

The Effect of CO₂ in Free-radical Polymerization of 2,2,2-Trifluoroethyl Methacrylate

Soyoung Kwon, Won Bae and Hwayong Kim[†]

School of Chemical Engineering & Institute of Chemical Processes, Seoul National University, Seoul 151-744, Korea

(Received 19 December 2003 • accepted 23 April 2004)

Abstract—Carbon dioxide is an effective diluent for increasing the free volume of polymer. It has useful advantages with reductions of viscosity, surface tension and with an increase of diffusion into polymer. These properties are available in polymer processing and particle designing. We carried out free-radical polymerization of 2,2,2-trifluoroethyl methacrylate (TFEMA) with AIBN as the initiator in carbon dioxide. This experiment was performed at fixed temperature (343 K), stirring speed and weight of monomer+initiator. Only weight ratios of carbon dioxide were changed. Molecular weight and T_g showed a minimum at 14.1 MPa and increased in the higher final pressure.

Key words: Carbon Dioxide, Free-radical Polymerization, 2,2,2-Trifluoroethyl Methacrylate, Plasticization

INTRODUCTION

Supercritical carbon dioxide has been widely investigated in the past decade as an alternative solvent for polymer synthesis. It has been possible to use both for radical chain polymerization and step polymerization [Ajzenberg et al., 2000; Kendall et al., 1999]. Main advantages to using CO₂ as a polymerization medium are that it is less-toxic, non-flammable, chemically inert and more naturally abundant than many other organic solvents [Song et al., 2002]. CO₂ can be removed by simple depressurization and the density of the solvent can be tuned by varying pressure [Ajzenberg et al., 2000; Cooper, 2000; Beckman, 2003].

CO₂ offers mass transfer advantages compared with conventional organic solvents because of its low viscosity and surface tension, but it has limitative solubilities. It is a poor solvent for most polymers of high molecular weight, whether polar or nonpolar [Ajzenberg et al., 2000; Cooper, 2000; Beckman, 2003]. Despite the fact that it has a poor solubility for high molecular weight polymers, CO₂ is an ideal solvent to use in polymerization because it does not support any detectable chain transfer to solvent during free-radical polymerization and it is non-reactive in process [Beckman, 2003].

An important feature of CO₂ on polymerization is plasticization, which results in the lowering viscosity of polymer melt by increasing free volume between the polymer segments [Kendall et al., 1999]. Particularly in heterogeneous free-radical polymerization, plasticization may facilitate diffusion of monomer and initiator into the polymer phase [Cooper, 2000; Kendall et al., 1999]. Plasticization effect is useful for polymer synthesis and processing. Because CO₂ is a non-toxic and easily separated material, it is more profitable than other solvents as a plasticizer while being a poor solvent for the polymer [Ajzenberg et al., 2000]. This plasticizing effect for polymer can be varied with the pressure of CO₂. Condensation polymerizations in various pressure of CO₂ have been already known. Many industrial condensation polymerizations are carried out without the use of organic solvents [Kendall et al., 1999]. They have difficulties in stirring and processing due to high viscosity of polymer melts.

But swelling and plasticization by CO₂ tend to produce a significant reduction of viscosity, enhancing mobility of both the condensate and polymer chain ends [Kendall et al., 1999]. The presence of CO₂ at various pressures would lower the reaction rate. But it might also allow the reaction to attain maximum conversion to product. Teng et al. [2002] have performed free-radical polymerization of acrylonitrile in supercritical carbon dioxide. They have shown the effect of CO₂ on molecular weight and molecular weight distribution in pressure range from 14.5 to 33.1 MPa [Teng et al., 2002]. It is found that the change of the pressure did not affect the polymer yield, but increased the average molecular weight as the pressure increased. With these effects of CO₂ on polymerization, we focused on synthesis of polymer containing fluorine group. In amorphous fluoropolymer polymerization, CO₂ has relatively a good solubility and may have special interactions with the fluorine group [Cooper, 2000; Kendall et al., 1999].

