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A Novel Approach to the Understanding of the Solvent Effects in Radical Polymerization Propagation Kinetics

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ABSTRACT: Propagation kinetics of isobornyl methacrylate (iBoMA) and methyl methacrylate (MMA) free-radical homopolymerization were studied by the PLP-SEC method, which consists of pulsed laser initiated polymerizations and subsequent polymer analysis by size-exclusion chromatography. The reactions were carried out in bulk and in solution of several organic solvents: toluene, tetralin, tetrahydrofuran (THF), methyl isobutyrate, and phenethyl isobutyrate. In all polymerization systems, the activation energy of the observed propagation rate coefficient, $k_{p,app}$, is not affected by either solvent type or solvent concentration. However, $k_{p,app}$ may be significantly different from the corresponding bulk values. In MMA polymerizations, $k_{p,app}$ values in solution were higher than in bulk, with the strongest enhancement of 50% observed for tetralin as solvent. In contrast, a solvent-induced lowering in propagation rate of up to 52% for THF as solvent was seen for iBoMA. The observed changes in propagation rate were assigned to the occurrence of a local monomer concentration in the vicinity of the free-radical chain end rather than to an intrinsic kinetic effect. The variation in local monomer concentrations is suggested to originate from differences in molar volume of the monomer and the solvent. Critical analysis of the results led to a linear correlation between solvent-induced changes in propagation rate and the difference in molar volumes of monomer and solvent. The correlation holds for both monomers.

Introduction

It has long been recognized that solvents may affect free-radical homo- and copolymerizations.[1−4] Despite the large number of articles covering this field, there is no common agreement not only on the origin of the solvent effect but also on the extent of its influence. Thus, the explanations are as diverse as the data, and it is not possible to generalize the findings.

Early experiments suffered from the fact that kinetic data were derived from techniques that did not give access to individual values of the propagation rate coefficient, k_p. Therefore, it is difficult to clearly identify the solvent influences on k_p. On the other hand, even in the case of direct k_p determination via pulsed laser initiated polymerization in combination with polymer analysis by size-exclusion chromatography (PLP-SEC experiments), no clear explanation of the experimentally observed solvent effect on k_p was given.

The majority of PLP data were derived only for methyl methacrylate (MMA) and styrene solution polymerizations. Early studies for MMA dissolved in methanol,[5] ethyl acetate,[5] ethanol,[6] toluene,[7] and 2-butanone[7] showed no significant change in k_p. More recently, Olaj et al.[8] measured propagation rate coefficients for styrene and MMA polymerizations in a wide variety of solvents (acetonitrile, dimethylformamide, anisole, methyl isobutyrate, bromobenzene, benzene, mesitylene, and 1,2-dichloroethane) at 50% v/v concentration. In these experiments, solvent-induced changes were mostly around 10%; in some cases, e.g., in poor solvents, at most 20% variation in k_p was seen. In addition, it has been reported that certain solvents, such as benzyl alcohol,[9,10] dimethyl sulfoxide,[10] diethyl phthalate,[10] *N*-methylpyrrolidinone,[10] or ionic liquids,[11] cause a significant increase in k_p when the monomer concentration decreases. MMA polymerizations for some of these latter solvents also show a considerable deviation of activation parameters compared to bulk values.

Polymerizations in solution have also been carried out for functional methacrylates, e.g., hydroxypropyl methacrylate (HPMA) and ethyl α-hydroxymethacrylate (EHMA). EHMA polymerizations were performed in a large number of solvents of different nature, and the resulting k_p values were correlated with the dielectric constant of the solvent.[12] A study on HPMA solution polymerizations[13] also indicates a significant solvent influence on the propagation rate coefficient and in addition on the activation energy. The results for HPMA were explained to be due to hydrogen bonding, which modifies the reactivity of monomer and radical. It has been suggested that an intrinsic kinetic effect occurs in the HPMA systems.[13]

On the other hand, it has been reported that the propagation rate for MMA and BA homopolymerizations in supercritical CO_2 ($scCO_2$) is reduced by up to 40% compared to the bulk value.[14] The experimental results did not show any significant changes in either the activation energy or the activation volume.[14]

Applying the PLP-SEC technique pioneered by Olaj et al.,[15] the propagation rate coefficient is derived according to eq 1:

$$L_1 = k_p c_M t_0 \tag{1}$$

where L_1 and t_0 are the number of propagation steps and the time interval between two successive laser pulses, respectively. L_1 is generally calculated from the position of the first inflection point of the molecular weight distribution (MWD).[15] With the experimentally accessible quantities L_1 and t_0, eq 1 allows for the determination of the product of k_p and monomer concentration, c_M. As a consequence, variations of k_p are implied if c_M at the site of the propagation reaction, which is denoted as the local monomer concentration $c_{M,loc}$, is not identical with the overall or analytical monomer concentration, $c_{M,a}$, in the system.

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The occurrence of local monomer concentrations was considered in order to explain the results from PLP-SEC experiments carried out in the presence of $scCO_2$.[14] Two types of interactions were discussed: intramolecular interactions between polymer segments of the same macroradical and intermolecular interactions between polymer segments and monomer or solvent molecules.

To test whether the occurrence of local monomer concentrations is responsible for the solvent influence on k_p in solution polymerizations, PLP-SEC experiments were performed for the systems described below. The monomers were methyl and isobornyl methacrylate, chosen because of their differences in size: the smallest ester group compared to a very hindered and bulky ester group. The solvents toluene, tetralin, tetrahydrofuran (THF), phenethyl isobutyrate (PhiBu), and methyl isobutyrate (MeiBu) were chosen according to the following criteria: (i) aromatic solvents of significantly different molar volume, (ii) saturated methacrylate analogues MeiBu and PhiBu, (iii) THF representing good solvents, and (iv) specific interactions between monomer and solvent molecules, e.g., such as H-bonding, are not expected to occur in these systems because the monomers and solvents studied do not carry any functional groups. Previously, it has been argued that especially for polymerizations in aromatic solvents the observed variation of k_p with monomer concentration may be related to complex formation between polymer radical and monomer or solvent.[2,16-18] The occurrence of such complexes has also been tested by carrying out experiments for a wide range of monomer concentrations and in mixtures of an aromatic and a nonaromatic solvent.

