is heated and operated at ambient pressure within this study. For details see, e.g., ref 13. FT-IR/NIR spectra are recorded with a resolution of 2 cm^{-1} using a tungsten halogen lamp, a silicon-coated CaF_2 beam splitter, and a liquid nitrogen cooled InSb detector in order to monitor the monomer conversion. The PLP−SEC experiments in solution of butanol were carried out for monomer concentrations (c_{BMA}) of around 0.8 and 1.5 mol·L^{-1}. For comparison, also bulk BMA polymerizations were carried out. The reaction mixture consisting of monomer, initiator, and solvent was irradiated by sequences of laser pulses (using a LPX 210i laser operated on the XeF-line at 351 nm, Lambda Physik) applied at repetition rates ν between 1 and 20 Hz, an energy of about 3 mJ per pulse, and a DMPA concentration of 1 or 2 mmol·L^{-1}. Depending on the reaction conditions, between 200 and 3300 pulses were applied to obtain BMA conversions of at most 4%. The resulting polymer is precipitated with an excess of methanol and isolated. The polymerization conditions and results are detailed in Table 1.

Size-Exclusion Chromatography (SEC). Molecular weight distributions were determined at 35 °C by SEC using a Waters 515 pump, a Waters 410 refractive index detector, three PSS−SDV-columns with nominal pore sizes of 10^5, 10^3, and 10^2 Å, respectively. Tetrahydrofuran was used as the eluent at a flow rate of 1 mL·min^{-1}. The polymer concentration was always at or below 3 mg/1 mL THF. Molecular weight calibration was established against narrow polydispersity polystyrene (PS) standards (MW = 410 to 2 000 000 g·mol^{-1}) from Polymer Standards Service (PSS, Mainz, Germany). Absolute molecular weights of the poly(BMA) samples are estimated via the principle of universal calibration[14] using the Mark−Houwink constants $K = 11.4 \times 10^5$ dL·mol^{-1} and $a = 0.716$ for PS and $K = 14.8 \times 10^5$ dL·mol^{-1} and $a = 0.664$ for poly(BMA).[15]

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Table 1. Polymerization Parameters and Experimental Results for BMA Polymerizations in Bulk and in Butanol at Ambient Pressure[a]

	T/°C	c_I/mmol·L^{-1}	c_M/mol·L^{-1}	ν/Hz	M_1/g·mol^{-1}	M_2/g·mol^{-1}	M_1/M_2	k_p/L·mol^{-1}·s^{-1}
bulk	1	2	6.46	20	8500	17 800	0.48	185
	1	2	6.46	20	8100	17 100	0.47	177
	25.3	2	6.27	20	20 000	37 600	0.53	449
	25.9	2	6.27	20	20 200	37 900	0.53	453
	50	2	6.07	20	35 900	69 900	0.51	831
	70	2	5.91	20	58 700	111 000	0.53	1398
	70	2	5.91	20	59 300	111 000	0.53	1411
BuOH	−11.7	1	0.8	2	12 000	25 100	0.48	211
	−11.1	1	0.8	2	12 300	25 700	0.48	216
	0.5	1	0.8	2	19 500	38 000	0.51	343
	0.6	1	0.8	2	19 500	38 900	0.50	343
	0.8	1	0.8	1	38 900	74 100	0.52	342
	0.8	1	0.8	1	38 000	72 400	0.52	334
	20.2	1	0.8	2	35 500	67 600	0.53	623
	20.2	1	0.8	2	36 300	67 600	0.54	637
	40.1	1	0.8	2	56 200	107 000	0.53	987
	40.3	1	0.8	2	57 500	112 000	0.51	1010
	60	1	0.8	10	20 000	38 900	0.51	1755
	60.5	1	0.8	10	20 400	38 900	0.52	1790
	80	1	0.8	10	28 200	53 700	0.53	2474
	80	1	0.8	10	28 200	51 300	0.55	2474
	80.3	1	0.8	10	28 800	53 700	0.54	2527
	0	2	1.6	20	3300	6500	0.51	291
	0.4	2	1.6	20	3400	6700	0.51	300
	25.5	2	1.55	20	7600	16 700	0.46	692
	25.7	2	1.55	20	7600	16 100	0.47	692
	50	2	1.52	20	12 500	25 200	0.50	1161
	50	2	1.52	20	12 600	25 200	0.50	1171
	70	2	1.48	20	19 700	37 100	0.53	1876
	70	2	1.48	20	20 000	37 600	0.53	1905

