# Propagation Rate Coefficients of Styrene and Methyl Methacrylate in Supercritical $CO_2$

**Alex M. van Herk* and Bart G. Manders**

*Eindhoven University of Technology,*
*Laboratory of Polymer Chemistry, P.O. Box 513,*
*5600 MB Eindhoven, The Netherlands*

**Dorian A. Canelas, Murat A. Quadir, and**
**Joseph M. DeSimone***

*University of North Carolina at Chapel Hill,*
*Department of Chemistry, CB# 3290, Venable and Kenan*
*Laboratories, Chapel Hill, North Carolina 27599-3290*

*Received March 12, 1997*
*Revised Manuscript Received June 11, 1997*

**Introduction.** Near-critical or supercritical carbon dioxide is rapidly becoming an attractive alternative as a continuous phase in homogeneous[1] and heterogeneous radical polymerizations.[2] A review on chain polymerizations in supercritical fluids appeared recently.[3] At present, $CO_2$ offers an environmentally sound solvent choice. Advantages offered include that the polymer can be easily separated from the reaction medium, the $CO_2$ can easily be recycled, and there is effectively no chain transfer to $CO_2$ for free-radical reactions.[3] In order to model the kinetics of homogeneous and heterogeneous free-radical polymerizations, it is necessary to obtain important kinetic coefficients like the initiation, propagation, and termination rate coefficients in $CO_2$. It must be realized that $CO_2$ is in general a poor solvent for most polymers except for amorphous or low-melting fluoropolymers and siloxanes. Therefore, the first references to free-radical polymerizations in $CO_2$ typically deal with precipitation polymerizations.[4]

Homogeneous polymerizations in supercritical $CO_2$ have been performed for fluorinated monomers.[1] The decomposition kinetics and initiator efficiencies in $CO_2$ differ from that in other media. The rate constant for AIBN decomposition was 2.5 times slower in $CO_2$ than in benzene. This was attributed to the low dielectric constant of $CO_2$ relative to benzene. Initiator efficiencies were very high ($>80\%$) as a consequence of negligible solvent cage effects in supercritical $CO_2$, as this medium has a very low viscosity.[1,6] Some early kinetic studies on the $\gamma$-radiation-induced precipitation polymerization of ethylene in liquid carbon dioxide[5] showed that there were no large effects on the propagation rate as compared to bulk polymerizations. In heterogeneous polymerization in the presence of $CO_2$, the large plasticization effects have a dramatic effect on diffusivities[7,8] and hence termination rate coefficients.

In order to understand dispersion polymerizations in $CO_2$,[1] as well as the effect of $CO_2$ in emulsion polymerizations in hybrid $CO_2$/aqueous media, the monomer partitioning needs to be determined. In the case of the hybrid system, it is very hard to determine the monomer concentrations in polymer particles under pressurized conditions. One method that might be successful is pulsed electron beam polymerization where the analysis of the molecular weight distribution yields the product of the propagation rate coefficient and the local monomer concentration.[9] This method is currently under investigation in the Eindhoven laboratories, but in order to successfully apply this method to hybrid systems we need to know the effect of the presence of $CO_2$ on the propagation rate coefficient ($k_p$). The method of choice for the determination of $k_p$ as recommended by the IUPAC working party on "Radical Polymerization Kinetics and Processes" is pulsed laser polymerization (PLP) in combination with size exclusion chromatography (SEC).[10−12]

This method comprises the generation of radicals through a photoinitiator, activated by a laser pulse. The time of growth of many polymer chains is directly determined by the time between pulses. Chains that are initiated at the moment that a pulse arrives and are terminated by radicals that are formed at the next pulse form the characteristic PLP peaks in the molecular weight distribution. From the chain length of these chains, this experiment gives direct access to $k_p$. This degree of propagation for the chains initiated and terminated by short pulses of radicals induced by light (in combination with a photoinitiator) or radical-generating radiation like electron beams or $\gamma$-radiation is given by the simple equation:[13]

$$L_{0,i} = ik_p[\mathrm{M}]t_p \qquad (1)$$

where $L_{0,i}$ is the chain length of the polymer formed in the time between two radical pulses, [M] is the monomer concentration, $t_p$ is the time between two subsequent radical pulses determined by the laser frequency ($\nu = 1/t_p$), and $i = 1, 2, 3, ...$ The higher order peaks ($i = 2, 3, ...$) may occur when growing chains survive termination by one or more subsequent pulses. In 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. Olaj[13] suggested that the inflection point at the low molecular weight side of the peaks gives a good measure for $k_p$.

