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Pulsed-Laser Polymerization of Methyl Methacrylate in Liquid and Supercritical Carbon Dioxide

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ABSTRACT: The free-radical propagation rate coefficients for methyl methacrylate (MMA) in liquid and supercritical carbon dioxide have been successfully determined using pulsed-laser polymerization (PLP) method. The effect of carbon dioxide solvency on the propagation rate coefficient, k_p, is examined at 180 bar for a temperature range of 20−80 °C. The temperature dependency of the obtained k_p data is evaluated by use of the Arrhenius equation. The resulting activation energy is (25.4 ± 1.2 kJ·mol^{-1}, and the preexponential factor is (5.2 ± 3.0 × 10^6 L·mol^{-1}·s^{-1}. These results are compared to the bulk activation parameters for the propagation rate coefficient of MMA as set forth by the IUPAC working party on “Modeling of Kinetics and Processes of Polymerization”. The discrepancy in the propagation rate coefficients at the lower temperature regime is attributed to a solvent effect of CO$_2$. This is consistent with the results from a recent PLP study of this monomer.

Introduction

Supercritical fluids, in particular supercritical carbon dioxide (scCO$_2$), have emerged as alternatives to traditional solvents for homogeneous[1] and heterogeneous free-radical polymerizations.[2−5] Several review articles on polymerizations in liquid and supercritical carbon dioxide have recently been published.[6−8] Much of the interest in scCO$_2$ has been driven by its inertness to free-radical reactions, relative low cost, environmentally benign potential, and its attraction as a replacement for many toxic liquid solvents. When CO$_2$ is raised above its critical point ($T_c = 31.1$ °C; $P_c = 73.8$ bar; $\rho_c = 0.472$ g/mL), its physicochemical properties (i.e., density, dielectric constant) can be tuned continuously between vaporlike and liquidlike limits by simply varying the system pressure and or temperature (Figure 1). Thus, scCO$_2$ offers an excellent means for controlling solvent properties over a considerable range without the need to physically change the solvent. Another intrinsic advantage of using carbon dioxide as a polymerization solvent is the fact that CO$_2$ can plasticize and swell many polymeric materials, allowing one to tune not only the solvent environment but potentially the glass transition temperature (T_g) and viscosity of the polymer-rich phases being formed.[9−13] Our recent studies from a series of heterogeneous systems[2−5] (e.g., dispersion polymerization) in CO$_2$ media indicate that the significant plasticization effects have a dramatic impact on diffusivities and hence termination rate coefficients. To quantify particle nucleation/growth kinetics in dispersion polymerizations in CO$_2$, as well as emulsion polymerizations in hybrid CO$_2$/aqueous media,[14] the effect of CO$_2$ on the propagation rate coefficient, k_p, needs to be determined. The *method of choice* for the determination of k_p as recommended by the IUPAC working party on *Modeling of Polymerization Kinetics and Processes* is pulsed-laser polymerization (PLP) in conjunction with size exclusion chromatography (SEC).[15−17]

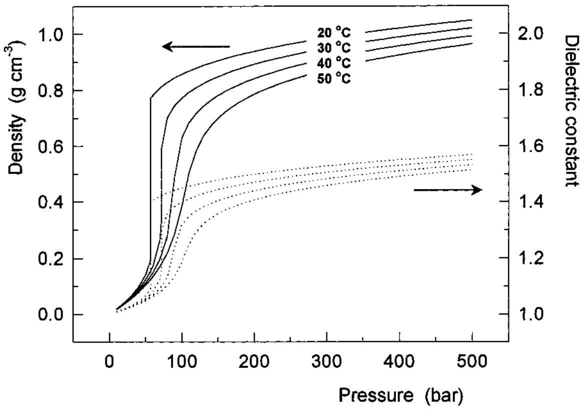

Figure 1. Dependence of CO$_2$ density and dielectric strength on pressure and temperature (solid line, calculated using the NIST equation of state;[29] dotted line, based on the Kirkwood−Frohlich equation[32]).