2,2,2-trifluoroethyl methacrylate (TFEMA) has features of typical methacrylate monomers and fluorine-containing monomer simultaneously. The homopolymer of TFEMA is a transparent and amorphous polymer that has excellent water repellency and stain resistance because it contains fluorine in its side chain [Kato, 2003]. Poly (TFEMA) is used in various coating applications because of excellent heat and chemical resistance, low refractive index, weatherability, non-cohesiveness, water and oil repellency, and electric insulating properties [Kato, 2003; Ciardelli et al., 1994]. It is easily produced by free radical polymerization using bulk, solution and emulsion polymerization methods [Ciardelli et al., 1994]. Feasible organic solvents in these polymerizations are THF, 1,4-dioxane and toluene etc. But these techniques using organic solvents except bulk polymerization require separation of the polymer from polymer-solvent mixture to obtain a free flowing powder. Then, large quantities of waste volatile organic compounds are generated and an additional process to separate and recycle these solvents is needed.

The objective of this study was to understand the effects of CO₂ on molecular weight, T_g and viscosity in free radical polymerization of 2,2,2-trifluoroethyl methacrylate at various pressures (from atmospheric pressure to 34.1 MPa).

EXPERIMENTS

[†]To whom correspondence should be addressed.

E-mail: hwayongk@snu.ac.kr

1. Materials

2,2,2-trifluoroethyl methacrylate (Aldrich, min 99+%) was pretreated through alumina column in order to remove inhibitor (MEHQ). 2,2'-azobisisobutyronitrile (AIBN, Junsei Chemical, min 98%) was recrystallized from methanol. Carbon dioxide (min 99.99%) was purchased from Korea Industrial Gases co. 1,4-dioxane (Daejung chemicals and metals Co., Ltd., min 99%) was degassed to remove residual gas under nitrogen. Tetrahydrofuran (THF, Samchun chemical, min 99.5%) and toluene (Junsei chemical co., LTD., min 99%) were used without further purification.

2. Polymerization

Polymerizations of 2,2,2-trifluoroethyl methacrylate (TFEMA) were carried out in a 30 mL SUS 316 reactor with two windows at both-sides. Typically 4.0 g of TFEMA and 0.04 g of AIBN (1 wt% of monomer) were added to the autoclave equipped with PTFE coated magnetic stirring bar. Then the reactor was purged by N₂ several times to remove residual air. CO₂ was charged with a cylinder at room temperature. Weight of adding CO₂ was determined with a difference of weighing cylinder before and after charging. The reactor was then heated to 343 K, which was held for 24 hrs. Pressure was measured with bourdon tube pressure gauge (WIKA, type 213.53.063, accuracy class 1.0). Temperature was measured with K (CA) type thermocouple (accuracy ± 0.05 K) and an indicator (Hanyoung Electronics Inc. Model DX-7). THF, toluene and 1,4-dioxane were used as polymerization media with same reaction conditions to compare with CO₂ for the solvent. After polymerization, the reactor was cooled down to room temperature and CO₂ was slowly vented through two glass traps. To prevent discharge of unreacted monomer to atmosphere during CO₂ separation, glass traps filled with cold methanol were used. A small amount of product was sampled to estimate conversion of monomer to polymer by using ¹H-NMR spectra. Equally, 1.0 g of remaining products in all experiments was washed with ethanol to remove unreacted monomer and collected by filtration. Finally, the resulting polymer was dried in vacuum at room temperature. Monomer conversion was determined with this gravimetric analysis.

3. Polymer Characterization

To confirm chemical structure of polymer, ¹H-NMR (Bruker, 300 MHz, CDCl₃ as a solvent) and FT-IR (AVATAR 360ESP) were used. Also, Residual monomer was detected by the relative intensities of polymer and monomer at the same functional group with NMR spectra. Thermal properties of polymers were investigated by using DSC (Perkin Elmer DSC7, heating and cooling rate of 10 K/min). Molecular weight and distribution of polymers were obtained by gel permeation chromatography (Waters, 600E controller) with a RI detector (Waters, 410) and three columns (Styragel[®] HT2, HT3, HT4). THF was used as the eluent at 40 °C. Narrow MWD PMMA was used as a standard material.