[a] Key: T, temperature; c_M, monomer concentration; c_I, initiator concentration; M_i ($i = 1, 2$), molecular weight at the first and second inflection points; k_p, propagation rate coefficient calculated from M_1.

Raman Spectrometer. Raman spectra are recorded on a FTIR-spectrometer (Bruker IFS 66/S) equipped with a Raman module FRA 106/S using a Nd:YAG laser operated at a power level of 0.4 W, a liquid N_2-cooled Ge-detector and a silicon-coated CaF_2 beam splitter. The resolution is 1 cm^{-1} and 500 scans are recorded at a rate of 5.0 kHz. The software Opus 3.1 is used to operate the spectrometer and to analyze the spectra. A Blackman-Harris-4-term apodization function is used for Fourier transformation.

Determination of Monomer Concentration. BMA concentrations for bulk experiments are calculated from the monomer densities, ρ (BMA), at the reaction conditions: The temperature dependence of ρ (BMA) is reported in ref 15. Initial monomer concentrations for polymerizations in organic solvents at ambient pressure are calculated from the known molar fractions of BMA and the solvents under the assumption of a negligible excess volume of the mixture. The densities ρ of the monomer and of the solvents were calculated according to the following equations.

$$\text{BMA:}^{15} \quad \rho/(\text{g}\cdot\text{cm}^{-3}) = (-9.19 \times 10^{-4})T/°\text{C} + 1.04786 \quad (1)$$

$$\text{butanol:} \quad \rho/(\text{g}\cdot\text{cm}^{-3}) = (-1.19 \times 10^{-3})T/°\text{C} + 0.8398 \quad (2)$$

Equation 2 is obtained from a linear fit of the densities at 25,[16] 50, and 90 °C.[17]

Determination of Propagation Rate Coefficients. Applying the PLP−SEC method k_p is derived according to eq 3 from a characteristic degree of polymerization, L_i, which is directly obtained from the molecular weight distribution (MWD).

$$L_i = ik_pc_Mt_0, \quad i = 1, 2, 3, ... \quad (3)$$

where c_M is the monomer concentration and t_0 is the time between two successive laser pulses. As detailed in the original paper,[3] L_1 is best identified with the position of the inflection point on the low molecular weight side of the MWD peak maximum. To obtain reliable k_p values, the existence of a second or even a third inflection point at degrees of polymerization around L_2 and L_3 is required. The occurrence of such higher order inflection points serves as a consistency check of the PLP−SEC method.[18,19]

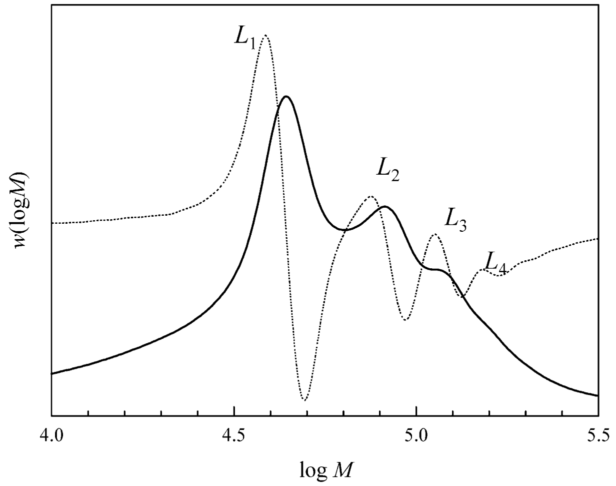


Figure 1. Polymer molecular weight distribution (full line) and associated derivative curve (dotted line) obtained from a BMA polymerization at 0.8 °C, ambient pressure, a laser pulse repetition rate of 1 Hz with c_{BMA} = 0.8 mol·L^{-1} in butanol.