The PLP method is a relatively new and easy tool for the measurement of k_p in radical polymerizations, which is without model assumptions.[18] During a PLP experiment, laser pulses are used to create radicals from a photoinitiator. An instantaneous and large increase of the radical concentration results, which starts the growth of many new polymeric radical chains. These radical chains will partly terminate bimolecularly, but a significant portion of the radicals will survive until a new laser pulse generates new, small radicals. These new, highly mobile radicals will predominately terminate polymer chains initiated from previous pulses or will initiate new polymeric chains. The degree of polymerization for the chain initiated and terminated

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via the short laser pulses can be calculated simply by

$$L_i = i k_p [M] t_p \qquad (1)$$

where L_i is the chain length of the polymer formed in the time between two pulses, [M] is the monomer concentration, t_p is the time between two subsequent laser pulses determined by the laser frequency ($\nu_R = 1/t_p$), and $i = 1, 2, 3, ...$. As polymeric radical chains may survive the first successive pulse, they can be eventually terminated by the second or third or more subsequent pulses, thus yielding a polymer with a chain length which is an integer multiplication of the chain length of the polymer resulting after the first successive pulse ($i = 2, 3, ...$). Between two pulses, bimolecular termination or transfer can occur, which results in a polymer of which the chain length has no relation to the time between the pulses, the so-called background polymer. Analysis of the resulting molecular weight distribution (MWD) with SEC shows peaks from which the chain length of the polymer can be determined. Numerous simulations[18−21] have suggested that the inflection point at the low-molecular-weight side of the peak is the best measure of L_1.

Although most of the PLP studies conducted thus far have been for bulk monomer only, some studies have examined the possibility of solvent effects during solution polymerization. Determination of k_p for methyl methacrylate and styrene in solvents such as ethanol, methanol, ethylbenzene, and ethyl acetate has shown no observable solvent effects on k_p.[22,23] More recently, Zammit et al. have demonstrated that certain solvents such as benzyl alcohol and *N*-methylpyrrolidinone (NMP) can have an effect on k_p of MMA and styrene.[24] These authors showed that the solvent influences both the activation energy ($E_{act.}$) and the preexponential factor (A) in the Arrhenius expressions for the propagation reactions. The authors also showed no solvent effect on MMA and styrene for a wide variety of other solvents including diethyl malonate, diethyl phthalate, bromobenzene, benzonitrile, chlorobenzene, and dimethyl sulfoxide (DMSO).

We have recently published our initial PLP experiments in carbon dioxide conducted on MMA and styrene.[27] Herein we will report the detailed studies for determination of the Arrhenius activation parameters for the propagation rate coefficients of methyl methacrylate in CO_2 solution. We have obtained significantly more data for k_p at a CO_2 pressure of 180 bar over a wide temperature range. We will compare the results to IUPAC benchmark values determined in bulk MMA monomer system.

Experimental Section

Pulsed-laser experiments were preformed using a Lambda Physik LPX110iMC pulsed excimer laser at 308 nm (XeCl line) at a pulse energy of 40−100 mJ/pulse. The laser beam (dimensions of the area of highest intensity, 18 mm × 7 mm) directly irradiated the largest part of the sample inside the high-pressure cell. Other parts of the cell receive somewhat lower light intensities, but it is believed that this does not lead to considerable amounts of "background" polymer as also can be inferred from the absence of a considerable amount of high molecular weight material in the observed molecular weight distributions (see results). The 3.0 mL high-pressure view cell with sapphire windows (diameter, 17.5 mm) has been previously described,[27] in which the path length was 12 mm. Temperature was monitored with a Pt-100 resistance element inside the cell and temperature was constant during the experiment within ±1.0 °C. All experiments are run with a desired pulse repetition rate for a total time or the number of pulses sufficient to allow 0.5−3.0% conversion of monomer to polymer.