Experimental Section

Materials. The monomers methyl methacrylate (MMA, Fluka, 99%) and isobornyl methacrylate (iBoMA, Aldrich, 98%) and the solvents methyl isobutyrate (MeiBu, Aldrich, 99%), phenethyl isobutyrate (PhiBu, Aldrich, 97%), tetrahydrofuran (THF, Fluka, 99.5%), 1,2,3,4-tetrahydronaphthalene (tetralin, Aldrich, 97%), and toluene (Fluka, >99%) were used as supplied. The photoinitiator 2,2-dimethoxy-2-phenylacetophenone (DMPA, Aldrich, 99%) was used without further purification. Methanol (Fluka Chemie AG, p.a.) with traces of the inhibitor hydroquinone (Merck-Schuchardt, >99% purity) served to precipitate the polymer. As eluent for size-exclusion chromatography, THF (Carl Roth, Rotipuran >99.5%, p.a., stabilized with 2,6-di-*tert*-butyl-4-methylphenol) was used.

Pulsed Laser Initiated Polymerizations. Polymerizations in bulk or in solution are carried out in an internal cell consisting of a Teflon tube closed by two quartz windows on each side. The internal cell is placed in an optical high-pressure cell, which may be heated and pressurized if required.[19] The DMPA concentrations were between 1×10^{-3} and 1×10^{-2} mol L^{-1}. DMPA decomposition was induced by excimer laser pulses (LPX 210i, Lambda Physik) at 351 nm with a laser pulse repetition rate, ν_{rep}, of 10 Hz. The samples were subjected to laser pulsing for times sufficient to convert around 3% of the monomer into polymer. The number of pulses applied depends on the monomer and on reaction conditions. Monomer conversion is monitored by NIR spectroscopy (IFS 88, Bruker) in the region of the first overtone of C−H stretching vibrations at around 6170 cm^{-1}.[14] The polymer is precipitated in methanol containing traces of hydroquinone in order to prevent further polymerization and is isolated prior to SEC analysis. Experimental details and results for each individual bulk and solution polymerization are available as Supporting Information.

Size-Exclusion Chromatography. Molecular weight distributions are determined by means of size-exclusion chromatography using a Waters 515 HPLC pump, a Waters 2410 refractive index detector, PSS-SDV columns with nominal pore sizes of 10^5, 10^3, and 10^2 Å, and THF at 35 °C as the eluent. The SEC setup is calibrated against polystyrene (PS) and poly(methyl methacrylate) (PMMA) standards of narrow polydispersity (MW = 410−2000 000 g mol^{-1}, Polymer Standards Service). Absolute molecular weights of the iBoMA polymer samples are estimated via the principle of universal calibration[20] using the Mark−Houwink constants $K = 0.0114$ mL g^{-1}, $a = 0.716$ for PS, and $K = 0.0135$ mL g^{-1} and $a = 0.560$ for poly(iBoMA) taken from the literature.[21]

Table 1. Coefficients Used To Calculate iBoMA and Solvent Densities According to Eq 2 and Dielectric Constant, ϵ, of the Solvents at 20 °C

	ρ_0/(g cm^{-3})	$10^4 b$/(g cm^{-3} °C^{-1})	ϵ(20 °C)
iBoMA	0.998[a]	7.96	
THF	0.912[b]	1.14	7.58
toluene	0.883[b]	9.05	2.38
MeiBu	0.914	11.67	5.6[c]
PhiBu	1.007	8.72	
tetralin	0.985[d]	7.52	2.77

[a] From ref 21. [b] From ref 13. [c] Dielectric constant value for methyl butyrate. [d] From ref 22.

Monomer Concentrations. The temperature, θ, dependence of iBoMA and solvent densities were calculated according to eq 2, using the coefficients reported in the literature[13,21,22] and listed in Table 1.

$$\rho = \rho_0 - b\theta/°C \qquad (2)$$

The variation of density with θ for the saturated monomer analogues PhiBu and MeiBu was not available from literature. Thus, the parameters ρ_0 and b were obtained by fitting of the densities measured between 25 and 80 °C with a Paar density meter, DMA 602 TP, Anton Paar GmbH, which was calibrated with air and water.

MMA densities were calculated according to eq 3.[23]

$$\rho/(\mathrm{g\ cm^{-3}}) = 0.9659 - 1.2129 \times 10^{-3}\theta/°C + 1.6813 \times 10^{-6}(\theta/°C)^2 - 1.0164 \times 10^{-8}(\theta/°C)^3 \qquad (3)$$

Additive volumes have been assumed in order to calculate initial monomer concentration in solution polymerizations. This assumption was shown to be appropriate by measuring the density of some monomer/solvent mixtures. The deviation between experimental and estimated density values of the solutions was always less than 5%.

Results

Polymerizations in solution were carried out at temperatures between 30 and 80 °C and at monomer concentrations between bulk and 12% of the bulk value. Although bulk k_p data for both monomers are well established,[24,25] a few bulk polymerizations were carried out in order to minimize uncertainties in k_p being simply due to the fact that the molecular weight distributions (MWDs) were measured on different SEC set ups. As outlined previously, uncertainties in k_p from PLP-SEC mostly originate from MWD determination.[24,26] The approach chosen here should allow for the detection of even small solvent effects.