The PLP method has been successfully applied in the Eindhoven group.[14]

IUPAC benchmark values are now published for styrene and methyl methacrylate.[11,12] Here we report the propagation rate coefficients of styrene (Sty) and methyl methacrylate (MMA) in a $CO_2$ solution.

**Experimental Section.** Pulsed laser experiments were performed using a Lambda Physik LPX110iMC pulsed excimer laser at 351 nm (XeF line) with pulse energies of 40 mJ. The laser beam (with dimensions of 18 mm × 7 mm) directly irradiated the sample inside the high-pressure cell. The 2.9 mL high-pressure view cell with sapphire windows (diameter 17.5 mm) has been previously described,[15] in which the path length was 12 mm. Temperature was monitored with a Pt-100 resistance element inside the cell and temperatures were constant during the experiment within ±0.2 °C.

Styrene (Sty, Shell, distilled under reduced pressure) and methyl methacrylate (MMA, Aldrich, 99%) were further purified by passage through an inhibitor-removing column (Aldrich). The monomer was added to the system using a glass syringe. Carbon dioxide (Hoekloos 5.5) was introduced in the cell, which already contained the photoinitiator 2,2-dimethoxy-2-phenylacetophenone (DMPA, Ciba Geigy) and the monomer, with a hand syringe pump. The concentration of the photoinitiator and the monomer was calculated with a cell volume of 2.9 mL. After the desired number of pulses, the reactor was cooled and the $CO_2$ was slowly vented from the cell, after which the product was collected. The cell was rinsed with tetrahydrofuran (THF, stabilized, Biosolve, A.R.) in order to collect the resulting polymer. Monomer

---

* Authors to whom correspondence should be addressed.

S0024-9297(97)00341-0 CCC: $14.00

**Table 1. Propagation Rate Coefficients in Supercritical Carbon Dioxide Obtained by the PLP Method**

| | *P*, bar | *T*, °C | $\nu$, Hz | [DMPA], M | [mon], M | no. of pulses | conv, % | infl point, g mol$^{-1}$ | $k_p^{obs}$, M$^{-1}$ s$^{-1}$ | $k_p^{theor}$, M$^{-1}$ s$^{-1}$ |
|---|---|---|---|---|---|---|---|---|---|---|
| MMA[a] | 153 | 25 | 2 | 0.01 | 3.2 | 1000 | 0.3 | | | 358 |
| MMA[b] | 169 | 63.3 | 2 | 0.01 | 6.4 | 1000 | 5.7 | ≈250 000 | 780 | 997 |
| MMA | 162 | 66.5 | 10 | 0.01 | 6.4 | 1000 | 3 | 73 700 | 1150 | 1069 |
| MMA | 156 | 66.4 | 50 | 0.01 | 3.2 | 1000 | 1.6 | 6 540 | 1020 | 1062 |
| MMA[c] | 196 | 67 | 50 | 0.01 | 6.4 | 1000 | 2.4 | 11 600 | 905 | 1103 |
| MMA[d] | 196 | 67 | 50 | 0.01 | 6.4 | 1000 | 2.4 | 24 300 | 948 | 1103 |
| Sty | 187 | 65.1 | 2 | 0.001 | 5.7 | 500 | 0.4 | 124 600 | 420 | 441 |
| Sty | 164 | 65.8 | 10 | 0.001 | 2.85 | 500 | 0.6 | 13 850 | 467 | 447 |
| Sty | 181 | 65.1 | 10 | 0.1 | 5.7 | 500 | 2.7 | 29 280 | 494 | 440 |

[a] No sharp peaks visible. [b] Unclear PLP peaks. [c] First low molecular weight inflection point ($i = 1$ in eq 1). [d] Second inflection point ($i = 2$ in eq 1).

conversions were determined gravimetrically and were generally below 3%.

To analyze the molecular weight distribution (MWD) of the polymer with SEC, 1 w/v-‰ solutions in THF were prepared of each sample. The solutions were filtered over 0.2 $\mu$m filters. The SEC analyses were carried out with four PL-Gel (mixed B) columns at 40 °C and a flow rate of THF of 1 cm$^3$ min$^{-1}$. A Waters 410 differential refractometer and a Waters 440 UV detector (operated at $\lambda = 254$ nm) were used for detection. Narrow-distribution polystyrene and poly(methyl methacrylate) standards (Polymer Labs) were used for calibration of the columns. The SEC chromatograms (refractometer signals) were converted into a differential log distribution [$w(\log M)$ vs $\log M$] according to the procedures described by Shortt[16] and fitted with a cubic spline for noise reduction. From these distributions the maximum of the analytically calculated first derivative of the cubic spline fit was used as a measure of $L_0$.