RESULTS AND DISCUSSIONS

The polymerization of TFEMA in various ratios of CO₂ to monomer resulted in different products from rigid solid state to very adhesive liquid-like state. Poly (TFEMA) was insoluble at this reaction pressure (by near 34.1 MPa). The initial pressure at 343 K was lower than about 24 MPa. It is found that the pressure in reactor increased with the progress of polymerization. When the pressure

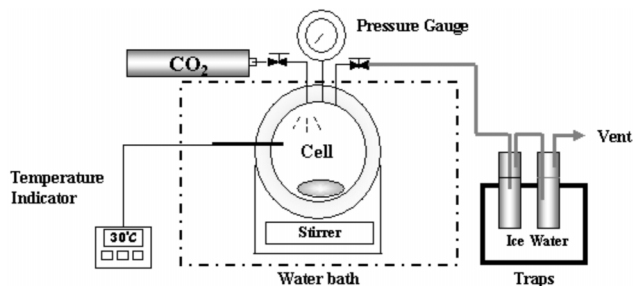


Fig. 1. Schematic diagram of the polymerization apparatus.

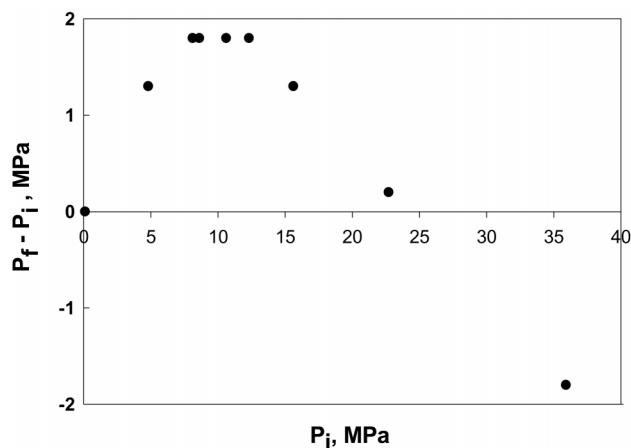


Fig. 2. Pressure variations in polymerization (P_i =initial pressure at 343 K, P_f =final pressure after 24 hrs (reaction time), $\Delta P = P_f - P_i$).

reached about 24 MPa, the final pressure decreased. Dispersion polymerization of methyl methacrylate showed a similar result with such pressure changes [Chatzidoukas et al., 2003]. Pressure changes can be explained by change of volume upon polymerization. The molar volume of a vinyl monomer is generally higher than that of the polymer. In constant volume system, the change of volume between the vinyl monomer and polymer upon polymerization prompted a change in pressure. Pressure variations might be attributed to the nonideal mixing behavior of monomer+CO₂+polymer system. Chatzidoukas et al. [2003] investigated such experimental tendency during polymerization of MMA. In Fig. 2, the pressure deviation between the final and initial pressures is plotted with P_i (initial pressure). Chemical structures of monomer, polymer, and residual monomer before ethanol washing were confirmed by ¹H-NMR in Fig. 3. Fig. 4 shows ¹H NMR spectrum during polymerization of TFEMA for various ratios of CO₂ to monomer. As increasing CO₂ weight ratio, monomer spectra ($-\text{CH}_2$, $-\text{CH}_2\text{CF}_3$) increased and again decreased. This tendency was similar to monomer conversion. Table 1 shows molecular weight of polymer, conversion and T_g with several ratios of CO₂ to monomer. These represented same tendency that again increased after showing the minimum value with gradually charging CO₂. This result is shown in Fig. 5 by various pressures. This reason might be the effect of high pressure of CO₂. Pressure had two competing effects on heterogeneous polymerization kinetics [Charpentier et al., 2000; Wang and Kanner, 1982]. Increasing pressure decreased the free volume of the polymer through a