Figure 1 shows molecular weight distributions of four polymers obtained from PLP experiments in solution at 40 °C. The MWDs of polymers resulting from MMA polymerizations in tetralin with c_M of 3 mol L^{-1} and in PhiBu with c_M of 4 mol L^{-1} are given in parts a and b of Figure 1, respectively. MWDs of poly(iBoMA) obtained from PLP in MeiBu with $c_M = 2$ mol L^{-1} and in THF with $c_M = 3$ mol L^{-1} are depicted in parts c and d of Figure 1, respectively. In all cases well-structured MWDs with at least three distinct peaks and an

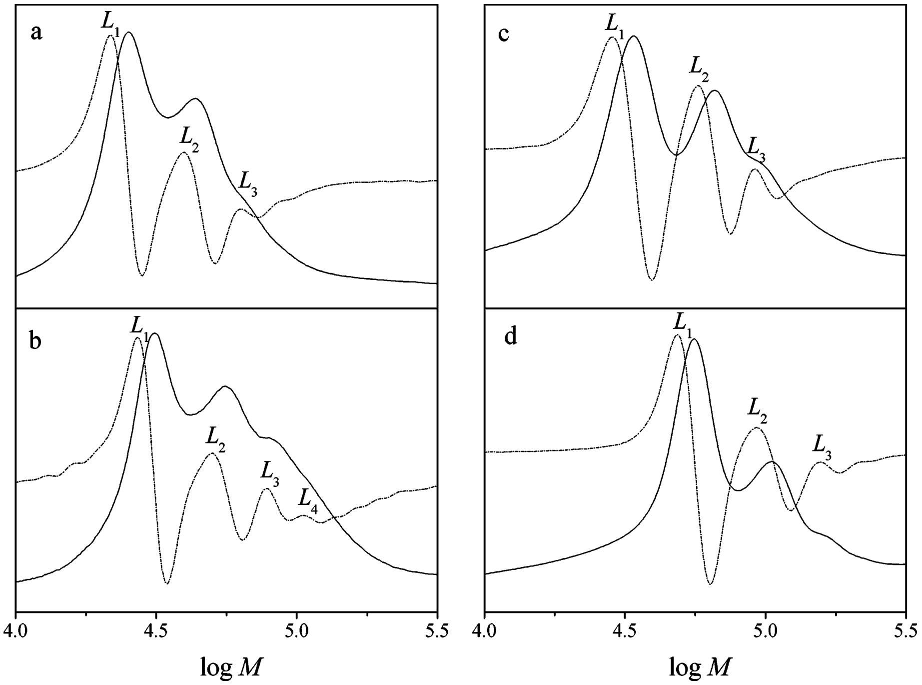


Figure 1. Molecular weight distributions, $w(\log M)$ (full line), and corresponding first derivate curves, $d(w(\log M))/d(\log M)$ (dashed line), of the polymer generated in pulsed laser polymerizations of methyl methacrylate (a) in tetralin and (b) in PhiBu solution and isobornyl methacrylate (c) in MeiBu and (d) in THF solution. Laser repetition rate was always 10 Hz and temperature 40 °C. For further details see text.

additional shoulder at higher molecular weights are obtained. The MWDs in Figure 1 are typical for the entire set of experiments. The dashed lines in Figure 1 represent the first-derivative curves of the MWDs, which clearly exhibit three or four maxima, indicated by L_1, L_2, etc. The higher-order inflection points are located at molecular weights which fulfill the consistency criteria: $L_2 \approx 2L_1$, $L_3 \approx 3L_1$, and $L_4 \approx 4L_1$. According to eq 1, propagation rate coefficients are calculated from the molecular weights $M_1 = L_1M_0$ (where M_0 is the monomer molecular weight) at the position of the first inflection point (M_1 and M_2 values for each individual experiment are contained in the Supporting Information).

The temperature dependence of the propagation rate coefficients observed for MMA polymerizations in bulk and in solution is presented in Figure 2. For comparison, the IUPAC recommended Arrhenius fit for bulk MMA polymerization,[24] according to eq 4, is included in Figure 2 (bold line).

$$\ln [k_p/(\mathrm{L\ mol^{-1}\ s^{-1}})] = 14.80 - 2694T^{-1}/\mathrm{K}^{-1} \quad (4)$$

The deviation of bulk k_p determined at 40 °C within the present work from the IUPAC benchmark value is 8%. Since in the case of PMMA direct calibration is used to derive MWDs and since Arrhenius parameters are usually less subject to variation if data sets from different laboratories are compared, here only MMA bulk k_p at 40 °C was determined (the average value is plotted in Figure 2).

Figure 2 shows that the values for the observed propagation rate coefficient, $k_{p,app}$, for MMA polymerizations in solution are always larger than the corresponding bulk value. The lines representing a fit of the individual data sets according to the Arrhenius relation $\ln k = \ln A - E_A/RT$ do not show significantly different slopes. The largest difference in slope and consequently in E_A from the bulk value is seen for polymerizations in PhiBu at 2 mol L^{-1}. The corresponding activation energy E_A (PhiBu, 2 mol L^{-1}) = 19.9 kJ mol^{-1} is 2.5 kJ mol^{-1} lower than the bulk value of 22.4 kJ mol^{-1} (eq 4). This difference is not considered to be significant in view of the limited number of data points. In contrast to bulk experiments, the structure of the MWDs starts to deteriorate with increasing temperature, thus limiting the temperature interval accessible at the chosen laser pulse repetition rate of 10 Hz.[27] The effect is most pronounced for polymerizations in tetralin, probably due to chain transfer to solvent. It should be noted that all k_p data presented within the present work are originating from experiments in which chain stopping is dominated by termination,[28] reflected by well-structured