Methyl methacrylate (Aldrich, 99%) was deinhibited by passage through an alumina column, degassed by purging with argon flow, and stored in sealed flasks. The monomer was added to the system using a glass syringe. Carbon dioxide (SCF/SFE grade provided by Air Products & Chemicals and used as received) was introduced in the cell, which already contained the photoinitiator 2,2-dimethyl-2-phenylacetophenone (DMPA, Aldrich) and the monomer, with a manual syringe pump. The concentrations of the photoinitiator and the monomer were calculated with a cell volume of 3.0 mL. After the certain number of pulses, the reactor was cooled, the CO_2 was slowly vented from the cell, and the product was collected. The cell was rinsed with tetrahydrofuran (THF; Biosolve A. R.) in order to collect the resulting polymer. Monomer conversions were then determined gravimetrically.

To analyze the molecular weight distribution (MWD) of the polymer formed during the PLP experiments with SEC, 1.0% (w/v) solutions in THF were prepared of each sample. The solutions were filtered using 0.45 μm filters. The SEC analyses were carried out at 30 °C with two Ultrastyragel columns (10^3 and 10^4 Å porosities) and a microstyragel HT linear column. THF was used as the eluent at a flow rate of 1.0 $cm^3\ min^{-1}$. A Waters 410 differential refractometer and a Waters 996 UV-detector ($\lambda = 254$ nm) were used for detection. Narrow-distribution poly(methyl methacrylate) standards (American Polymer Standards Corp.) were used for calibration of the columns. The SEC chromatograms were converted into a differential log distribution [$w(\log M)$ vs $\log M$] according to the procedures described by Shortt[26] and curve smoothing for noise reduction. From these distributions the maximum of the analytically calculated first derivative of the curve was used as a measure of L_1.

Results and Discussion

To avoid the precipitation of the formed polymer in the solution during the PLP experiment, either relatively high monomer concentrations should be used (where the monomer will act as a cosolvent for the forming polymer) and/or higher laser frequencies where consequently low molecular weight samples are produced. When other conditions applied, broad featureless MWDs are generated. A typical SEC molecular weight distribution for MMA pulsed in carbon dioxide solution is shown as Figure 2, with the corresponding derivative plot. Duplicate experiments were performed at each temperature and pressure; agreement among each pair is excellent. The samples collected in the temperature range up to 80 °C exhibit MWD traces with clear, well-defined primary inflection points and observable second inflection points at twice the molecular weight. The molecular weight distributions are very similar to MWDs prepared in bulk PLP experiment, and the width of the peaks is also comparable.

Also seen are the effects of monomer concentration and laser frequency to the forming polymer chain length L_i according to eq 1. Figure 3 shows the impact of varying the MMA concentration on the molecular weight of the PMMA obtained at 25 °C. Decreasing the MMA concentration results in a decreased molecular weight and a decreased inflection point shifting to the lower molecular weight region. The same is true when the laser frequency was varied. Changing the laser frequency leads to consistent shifts in the position of the peaks[25] (Figure 4). Additionally, changes in laser energy and photoinitiator concentration do not seem to lead to systematic changes on the observed k_p values.[27]

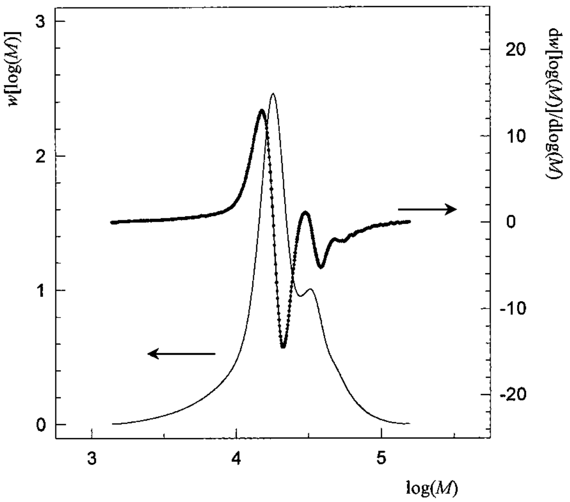

Figure 2. Molecular weight distribution (MWD) of poly(methyl methacrylate) (PMMA) prepared in $scCO_2$ by pulsed-laser polymerization with [DMPA] = 6.7 mmol·L^{-1}, [MMA] = 6.2 mol·L^{-1}, t_p = 0.1 s, T = 25 °C, and P = 180 bar. The inserted derivative d[w(log M)]/d(log M) is computed by analytically taking the first derivative of the MWD and plotted in arbitrary units (dotted line). w(log M) is the polymer weight fraction of the molecular weight.