Results and Discussion

As an example, Figure 1 gives the molecular weight distribution (MWD) for a polymer obtained at 0.8 °C applying a pulse repetition rate of 1 Hz and an initiator concentration of 1 mol·L^{-1}. The monomer concentration was 0.8 mol·L^{-1}. The MWD shows a typical PLP structure and the associated first derivative, given by the dotted line, shows 4 distinct peaks. The positions of these peaks, marked by L_1 to L_4, indicate the inflection

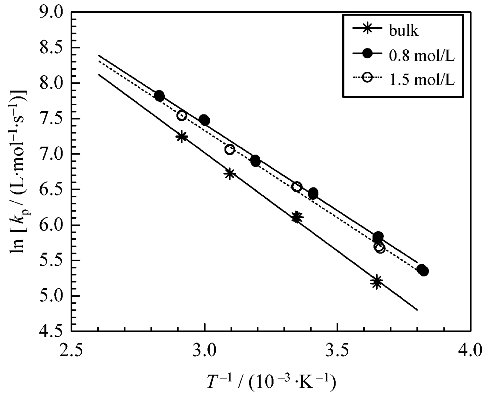


Figure 2. Temperature dependence of k_p for BMA polymerizations in bulk and in butanol at the indicated monomer concentrations. The lines refer to Arrhenius fits of the individual data sets.

points on the MWD. The positions of the points of inflection are related to L_1 as follows: $L_2 = 1.9L_1$, $L_3 = 2.9L_1$, $L_4 = 3.9L_1$, thus fulfilling the consistency criteria of $L_n \sim nL_1$.[18] For all k_p values reported in this publication, MWDs with at least two well-defined maxima in the derivative were obtained. The positions of the first and second inflection points are listed in Table 1. In addition, Table 1 contains the k_p values, which are all calculated from L_1.

The temperature dependence of k_p for bulk polymerizations and for polymerizations in BuOH with BMA concentrations of around 1.5 and 0.8 mol·L^{-1} is given in Figure 2. It is clearly seen that k_p increases with decreasing monomer concentration to 1.5 mol·L^{-1}. A further reduction of the monomer concentration to 0.8 mol·L^{-1} results only in a slight enhancement of k_p.

The k_p data for polymerizations in bulk and in solution of butanol are fit by the Arrhenius equation, $\ln k_p = \ln A - E_A/RT$. The fits are given by the lines in Figure 2, which are associated with the following activation energies E_A and preexponential factors A:

$$E_A = 23.0\ \text{kJ·mol}^{-1},\quad A = 4.52 \times 10^6\ \text{L·mol}^{-1}\text{·s}^{-1}\ \text{(bulk)}$$

$$E_A = 20.4\ \text{kJ·mol}^{-1},\quad A = 2.41 \times 10^6\ \text{L·mol}^{-1}\text{·s}^{-1}\ (1.5\ \text{mol·L}^{-1}\ \text{BMA})$$

$$E_A = 20.5\ \text{kJ·mol}^{-1},\quad A = 2.77 \times 10^6\ \text{L·mol}^{-1}\text{·s}^{-1}\ (0.8\ \text{mol·L}^{-1}\ \text{BMA})$$

The Arrhenius parameters for bulk polymerizations are in very good agreement with previously published data[20] of $E_A = 22.9$ kJ·mol^{-1} and $A = 3.8 \times 10^6$ L·mol^{-1}·s^{-1}. The difference in activation energies for polymerizations in bulk and with $c_{BMA} = 0.8$ mol·L^{-1} is around 2.5 kJ·mol^{-1}. The preexponential factor A is decreased by a factor of 1.6 due to the presence of the alcohol.