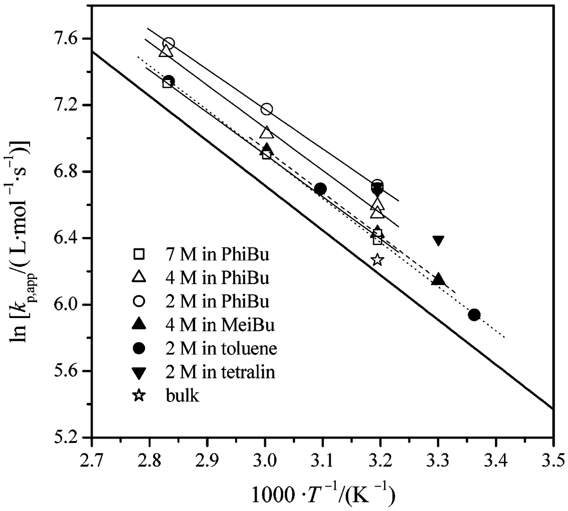


Figure 2. Temperature dependence of $k_{p,app}$ for MMA polymerizations in solution (solvents and c_{MMA} as indicated). The bold line represents the IUPAC recommended values for bulk MMA polymerization.[24] See text for further details.

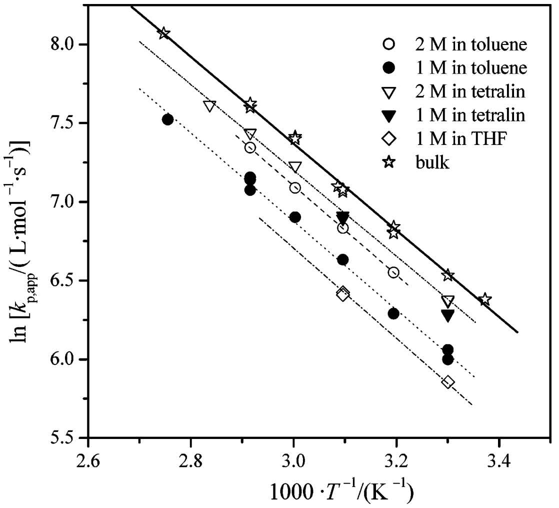


Figure 3. Temperature dependence of $k_{p,app}$ for iBoMA polymerizations in bulk and in solution (solvents and c_{iBoMA} as indicated). See text for further details.

MWDs as presented in Figure 1a−d. Because of the low boiling temperature of THF, solution polymerizations in THF were only carried out at 40 °C.

To obtain a better understanding of the solvent influence on the propagation reaction, additional experiments with iBoMA were carried out. First, the temperature dependence of $k_{p,app}$ for iBoMA polymerizations in different solvents was investigated. The results are shown in Figure 3. iBoMA polymerizations were performed in toluene and in tetralin at different temperatures with monomer concentrations of 1 and 2 mol L^{-1}. For polymerizations in THF at 30 and 50 °C, the concentration of iBoMA was 1 mol L^{-1}. In addition, Figure 3 contains bulk values. The Arrhenius fit of the bulk data is described by eq 5:

$$\ln [k_p/(\mathrm{L\ mol^{-1}\ s^{-1}})] = 15.73 - 2754 T^{-1}/\mathrm{K}^{-1} \quad (5)$$

According to eq 5, E_A for bulk polymerizations is 22.9 kJ mol^{-1}. As expected from the generally observed family-type behavior,[4] this value is very close to the corresponding MMA E_A of 22.5 kJ mol^{-1}. However, in contrast to the MMA data, Figure 3 shows that iBoMA $k_{p,app}$ values obtained in solution polymerizations are lower than in bulk. iBoMA $k_{p,app}$ values at $c_M = 1$ mol L^{-1} in THF are by about 50% and in toluene by about 40% below the bulk values. The variations in $k_{p,app}$ are the smallest for polymerizations in tetralin, which yield values that are by 12% below bulk k_p. It should be noted that the activation energy is independent of monomer concentration and solvent type. This is demonstrated in Figure 3 by the invariant slopes of the Arrhenius fits to the individual data sets, given by the dashed and dotted lines.

In addition to the temperature dependence of $k_{p,app}$, the variation of $k_{p,app}$ with monomer concentration was studied at a constant temperature of 40 °C.

In Figure 4, the variation of $k_{p,app}$ with initial monomer concentration for MMA (a) and iBoMA (b) polymerizations in solution is shown. Results are presented as relative propagation rate coefficients, $k_{p,app}/k_{p,bulk}$, plotted vs relative monomer concentration, $c_M/c_{M,bulk}$. The symbols in the diagrams represent the average value of several experiments. The individual data are given in the Supporting Information. As already pointed out in Figures 2 and 3, both monomers show a completely different behavior in solution. Solvents, such as tetralin or PhiBu, which induce a significant increase in $k_{p,app}$ for MMA polymerizations, have the smallest influence on $k_{p,app}$ for iBoMA polymerizations. On the contrary, THF causes nearly no effect on $k_{p,app}$ in MMA polymerizations, whereas iBoMA $k_{p,app}$ is significantly decreased.

Figure 4 clearly indicates that the dependence of $k_{p,app}$ on monomer concentration is linear for all the solvents, with the exception of MMA polymerizations in tetralin, where the data are better fitted by an exponential function. At first sight, the deviating finding for tetralin could be assigned to chain transfer reactions. However, if this were true, the same trend as for MMA would be expected to occur for iBoMA polymerizations. Thus, a more feasible explanation is required, taking also into account that, in the case of significant chain transfer, monomodal MWDs instead of well-resolved PLP structures (at 40 °C) would have been obtained.[28] At room temperature solubility of both polymers in the solvents used here was checked. Only for the PMMA−tetralin case was poor solubility seen, which may explain the special behavior for this system.