**Results and Discussion.** The IUPAC-recommended activation parameters for the propagation rate coefficient of styrene are[11] $A = 4.27 \times 10^7$ mol$^{-1}$ L s$^{-1}$ and $E_a = 32.51$ kJ mol$^{-1}$. And for methyl methacrylate they are[12] $A = 2.65 \times 10^6$ mol$^{-1}$ L s$^{-1}$ and $E_a = 22.34$ kJ mol$^{-1}$. Values for the volume of activation are $\Delta V^\ddagger$ (Sty) $= -12$ cm$^3$ mol$^{-1}$ (30 °C)[17] and $\Delta V^\ddagger$ (MMA) $= -17$ cm$^3$ mol$^{-1}$ (30 °C).[18] With these activation parameters, the expected propagation rate coefficients under our reaction conditions were calculated (Table 1, $k_p^{theor}$) by assuming that the activation parameters are independent of pressure and temperature.

In order keep the formed polymer in solution during the PLP experiment, either relatively high monomer concentrations are needed (where the monomer acts as a cosolvent for the forming polymer) and/or conditions where relatively low molecular weight material is produced (higher frequencies). When other conditions were applied, broad featureless MWDs were obtained. In Figure 1 MWDs of polymer from PLP experiments with styrene and MMA are shown. The MWDs are very similar to MWDs produced in bulk PLP experiments, and the width of the peaks is also very similar.[14] In Table 1 a summary of the experimental results is given. Changes in frequency and monomer concentration lead to the expected shifts in the low molecular weight inflection points according to eq 1. Also, changes in photoinitiator concentration do not lead to systematic changes in the observed $k_p$ values, complying with the consistency checks as recommended by the IUPAC.[11]

From the table it can be concluded that the propagation rate coefficients of styrene and methyl methacrylate in supercritical CO$_2$ do not change as compared to the bulk propagation rate coefficients (corrected for pressure effects with the volumes of activation). At an average temperature of 65 °C and an average pressure of 180 bar for styrene, an average over three experiments gives $k_p = 460(\pm 15\%)$ L mol$^{-1}$ s$^{-1}$. At an average temperature of 67 °C and an average pressure of 180 bar for MMA, an average over three experiments (four inflection points) gives $k_p = 1030(\pm 15\%)$ L mol$^{-1}$ s$^{-1}$. Both values compare well with the expected values, when averaged over the experimental conditions. In bulk the values are 440 and 1080 L mol$^{-1}$ s$^{-1}$ for Sty and MMA, respectively.