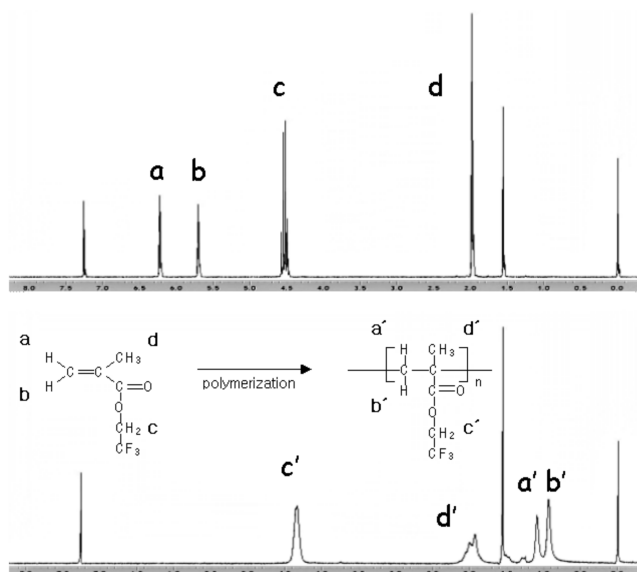


Fig. 3. ^1H -NMR spectra of TFEMA and poly (TFEMA).

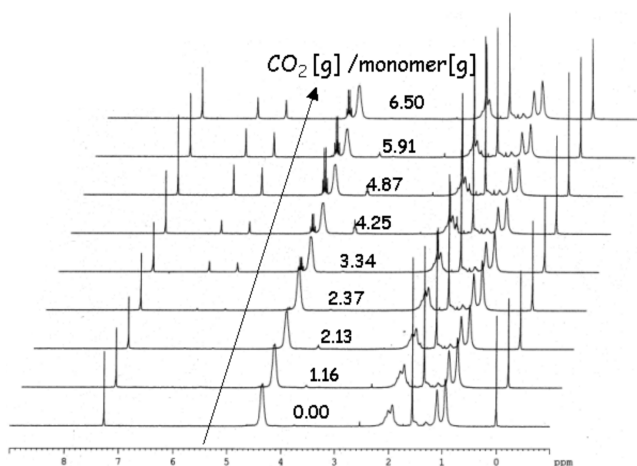


Fig. 4. ^1H -NMR spectra during polymerization of TFEMA for various ratios of CO_2 .

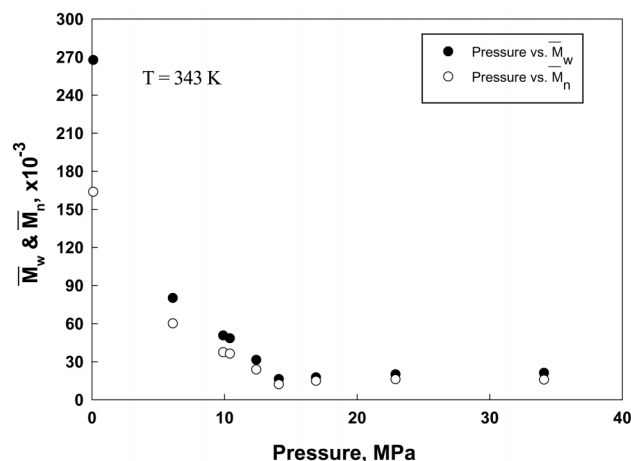


Fig. 5. Varied pressure and density of pure CO_2 and molecular weight by pressure.

hydrostatic effect. On the other hand, increasing pressure increased sorption of CO_2 with increasing the free volume of the polymer. Poly (TFEMA) was more influenced by the latter effect until pressure increased to 14.1 MPa. Molecular weight and T_g were minimized near at 14.1 MPa. Above this pressure, hydrostatic pressure effect took over and molecular weight and T_g were increased at higher pressure.

The T_g of a homopolymer generally increases with increasing molecular weight up to a limiting value, known as the limiting or persistent T_g value. Molecular weight distribution has also the same effect on T_g as molecular weight does [Brandrup et al., 1999]. Fig. 6 shows molecular weight dependence of T_g . The classical model for the effect of molecular weight on T_g is expressed in Eq. (1) [Brandrup et al., 1999].

$$T_g = T_g^\infty - \frac{A}{\bar{M}_n} \quad A = \text{constant} \quad (1)$$

This model suggests that the glass transition temperature (T_g) reaches a limiting value (T_g^∞) as the number average molecular weight ($\bar{M}_n$) of the polymer becomes large. There is no further increase in