In contrast to many PLP investigations into the solvent influence on the propagation rate coefficients summarized in the Introduction, the experimental findings depicted in Figure 4 show a significant solvent effect for both monomers.

Discussion

The solvent effect on k_p has been generally discussed in terms of the following points:[2] (1) copolymerization of monomer and solvent, (2) chain-transfer reaction with solvents, (3) polarity and polarizability of the medium, (4) change in monomer reactivity by interaction of the monomer with solvents, (5) reversible complex formation of the propagating radical with solvent molecule, and (6) selective solvation of polymer by monomer. In the following, these points will be discussed with respect to our experimental observations.

Copolymerization between monomer and solvents are not likely to occur in the systems considered in this work. In addition, a solvent influence due to chain transfer may also be excluded because experiments were designed to yield well-structured MWDs. Polarity does not seem to play a major role since the results for both monomers are different in a given solvent. Besides, while the solvents used in this study have similar dielectric constants, ϵ (listed in Table 1), the extent of the variation in $k_{p,app}$ is different in every solvent. In addition, Zammit et al.[10] showed that for MMA solution polymerization the largest solvent effect was found for DMSO ($\epsilon = 48$) and benzyl alcohol ($\epsilon = 13$). For solvents such as bromobenzene ($\epsilon = 5.4$) and benzonitrile ($\epsilon = 26$) the solvent effect was not as pronounced as for benzyl alcohol. In addition to points 1−3, specific interactions between monomer and solvent molecules are also not likely to occur in our polymerizations and thus cannot explain the observed solvent influence on the propagation reaction.

To explain the solvent influence on propagation rate, the formation of reversible complexes between radical and solvent molecules has been considered in several publications. Since Henrici-Olivé and Olivé proposed the occurrence of such complexes,[16] a number of papers with experimental and theoretical data have been published, which support this idea.[2,9] It has been pointed out that the electron affinities of the polymer radical are of the

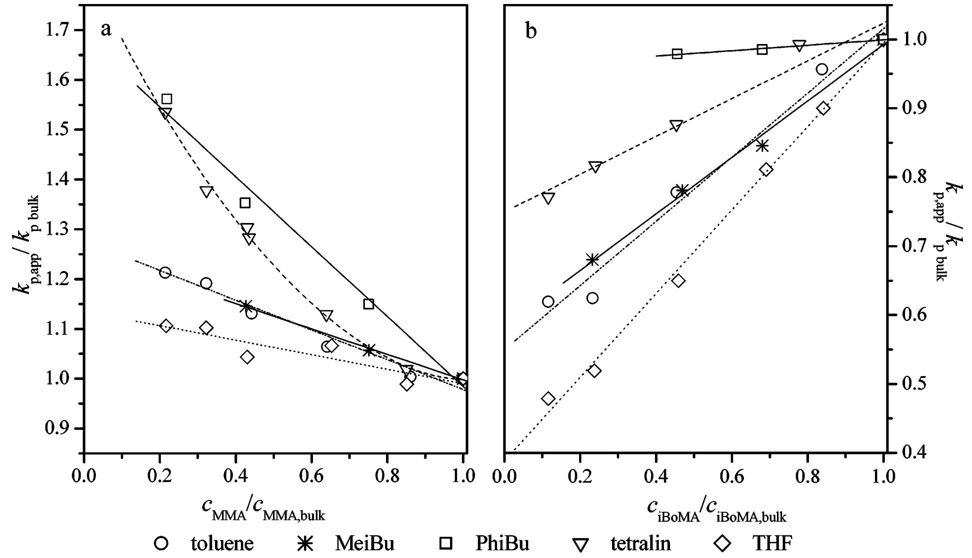
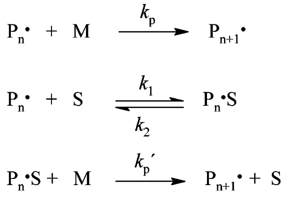


Figure 4. Variation of the propagation rate coefficient $k_{\mathrm{p,app}}$ with monomer concentration for MMA (a) and iBoMA (b) polymerizations in solution at 40 °C. $k_{\mathrm{p,app}}$ values and monomer concentrations are given relative to the corresponding bulk values.

Scheme 1



same order as for molecules such as tetracyanoethylene and chloranile which are known to form charge-transfer complexes with typical aromatic solvents.[2] Considering an equilibrium between complexed and noncomplexed radicals, the contribution of the complexed radical to propagation rate should only be significant if the radical is more stable in the complexed form. Therefore, solvent effects would be reflected by stabilization of the radical, and most likely not only a change in $k_{\mathrm{p,app}}$ but also a variation in the activation energy should occur.[10]

In the next section, it is checked whether the experimental results of this work may be explained in terms of a complexation of the radical. The mechanism of such a complexation is shown in Scheme 1, as proposed in the literature.[9,18]

According to Scheme 1, a propagating polymer chain either adds monomer with the rate coefficient k_{p} or forms a reversible complex with solvent S. The complexed radical $\mathrm{P}_n{\cdot}\mathrm{S}$ may add monomer, thus displacing the solvent and forming a chain end $\mathrm{P}_{n+1}{\cdot}$ with a rate coefficient k_{p}'. This mechanism has been used to explain solvent effects on the propagation rate of MMA, styrene, or vinyl acetate homo- and copolymerizations in several aromatic solvents.[2,9,18] Depending on the strength of the complex and based in Scheme 1, O'Driscoll et al.[9] proposed two different equations for the observed propagation rate coefficient $k_{\mathrm{p,app}}$. In the case of weak complexation, eq 6 was applied.

$$k_{\mathrm{p,app}} = k_{\mathrm{p}} + k_{\mathrm{p}}'\left(\frac{k_1 c_{\mathrm{S}}}{k_2}\right) \tag{6}$$

In eq 6, k_1 and k_2 represent the rate constants of the formation and decomposition of the complex $\mathrm{P}_n{\cdot}\mathrm{S}$, respectively. Equation 6 is deduced for formation of a weak complex assuming that $k_1/k_2 \ll 1$ and $k_2 \gg k_{\mathrm{p}}' c_{\mathrm{M}}$.