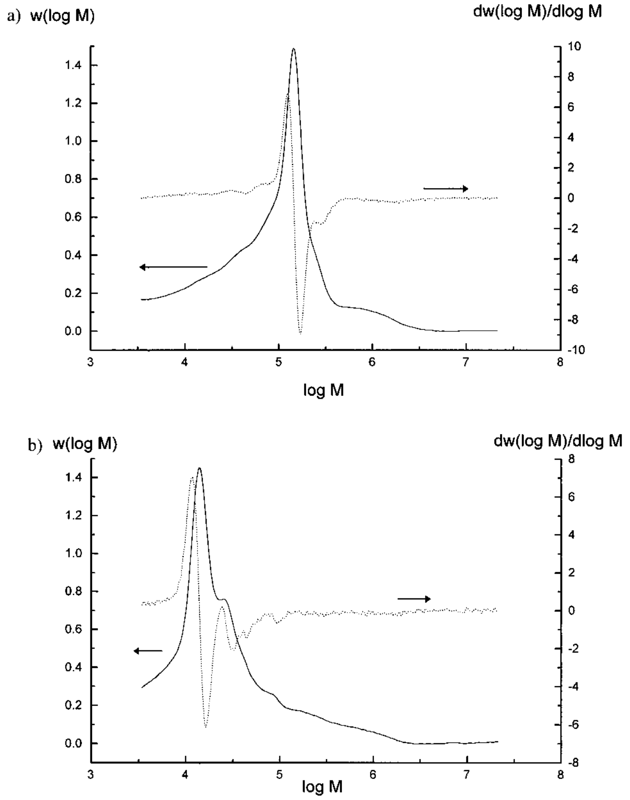

**Figure 1.** Experimental molecular weight distribution (MWD) for a pulsed laser polymerization in supercritical CO$_2$: (a) 5.7 mol L$^{-1}$ Sty, laser frequency 2 Hz, $T = 65.1$ °C, $P = 187$ bar, [DMPA] = 0.001 mol L$^{-1}$; (b) 6.4 mol L$^{-1}$ MMA, laser frequency 50 Hz, $T = 67$ °C, $P = 196$ bar, [DMPA] = 0.01 mol L$^{-1}$. The inserted derivative d($w(\log M)$/d($\log M$) is computed by analytically taking the first derivative of a cubic spline function fitted through the MWD and plotted in arbitrary units (dotted line). $w(\log M)$ is the polymer weight fraction of the molecular weight.

In principle, solvent effects for the propagation rate coefficients of styrene and methyl methacrylate are not expected to be large. These experiments in supercritical CO$_2$ confirm this theory, although one must realize that the density (≈0.5 g cm$^{-3}$) and the dielectric constant of pure $CO_2$ under these conditions are much lower than conventional solvents.

Although an extensive study of temperature and pressure effects on the propagation rate coefficients in supercritical $CO_2$ is under way, no large solvents effects are to be expected and bulk propagation rate coefficients apparently can be used for $CO_2$. Such observations should facilitate the design of pilot scale equipment and processes that utilize $CO_2$ as the polymerization medium.

## References and Notes

(1) DeSimone, J. M.; Guan, Z.; Elsbend C. S. *Science* **1992**, *257*, 945.

(2) See for example: DeSimone, J. M.; Maury, E. E.; Menceloglu, Y. Z.; McClain, J. B.; Romack, T. R.; Combes, J. R. *Science* **1994**, *265*, 356. Canelas, D. A.; Betts, D. E.; DeSimone, J. M. *Macromolecules* **1996**, *29*, 2818.

(3) Shaffer, K. A.; DeSimone, J. M. *Trends Polym. Sci.* **1995**, *3*, 146.

(4) Fukui, K.; Kagiya, T.; Jokota, H.; Toriuchi, Y.; Kuaiyoshi, F. U.S. Patent 3,522,228, 1970.

(5) Hagiwara, M.; Mitsui, H.; Machi, S.; Kagiya, T. *J. Polym. Sci., Polym. Chem. Ed.* **1968**, *6*, 721.

(6) Guan, Z.; Combes, J. R.; Menceloglu, Y. Z.; DeSimone, J. M. *Macromolecules* **1993**, *26*, 2663.

(7) Condo, P. D.; Paul, D. R.; Johnston, K. P. *Macromolecules* **1994**, *27*, 365.

(8) Chapman, B. R.; Gochanour, C. R.; Paulaitis, M. E. *Macromolecules* **1996**, *29*, 5635.

(9) van Herk, A. M.; de Brouwer, H.; Manders, B. G.; Luthjens, L. H.; Hom, M. L.; Hummel, A. *Macromolecules* **1996**, *29*, 1027.

(10) Gilbert, R. G. *Pure Appl. Chem.* **1996**, *68*, 1491.

(11) Buback, M.; Gilbert, R. G.; Hutchinson, R. A.; Klumperman, B.; Kuchta, F. D.; Manders, B. G.; O'Driscoll, K. F.; Russell, G. T.; Schweer, J. *Macromol. Chem. Phys.* **1995**, *96*, 3267.

(12) Beuermann, S.; Buback, M.; Davis, T. P.; Gilbert, R. G.; Hutchinson, R. A.; Olaj, O. F.; Russell, G. T.; Schweer, J.; Van Herk, A. M. *Macromol. Chem. Phys.* **1997**, *198*, 1545.

(13) Olaj, O. F.; Bitai, I.; Hinkelmann, F. *Makromol. Chem.* **1987**, *188*, 1689.

(14) Manders, B. G.; Chambard, G.; Kingma, W. J.; Klumperman, B.; van Herk, A. M.; German, A. L. *J. Polym. Sci., Polym. Chem. Ed.* **1996**, *34*, 2473.

(15) Lemert, R. M.; DeSimone, J. M. *J. Supercrit. Fluids* **1991**, *4*, 186.

(16) Shortt, D. W. *J. Liquid Chromatogr.* **1993**, *16*, 3371.

(17) Buback, M.; Kuchta, F. D. *Macromol. Chem. Phys.* **1996**, *196*, 1887.

(18) Beuermann, S.; Buback, M.; Russell, G. T. *Macromol. Rapid Commun.* **1994**, *15*, 351.

MA9703416