Table 1. Free-radical polymerization in carbon dioxide as a solvent at 343 K, 24 hrs^a

No	CO_2 (g)	Relative ratio ^b	Pressure (MPa)	Conversion (%) ^c	$\bar{M}_w$ ^d	PDI ^d	T_g (K) ^e
1	0.00	0.00	0.1	92.8	268,000	1.6	350
2	4.67	1.16	6.1	97.8	80,000	1.3	339
3	8.56	2.13	9.9	96.1	51,000	1.4	338
4	9.50	2.37	10.4	96.9	48,000	1.3	334
5	13.36	3.34	12.4	89.0	31,000	1.3	334
6	17.00	4.25	14.1	87.1	16,000	1.4	325
7	19.75	4.87	16.9	69.2	18,000	1.2	338
8	23.30	5.91	22.9	64.8	20,000	1.2	335
9	26.51	6.50	34.1	78.6	21,000	1.3	330

^aTFEMA=4.0 g and AIBN=0.04 g in all reactions.

^bRelative ratio= CO_2 (g)/ monomer (4.0 g).

^cDetermined as the ratio of residual mass after ethanol-washing to initially charged monomer mass.

^dDetermined by GPC (PMMA standards).

^eDetermined by DSC.

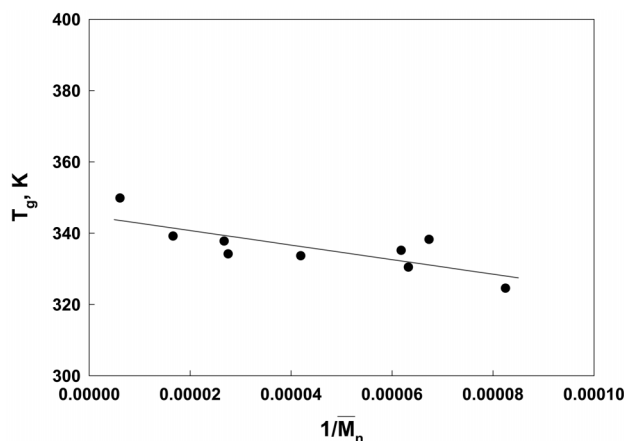


Fig. 6. T_g as a function of the number-average molecular weight ($\bar{M}_n$).

T_g when the molecular weight is above a critical value. A is the slope of Eq. (1).

The diversities of molecular weight and T_g by changing quantity of CO₂ are useful advantages to polymer reactions and processes. 17.00 g of CO₂ (monomer basis=4.0 g) could change $\bar{M}_w$ from 268,000 to 16,000 and T_g from 350 to 325 K.

We carried out free-radical polymerization of TFEMA with substituting organic solvents for CO₂ at same reaction conditions. The results are shown in Table 2. Poly (TFEMA) was soluble in THF and 1,4-dioxane, but precipitated in toluene. As shown in Fig. 7, conversion of monomer to polymer is similar in all solvents. But

Table 2. Effects of the organic solvents on the polymerization of TFEMA

Solvent	(g)	Conversion (%)	$\bar{M}_w$	PDI
THF	17.00	76.6	30,000	1.7
Toluene	17.00	82.3	34,000	1.5
1,4-Dioxane	17.00	89.1	54,000	1.9
CO ₂	17.00	87.1	16,000	1.4
None	0	92.8	268,000	1.6

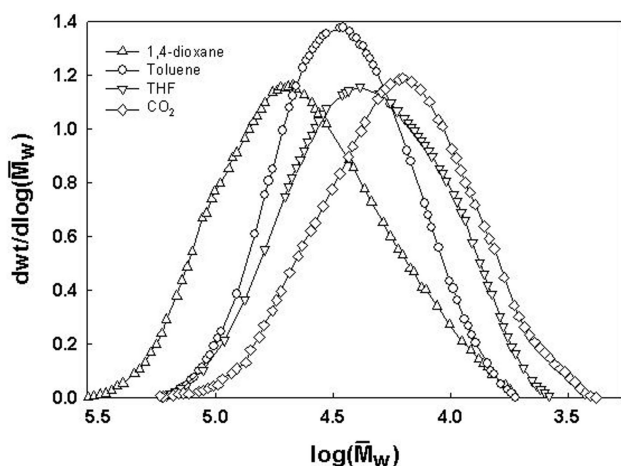


Fig. 7. Effect of solvents on the MWD of polymerization.

molecular weight and molecular weight distribution are the lowest when CO₂ is used as a solvent. The larger sorption of CO₂ in comparison with other solvents, which increases the free volume of the polymer, yields low molecular weight with small MWD. It can be applied to control molecular weight for various purposes in the industrial polymer process.