Equation 6 would allow for fitting of our experimental data resulting in similar graphs as the ones shown in Figure 4, leading to the physically not meaningful conclusion that, independent of the solvent (aromatic or nonaromatic), weak complexes between polymer radicals and solvent would be formed. Besides, for iBoMA polymerizations linear graphs with negative slopes would be obtained, which is in conflict with eq 6, allowing only for positive slopes in a plot of $k_{\mathrm{p,app}}$ vs c_{S}.

To account for strong complexes, eq 7 was derived:[9]

$$k_{\mathrm{p,app}} = k_{\mathrm{p}} + \left(\frac{k_1 c_{\mathrm{S}}}{c_{\mathrm{M}}}\right) \tag{7}$$

However, plotting of the experimental $k_{\mathrm{p,app}}$ values as a function of $c_{\mathrm{S}}/c_{\mathrm{M}}$ does not result in a linear dependence (see Figure S1 in Supporting Information). Therefore, eq 7 does not allow for an interpretation of the experimental data. The use of eq 8, derived by Kamachi et al.[18] from the same complexation scheme as given in Scheme 1, is also not successful in describing our results.

$$k_{\mathrm{p,app}} = \frac{k_{\mathrm{p}}}{1 + \dfrac{k_1}{k_2} c_{\mathrm{S}}} \tag{8}$$

According to eq 8, straight lines should be obtained when plotting $(k_{\mathrm{p,app}})^{-1}$ as a function of solvent concentration. The value of k_1/k_2 for different solvents should directly be determined by the slopes of the lines. The resulting graphs of the experimental data presented here do not provide a linear dependence of $(k_{\mathrm{p,app}})^{-1}$ on c_{s} (see Figure S2 in Supporting Information). This observation is in disagreement with what would be expected if complexes between propagating radicals and solvent molecules occurred. Therefore, it is concluded that radical complexation is not operative in the monomer–solvent systems considered in this work. This finding is important since $k_{\mathrm{p,app}}$ for MMA and iBoMA polymerizations may be predicted, a priori, by knowing the monomer concentration of the polymerization mixture. Additional parameters are not required in order to estimate $k_{\mathrm{p,app}}$ as a function of monomer concentration.

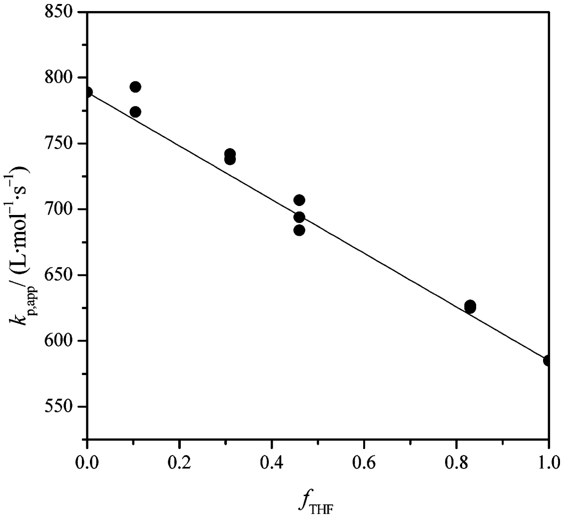


Figure 5. Observed propagation rate coefficients for iBoMA polymerization at 40 °C with a monomer concentration of 2 mol L^{-1} as a function of f_{THF}. The full line represents a straight line which connects $k_{p,app}$ values in both pure solvents.

To further support the conclusion that radical–solvent complexes do not affect propagation rate coefficients, $k_{p,app}$ for iBoMA polymerizations was determined for a mixture of THF with the aromatic solvent tetralin. In the case of no complexation it is anticipated that $k_{p,app}$ should be calculated taking only into account the fraction of solvents in the mixture. For this purpose, iBoMA was polymerized in mixtures of tetralin and THF at 40 °C and with a monomer concentration of 2 mol L^{-1}. In Figure 5, $k_{p,app}$ is plotted as a function of the mass ratio of THF, f_{THF}, with f_{THF} calculated as THF weight divided by the sum of THF and tetralin weight. The experimental data are well represented by a straight line, which links $k_{p,app}$ for polymerizations in pure THF and in pure tetralin.

Because all the aspects previously reported as being responsible for a solvent influence on the propagation rate fail to explain the experimental results presented in this work, now a novel concept will be discussed. As stated in the Introduction, $k_{p,app}$ may change as a consequence of the occurrence of local monomer concentrations at the active site of the propagating radical. $c_{M,loc}$ may result from intra- and/or intermolecular interactions between polymer segments or between polymer and solvent molecules. Alterations in the interactions involving polymer molecules might be caused by solvents which are poor solvents for the polymer[14] or which can undergo specific interactions, e.g., H-bonding with monomer or polymer.[12,13] However, even if the solvent does not change these interactions, the occurrence of $c_{M,loc}$ might be caused by differences in size of monomer and solvent molecules. In solution polymerizations, a competition with respect to which molecule (solvent or monomer) is positioned close to the radical chain end occurs. If the volume of the solvent molecule is smaller than the volume of the monomer, the local monomer concentration in the vicinity of the propagating radical should be smaller than the overall monomer concentration, leading to lower values of $k_{p,app}$. On the other hand, if solvent molecules were bigger than monomer molecules, the active site would be easily reached by monomer. As a consequence, the local monomer concentration would be higher than the analytical monomer concentration, giving rise to larger $k_{p,app}$ values.