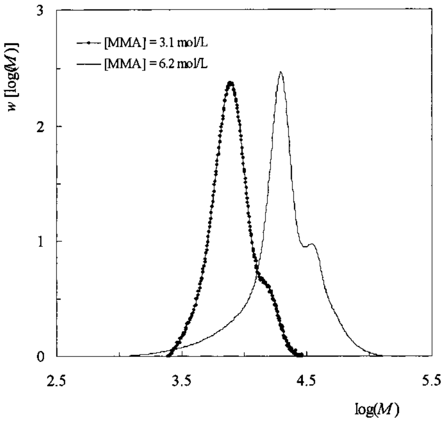

Figure 3. Molecular weight distribution (MWD) for PMMA produced in $scCO_2$ by pulsed-laser polymerization at two different monomer concentrations: [DMPA] = 6.7 mmol·L^{-1}, t_p = 0.1 s, T = 25 °C, and P = 180 bar.

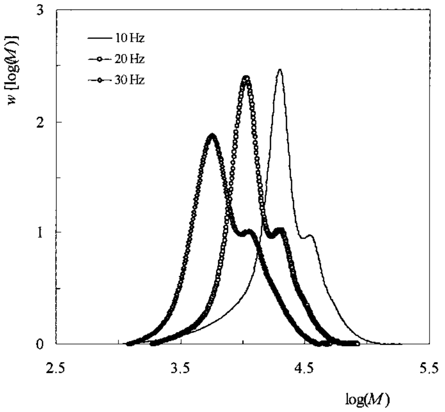

Figure 4. Molecular weight distribution (MWD) for PMMA produced in $scCO_2$ by pulsed-laser polymerization at various laser repetition frequencies: [DMPA] = 6.7 mmol·L^{-1}, [MMA] = 6.2 mol·L^{-1}, T = 25 °C, and P = 180 bar.

Our findings are in very good agreement with the consistency checks as recommended by the IUPAC.[16]

Table 1. Inflections Points and k_p Estimates for MMA in Carbon Dioxide Solution (Pulse Energy = 100 mJ/Pulse and [DMPA] = 6.7 mmol·L^{-1} [a])

T/°C	P/bar	[MMA]/-(mol·L^{-1})	ν_R[e]/s^{-1}	L_1	L_2	k_p/(L·mol^{-1}·s^{-1})
18.7	188	6.2	10	137	269	221[b]
19.9	174	6.2	10	123	253	198
20.5	174	6.2	10	125	256	202[b]
21.1	187	3.1	10	68	163	219[b,c]
21.2	184	3.1	10	57	143	184[b,c]
21.4	207	6.2	10	152	300	245
21.4	202	3.1	10	61	147	197[b,c]
21.7	164	3.1	10	61	171	197[b,c]
21.9	161	6.2	10	148	300	239
22.7	237	6.2	30	42	104	203[b]
23.2	153	6.2	10	147	296	237
23.3	204	6.2	25	57	134	230[b]
23.5	159	6.2	10	149	296	240
23.6	199	6.2	40	33	90	213[b]
23.7	168	6.2	10	156	319	252
23.8	171	6.2	10	140	283	226
23.9	160	6.2	10	168	327	271[b]
25.2	180	6.2	15	140	279	339[b]
25.3	195	6.2	20	84	184	271[b]
32.5	239	6.2	10	235	443	379[b]
33.6	155	6.2	10	203	382	327
34.8	151	6.2	10	211	411	340
40.1	162	6.2	10	253	462	408
40.8	223	6.2	10	285	522	460
41.9	153	6.2	10	318	580	513[b]
42.1	170	6.2	10	296	548	477[b]
44.5	181	6.2	10	329	605	531[b]
45.3	208	6.2	10	303	566	489
46.7	147	6.2	10	292	542	471
50.1	138	6.2	10	283	522	457
50.2	292	6.2	10	314	581	507
50.7	182	6.2	10	419	788	676[b]
50.9	218	6.2	10	330	606	532
53.7	148	6.2	10	296	574	477
55.1	158	6.2	10	371	707	598
60.0	160	6.2	10	348	671	561
60.6	159	6.2	10	544	1041	877[b]
60.8	181	6.2	10	394	752	636
62.9	231	6.2	10	570	1106	919[b]
63.0	192	6.2	20	337	618	1087[b]
63.6	148	6.2	30	246	456	1190[b]
66.4	156	6.2	50	65	126	1020[d]
66.5	162	6.2	10	736	1502	1150[d]
67.0	196	6.2	50	116	243	905[d]
65.3	143	6.2	10	462	878	745
67.7	179	6.2	10	618	1250	997[b]
66.3	151	6.2	10	417	780	673
69.0	160	6.2	10	458	928	739
76.3	150	6.2	10	562	1178	907