To estimate the error of the activation parameters, 95% joint confidence intervals of E_A and A were calculated assuming a constant but unknown relative error. Details on this procedure are given elsewhere.[18,21] The joint confidence intervals (JCIs) for E_A and A for polymerizations in bulk and in solution are depicted in Figure 3. The JCI for data from bulk polymerizations is clearly not overlapping with the other JCIs, thus indicating a significant difference in Arrhenius parameters for polymerizations in butanol. The JCI for $c_{BMA} = 0.8$ mol·L^{-1} is located slightly below the JCI for data derived from polymerizations with $c_{BMA} = 1.5$ mol·L^{-1}.

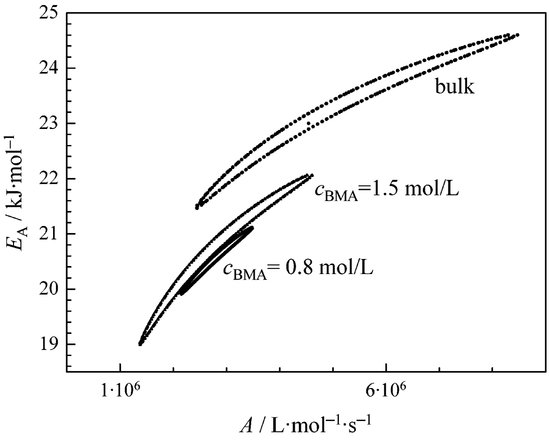


Figure 3. 95% joint confidence intervals for Arrhenius parameters A and E_A for BMA polymerizations in bulk and in solution of butanol; for details see text.

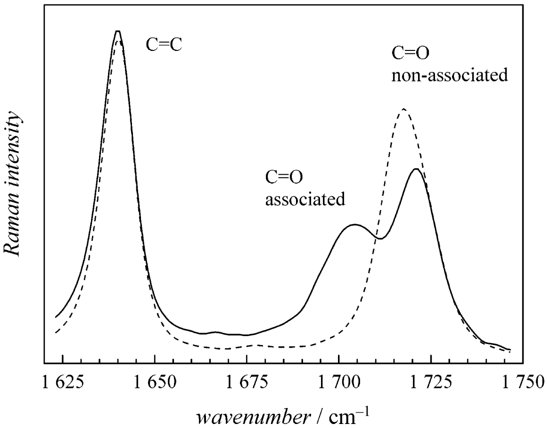
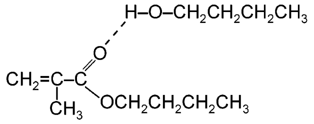


Figure 4. Raman spectra of BMA and of a binary mixture of BMA in butanol (c_{BMA} = 1.6 mol·L^{-1}) recorded at room temperature.

Scheme 1



Corresponding to the observed change in activation energy, the influence of alcohol on k_p depends on temperature: k_p in solution of butanol ($c_{BMA} = 0.8$ mol·L^{-1}) is 80% higher at 0 °C and 42% at 80 °C than in bulk. Thus, the solvent influence is weaker at higher temperatures. As for HPMA polymerizations, the influence of BuOH on BMA may be explained by the occurrence of H bonds between the OH group of the alcohol molecules and the carbonyl group of the monomers, as depicted in Scheme 1.

The association of the carbonyl group may be monitored by Raman spectroscopy in the range of the carbonyl vibrations at around 1700 to 1720 cm^{-1}.[22] The carbonyl group in alkyl methacrylates gives rise to a peak at around 1720 cm^{-1} in the Raman spectrum. As previously discussed, interactions of the carbonyl group with an OH group leads to the occurrence of a carbonyl vibration at around 1700 cm^{-1}.[12,22] Figure 4 presents Raman spectra for BMA and a mixture of BMA and

BuOH with a BMA concentration of 1.6 mol·L^{-1}. The peak at 1640 cm^{-1} assigned to the double bond of the monomer is not significantly changed due to the presence of the alcohol. The spectrum of pure BMA shows a single peak at 1718 cm^{-1}, which is assigned to the carbonyl group in the absence of any H bonds. In contrast, the spectrum for the mixture of BMA and BuOH shows a second peak at 1704 cm^{-1}. The new peak is related to vibrations of the carbonyl group, which forms hydrogen bonds to the OH group of the alcohol. In addition, the peak of the nonassociated carbonyl group is shifted by 3 cm^{-1} to higher wavenumbers.