Table 2. Solvent Molar Volume V_{solv} at 40 °C and the Ratio of Propagation Rate Coefficients at Infinite Dilution over Bulk k_p

		$k_{p,\infty}/k_{p,bulk}$	
	V_{solv}/cm^3 mol^{-1}	MMA	iBoMA
THF	83.22	1.14	0.39
toluene	108.79	1.28	0.55
MeiBu	117.73	1.25	0.58
tetralin	138.80		0.75
PhiBu	197.79	1.69	0.96

This interpretation is in agreement with the experimental findings: for all MMA systems considered in this work $k_{p,app}$ in solution is higher than in bulk, all the solvents, with the exception of THF, being bigger in volume than the monomer. $k_{p,app}$ of MMA derived in MeiBu is lower than in PhiBu, molecular size being the most important difference between both solvents. The smallest solvent effect occurs in THF, which is the solvent with the smallest volume. According to the above presented argument, it had been assumed that in the case of MMA solution polymerizations in THF, lower $k_{p,app}$ values than in bulk polymerizations would have been obtained, since the THF molar volume is smaller than the MMA molar volume. However, the experimental data show a slight increase in the coefficient. Although it cannot be ruled out that the increase is due to experimental uncertainties, it appears to be rewarding to study in future work whether other effects have to be considered.

Sterical arguments can also be used to explain the experimental data for the bulky monomer iBoMA. In all the cases, the solvent molecules are smaller than the monomer molecules, and $k_{p,app}$ for iBoMA solution polymerizations are always reduced. The extent of this reduction depends on the solvent size, being more pronounced in the case of THF and less pronounced for PhiBu (the solvent which is the most similar in size with monomer). Thus, the solvent influence on $k_{p,app}$ should be correlated with the size of solvents and monomer.

To demonstrate the importance of molecular sizes discussed above, the molar volumes (V_m) of the monomers and solvents are considered as a measure of size. V_m is calculated dividing the molar mass by the density at 40 °C. The values for MMA and iBoMA are 108.90 and 230.12 cm^3 mol^{-1}, respectively. The molar volumes of the solvents are listed in Table 2.

The propagation rate coefficient at infinite dilution, $k_{p\infty}$, is used to test whether a correlation between the solvent influence on the propagation rate and the molar volumes of monomer and solvent is operative. The use of $k_{p\infty}$ is advantageous because contributions from variation of $k_{p,app}$ with monomer concentration, which is different for the solvents studied here, are omitted. $k_{p\infty}/k_{p,bulk}$ is determined by extrapolation of the experimental data presented in Figure 4 to infinite dilution, given by the intercept with the y-axis. The resulting values for all systems are included in Table 2. Note that $k_{p\infty}/k_{p,bulk}$ was not determined for the MMA–tetralin system because a nonlinear variation of $k_{p,app}$ with monomer concentration was found (see Figure 4).

The ratio of $k_{p\infty}$ over $k_{p,bulk}$ is plotted as a function of the difference between molar volume of monomer (V_{mon}) and solvent (V_{solv}) in Figure 6. The data presented in Figure 6 clearly indicate a linear correlation between $k_{p\infty}/k_{p,bulk}$ and $V_{mon} - V_{solv}$. The dotted line in Figure 6 is obtained by fitting the data for iBoMA and MMA reported in this publication. The closer the molar

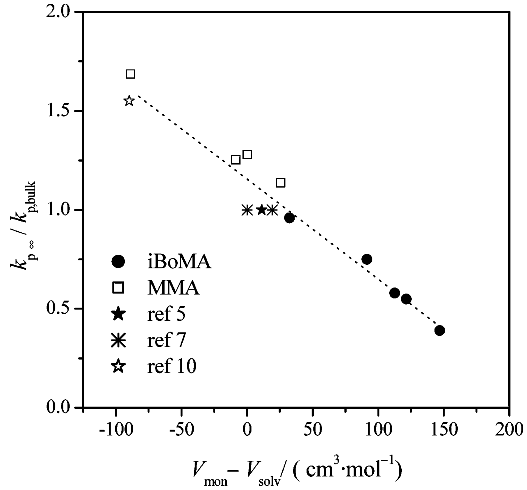


Figure 6. Ratio $k_{p\infty}/k_{p,bulk}$ for MMA and iBoMA solution polymerizations at 40 °C vs difference in molar volume of monomer, V_{mon}, and solvent, V_{solv}. The dotted line represents the combined linear fit of the data, including data from the literature. Literature data refer to MMA solution polymerizations in toluene,[7] 2-butanone,[7] ethyl acetate,[5] and diethyl phthalate.[10]

volumes of monomer and solvent, the smaller the solvent effect on k_p reflected by $k_{p\infty}/k_{p,bulk} \sim 1$. On the other hand, the influence on $k_{p,app}$ is more pronounced if the differences in V_{mon} and V_{solv} are bigger.

In addition, some literature data for MMA polymerizations in solution have been included in Figure 6. The data refer to systems with good polymer solubility, in which specific interactions between solvent and monomer are not expected to occur and for which a linear dependence of $k_{p,app}$ on monomer concentration was determined. Data for MMA solution polymerizations are available for reactions in toluene,[7] 2-butanone,[7] and ethyl acetate.[5] These solvents are very similar in size to MMA, and no significant variation of $k_{p,app}$ was observed. Literature data for MMA polymerizations in diethyl phthalate,[10] which is larger in size than MMA, show a significant increase in $k_{p,app}$. For these systems $k_{p\infty}/k_{p,bulk}$ was calculated, and the data are also contained in Figure 6. These data are in excellent agreement with the correlation between $k_{p\infty}/k_{p,bulk}$ and $V_{mon} - V_{solv}$ derived in this work. It goes without saying that an analogues correlation is obtained if the ratio of ($k_{p\infty}c_M$) and ($k_{p,bulk}c_{M,bulk}$) is plotted as a function of $V_{mon} - V_{solv}$.