[a] DMPA, 2,2-dimethoxy-2-phenylacetophenone. [b] Pulse energy = 40 mJ/pulse. [c] [DMPA] = 3.3 mmol·L^{-1}. [d] Reference 27. [e] $\nu_R = 1/t_p$.

The results for the inflection points and the k_p estimates are given in Table 1. To cancel out the differences in pressure, we used the activation volume determined by Buback et al.[28] at 30 °C ($\Delta V^{\ddagger}$ (k_p) = −(16.7 ± 1.1) cm^3·mol^{-1}) and corrected the k_p values to a pressure of 1 bar assuming a temperature independent value of $\Delta V^{\ddagger}$. The corrected data are shown in Figure 5. These data were then fitted with the Arrhenius equation using a nonlinear regression procedure with relative error minimization.[30] The resulting Arrhenius parameters are $A = (5.2 \pm 3.0) \times 10^6$ L·mol^{-1}·s^{-1} and $E_{act.} = 25.4 \pm 1.2$ kJ·mol^{-1} (quoted errors are estimated standard deviations); the parameters with the corresponding joint confidence interval are shown in Figure 6. The Arrhenius parameters for bulk polymerization[17] are $A = (2.65 \pm 0.30) \times 10^6$ L·mol^{-1}·s^{-1} and $E_{act.} = 22.35 \pm 0.31$ kJ·mol^{-1}.

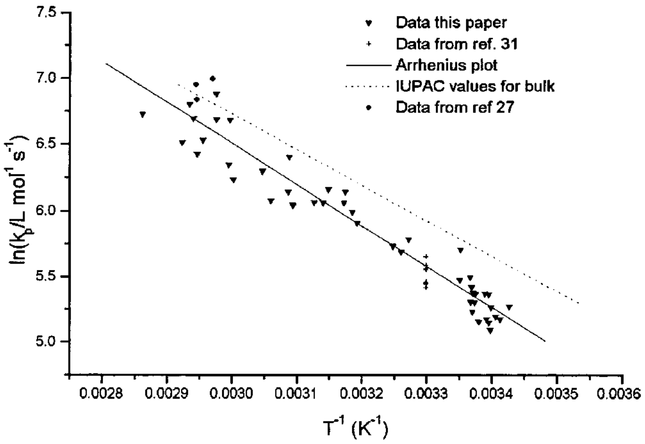

Figure 5. Arrhenius plot of the propagation rate coefficient k_p for methyl methacrylate as determined by PLP.

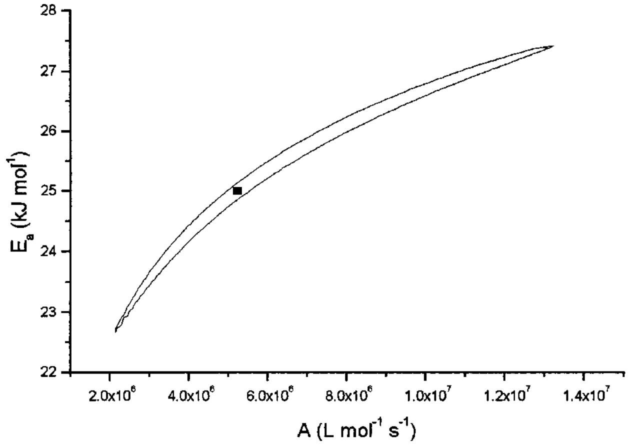

Figure 6. 95% confidence interval for the activation parameters A (preexponential factor) and $E_{act.}$ (activation energy) for the propagation rate constant k_p of methyl methacrylate obtained from nonlinear regression with relative error minimization.