Because of the formation of an H bond between the carbonyl and the OH groups the electron density at the carbonyl C atom is changed compared to the carbonyl group not engaged in any association. Since the carbonyl group and the double bond form a conjugated system, the electron density of the double bond should be varied as well. Thus, the reactivity of the double bond toward the addition of a radical should be altered. In addition, the reactivity of the radical should also be varied due to the formation of H bonds. To find out how the reactivity of the monomer is altered, first bulk BMA is considered. Because of the $-I$ effect of the carbonyl O atom, the carbonyl C atom carries a partial positive charge and the double bond is electron deficient. If the carbonyl oxygen undergoes H bonding with the hydroxyl group, the formation of the hydrogen bond shifts some of the electron density of the carbonyl oxygen to the hydrogen bond. To adjust for this loss in electron density, the partial positive charge at the carbonyl carbon will be enhanced[23] and consequently resulting in a stronger electron-deficiency at the double bond. As previously discussed for the reaction of low molecular weight species a higher electron deficiency of a double bond leads to an increase in radical addition rate.[24]

Thus, the solvent influence on the propagation rate coefficient is a true kinetic effect and not an influence on the environment of the free-radical chain end, as discussed for the solvent influence of scCO$_2$[25] or, e.g., toluene.[8] The variation in activation energy is suggested to be due to the temperature dependence of the H-bond formation. H bonds are weaker at higher temperatures, thus, the difference in monomer and/or radical reactivity between the bulk and the BMA/BuOH system is less pronounced at higher temperatures. This idea is in agreement with the experimental data shown in Figure 2, which indicate a diminishing solvent influence at higher temperatures. The influence of temperature on the association behavior and on the propagation kinetics is currently under investigation in our laboratory.

The implications of the alcohol influence on propagation kinetics are also of importance for the understanding of other elementary reactions occurring in a free-radical polymerization. As an example, the catalytic chain-transfer reaction will be considered. As recently reviewed, the chain-transfer constants (C_T) for the catalytic chain-transfer reaction of bis[(difluoroboryl)-dimethylglyoximato]cobalt(II) in MMA polymerizations shows a solvent influence.[26] For reactions in methanol or in ethanol C_T is significantly lower than for reactions in bulk or in solvents not undergoing H bonding. It was suggested that the smaller C_T values are due to some interactions between the OH group of the solvent and the Co center. However, considering the enhancement of k_p for polymerizations in an alcohol, the decrease in C_T, which is defined as $C_T = k_{tr}/k_p$ with the catalytic chain-transfer rate coefficient k_{tr}, may at least partly be due to a higher k_p value. Thus, to understand the solvent influence on k_{tr} it should be identified whether k_p is changed due to the presence of the alcohol.

Conclusions

Butyl methacrylate polymerizations carried out in bulk and in butanol indicate that the formation of hydrogen bonds between the carbonyl group of the monomer and the OH group of the alcohol has a significant impact on the propagation rate coefficient. Because of the presence of the alcohol an enhancement of k_p is observed, which is more pronounced at lower temperatures. Thus, the activation energy E_A and the preexponential factor A are varied by the presence of BuOH in the reaction mixture. Calculation of joint-confidence intervals shows that the differences are significant. It goes without saying that the observed solvent influence is not restricted to the system under investigation, but should occur with other methacrylates and alcohols. Knowledge of the solvent influence on k_p is also important for gaining better insights into other elementary reactions occurring during free-radical polymerizations, whose rate coefficients are frequently measured coupled to the propagation rate coefficient k_p.

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