To test the correlation between solvent-induced changes in $k_{p,app}$ and the size of the monomer and solvent molecules, an additional approach was used to derive the volumes. Using the molecular modeling program Spartan ES, the monomer and solvent molecules were generated. Applying a MMFF94 force field, the geometries were optimized with respect to the conformation of the lowest energy. The coordinates of the atoms are used to calculate Connolly surfaces of each molecule with the program Molekel.[29,30] From these surfaces, the volumes of monomers and solvents are derived. Plotting $k_{p\infty}/k_{p,bulk}$ as a function of the difference in these volumes also results in a linear correlation, which is very close to Figure 6. The methods used to get a measure of the molecule volumes will be discussed in more detail in an upcoming paper.

If the data reported for MMA polymerizations in DMSO,[10] benzyl alcohol,[9] or an ionic liquid[11] are treated in the same way, the resulting values of $k_{p\infty}/k_{p,bulk}$ as a function of $V_{mon} - V_{solv}$ do not fit to the data presented in Figure 6. This is not overly surprising, since in these systems strong specific interactions are expected to occur. First results for systems where solvent and monomer molecules may undergo specific interactions also show a correlation of $k_{p\infty}/k_{p,bulk}$ with $V_{mon} - V_{solv}$; however, this correlation is different from the one presented in Figure 6. These results will be presented in an upcoming paper.

At first sight it may be anticipated that the correlation presented in Figure 6 may also serve as an explanation for the observed decrease in $k_{p,app}$ for MMA polymerizations in $scCO_2$. The difference in molar volumes of monomer and solvent is 60.5 $cm^3\ mol^{-1}$ at 40 °C. According to Figure 6, a decrease in k_p by about 20% is predicted. However, the reported CO_2 influence is significantly larger.[14] It should also be noted that, contrary to most systems studied in this publication, the variation of $k_{p,app}$ with MMA concentration in the MMA−CO_2 system does not follow a linear relation. As for the MMA−tetralin system studied here, this may be explained by the limited polymer solubility in $scCO_2$.[14] It is also noteworthy to point out that the values for MMA polymerizations in tetralin, $k_{p\infty}/k_{p,bulk} > 1.5$ and $V_{mon} - V_{solv} = -29.9$ $cm^3\ mol^{-1}$, do not fit to the correlation presented in Figure 6. The results for MMA $k_{p,app}$ in $scCO_2$[14] and in tetralin demonstrate that the correlation presented in Figure 6 does not hold for systems in which the polymer is only of limited solubility in the reaction medium.

All the data included in Figure 6 can be fitted by a straight line which may be used to predict $k_{p,app}$, at least qualitatively, for polymerizations in solution. It should be noted that the correlation shown in Figure 6 may be used to predict the solvent influence on the propagation rate to model polymerizations, as long as local monomer concentration at the active site is not yet available. It is remarkable that the solvent influence for these two rather different methacrylates may be described by the same linear fit.

The investigation into the solvent influence on the propagation rate will be extended to other methacrylate systems in order to check whether the findings presented in this work may be generalized. Besides using additional methacrylates with cyclic and alkyl ester groups, it is particularly interesting to study systems in which the difference in molar volumes of the monomer and the solvent, $|V_{mon} - V_{solv}|$, is very large. On the basis of the correlation depicted in Figure 6, formally a physically not meaningful negative value of $k_{p\infty}/k_{p,bulk}$ may be reached for $|V_{mon} - V_{solv}| > 226$ $cm^3\ mol^{-1}$. It may be anticipated that $k_{p\infty}/k_{p,bulk}$ deviates from the linear correlation at very large differences in V_{mon} and V_{solv}. In addition to the systems considered so far, it will be interesting to study systems in which the monomers carry long highly flexible groups, e.g., *n*-alkyl or Si-containing ester groups. Further, the use of highly flexible solvents, e.g., in the case of *n*-dodecyl methacrylate polymerizations, should be investigated.

The explanation of the solvent-induced changes of $k_{p,app}$ by the differences in molar volume is supported by the experimentally determined invariance of E_A for polymerizations in solution and in bulk. The difference in molar volumes of monomer and solvent is not expected to depend on temperature to a large extent for the temperatures applied in methacrylate PLP-SEC.

Conclusions

Solvent-induced changes in the experimentally derived propagation rate coefficients $k_{p,app}$ were observed for MMA and iBoMA homopolymerizations. While an enhancement of MMA $k_{p,app}$ was seen, a reduction in iBoMA $k_{p,app}$ of up to 52% was observed. For the systems under consideration, specific interactions between monomer and solvent were not expected, and the changes in $k_{p,app}$ were explained by the occurrence of local monomer concentrations $c_{M,loc}$ in the vicinity of the free-radical chain end. Thus, in the case of MMA solution polymerizations, $c_{M,loc}$ may be higher than the analytical monomer concentration and, on the contrary, in the case of iBoMA lower than c_M. The explanation is supported by the invariance of the activation energy in all cases. The variation in local monomer concentrations is suggested to originate from differences in molar volume of the monomer and the solvent. The data for both monomers may be represented by a linear correlation between $k_{p,\infty}/k_{p,bulk}$ and the difference in size of the molar volumes of monomer and solvent.

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Supporting Information Available: Tables S1 and S2 listing experimental conditions and results from pulsed laser free-radical polymerization of MMA and iBoMA, Figure S1 showing variation of $k_{p,app}$ with ratio of solvent and monomer concentration for iBoMA and MMA, and Figure S2 showing variation of $k_{p,app}{}^{-1}$ with solvent concentration for iBoMA and MMA. This material is available free of charge via the Internet at http://pubs.acs.org.

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