In Figure 5 the original data from ref 27 are also included. Recently Beuerman et al. investigated the k_p values of MMA in CO_2 at high pressure (1000 bar) and found a lowering of k_p as compared to the bulk values.[31] For comparison these data were also corrected for pressure. From Figure 5 it can be seen that at higher temperatures the k_p values in CO_2 and in bulk do not differ very much. However, at lower temperatures a clear trend is observed. The k_p values in CO_2 are lower than in bulk. This is consistent with the fact that the main difference between the bulk and the CO_2 activation parameters can be found in the activation energy. A similar conclusion was reached by Beuerman et al.[31] This solvent effect is also illustrated by the fact that these authors found that there is a slight dependence on monomer concentration of k_p in CO_2. After correction for pressure, the k_p data of Beuerman et al. obtained at 1000 bar and 30 °C coincide nicely with our data.

Some of the data in Table 1 and Figure 5 are obtained independently in a different laboratory (see ref 27) with other GPC equipment. This introduces additional small systematic differences stemming from differences in calibration and instrumental broadening for example. Excluding these data from the fit could lead to smaller joint confidence intervals for the activation parameters ($A = (3.8 \pm 2) \times 10^6\ \mathrm{L{\cdot}mol^{-1}{\cdot}s^{-1}}$ and $E_{act.} = 24.2 \pm 1.3\ \mathrm{kJ{\cdot}mol^{-1}}$), but we believe this would lead to an overestimation of the accuracy of the activation parameters.

The reduction of k_p upon adding CO_2 to pure MMA may, at least in part, be attributed to the compressibility of the supercritical phase: Increasing the density at constant volume leads to an increasing number of inert solvent molecules and mimics the effect of dilution in conventional solvents[33] ("Ziegler–Ruggli's dilution principle"), favoring intramolecular interaction or other reaction pathways. Since CO_2 is a poor solvent for poly(methyl methacrylate), it may significantly cause a globule-to-coil transition leading to a more collapsed coil state with higher segmental density. Consequently, the free-radical chain end may be shielded within the tightly coiled macroradical, and thus monomer diffusion into the free-radical site may be hindered to a certain extent.

Because of the presence of this solvent effect, it may be expected that the pressure, which clearly can affect the solvent quality of CO_2, also will influence the activation parameters. Therefore a more extensive study, where also pressure is varied, is needed. A remark can be made about the scatter in the data, which is somewhat larger than usual. The fact that there is a solvent effect means that the corrections for pressure assuming a constant volume of activation are not completely correct. Furthermore comparing k_p values obtained at different monomer concentrations can also introduce differences as a consequence of the observed solvent effects.

Conclusions

Propagation rate coefficients of methyl methacrylate have been determined over a temperature range of 20–80 °C at 180 bar in carbon dioxide. The obtained k_p data were fitted with the Arrhenius equation. The resulting Arrhenius parameters are $A = (5.2 \pm 3.0) \times 10^6\ \mathrm{L{\cdot}mol^{-1}{\cdot}s^{-1}}$ and $E_{act.} = (25.4 \pm 1.2)\ \mathrm{kJ{\cdot}mol^{-1}}$ converted to a pressure of 1 bar using a volume of activation of $-16.7\ \mathrm{cm^3{\cdot}mol^{-1}}$. At lower temperatures the k_p values are somewhat lower than the corresponding bulk values indicating a solvent effect. These data are in agreement with other literature data. It is expected that, because of the presence of a solvent effect, changing the pressure will affect the activation parameters.

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