CONCLUSION

The radical polymerization of poly (TFEMA) was carried out in various ratios of CO₂ to monomer heterogeneously. Weight changes of CO₂ had an influence on conversion, molecular weight, PDI and T_g of resulting polymer. At 343 K, molecular weight and T_g became minimum near at 14.1 MPa and increased at the higher pressure.

We also carried out free-radical polymerization of TFEMA in organic solvents to compare with CO₂ under same reaction conditions. Molecular weight was the lowest and molecular weight distribution was the most narrow in CO₂. It can be described by the largest free volume of polymer in CO₂ and special interaction between perfluorine group and CO₂.

The future research is to understand polymerization of perfluoro methacrylate polymerization in CO₂ as a solvent. Through this further research, we may assimilate unknown interactions between perfluorine group and CO₂ in radical polymerization.

ACKNOWLEDGMENT

This work was supported by the BK21 project of Ministry of Education and the Cleaner Production Program of KNCPC.

REFERENCES

- Ajzenberg, N., Trabelsi, F. and Recasens, F., "Whats New in Industrial Polymerization with Supercritical Solvents? A Short Review," *Chem. Eng. Technol.*, **23**, 10 (2000).
- Beckman, E. J., "Supercritical and Near-critical CO₂ in Green Chemical Synthesis and Processing," *Journal of Supercritical Fluids*, **1** (2003).
- Brandrup, J., Immergut, E. H. and Grulke, E. A., "Polymer Handbook," 4th edition, John Wiley & Sons, Inc. (1999).
- Charpentier, P. A., Desimone, J. M. and Robers, G. W., "Continuous Precipitation Polymerization of Vinylidene Fluoride in Supercritical Carbon Dioxide: Modeling the Rate of Polymerization," *Ind. Eng. Chem. Res.*, **39**, 4588 (2000).
- Chatzidoukas, C., Pladis, P. and Kiparissides, C., "Mathematical Modeling of Dispersion Polymerization of Methyl Methacrylate in Supercritical Carbon Dioxide," *Ind. Eng. Chem. Res.*, **42**, 743 (2003).
- Ciardelli, F., Agleitto, M., Montagnini di Marabello, L., Passaglia, E., Giancristoforo, S., Castelvetro, V. and Ruggeri, G., "New Fluorinated Acrylic Polymers for Improving Weatherability of Building Stone Materials," *Progress in Organic Coatings*, **32**, 43 (1994).
- Cooper, A. I., "Polymer Synthesis and Processing Using Supercritical Carbon Dioxide," *Journal of Materials Chemistry*, **10**, 207 (2000).
- Kato, K., "New Fluorinecontaining Monomer," <http://www.pcimag.com/> (Accessed 17 sep. 2003).
- Kendall, J. L., Canelas, D. A., Young, J. L. and Desimone, J. M., "Polymerization of Supercritical Carbon Dioxide," *Chem. Rev.*, **99**, 543

- (1999).
- Song, K. H., Lee, C. H., Lim, J. S. and Lee, Y. W., "Preparation of L-PLA Submicron Particles by a Continuous Supercritical Antisolvent Precipitation Process," *Korean J. Chem. Eng.*, **19**(1), 139 (2002).
- Teng, X. R., Shao, H. L. and Hu, X. C., "Molecular Weight Distribution of Polyacrylonitrile Produced in Supercritical CO₂," *Journal of Applied Polymer Science*, **86**, 2338 (2002).
- Wang, W. and Karmer, E., "Effects of High-pressure CO₂ on the Glass Transition Temperature and Mechanical Properties of Polystyrene," *Journal of Polymer Science*, **20**, 1371 (1982).