

## The Effect of CO<sub>2</sub> in Free-radical Polymerization of 2,2,2-Trifluoroethyl Methacrylate

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**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 CO<sub>2</sub> 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]. CO<sub>2</sub> 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].

CO<sub>2</sub> 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, CO<sub>2</sub> 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 CO<sub>2</sub> 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 CO<sub>2</sub> 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 CO<sub>2</sub>. Condensation polymerizations in various pressure of CO<sub>2</sub> 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 CO<sub>2</sub> 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 CO<sub>2</sub> 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 CO<sub>2</sub> 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 CO<sub>2</sub> on polymerization, we focused on synthesis of polymer containing fluorine group. In amorphous fluoropolymer polymerization, CO<sub>2</sub> 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 CO<sub>2</sub> 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).

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### EXPERIMENTS

## 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 N<sub>2</sub> several times to remove residual air. CO<sub>2</sub> was charged with a cylinder at room temperature. Weight of adding CO<sub>2</sub> 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  $\pm 0.05$  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 CO<sub>2</sub> for the solvent. After polymerization, the reactor was cooled down to room temperature and CO<sub>2</sub> was slowly vented through two glass traps. To prevent discharge of unreacted monomer to atmosphere during CO<sub>2</sub> 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 <sup>1</sup>H-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, <sup>1</sup>H-NMR (Bruker, 300 MHz, CDCl<sub>3</sub> 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<sup>®</sup> 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 CO<sub>2</sub> 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

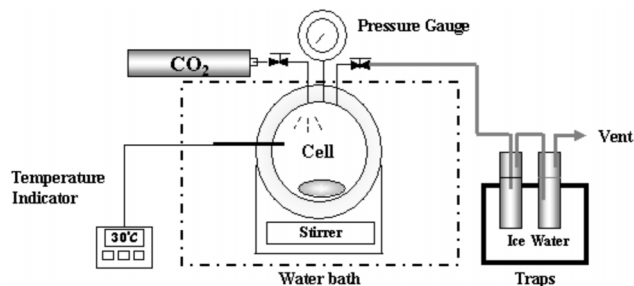


Fig. 1. Schematic diagram of the polymerization apparatus.

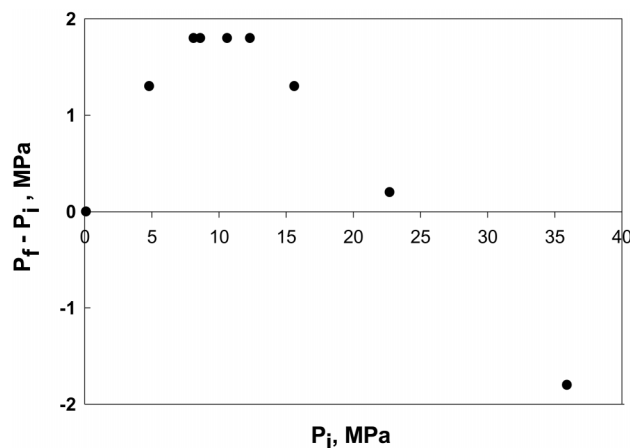


Fig. 2. Pressure variations in polymerization ( $P_i$ =initial pressure at 343 K,  $P_f$ =final pressure after 24 hrs (reaction time),  $\Delta P = P_f - P_i$ ).

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+CO<sub>2</sub>+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 <sup>1</sup>H-NMR in Fig. 3. Fig. 4 shows <sup>1</sup>H NMR spectrum during polymerization of TFEMA for various ratios of CO<sub>2</sub> to monomer. As increasing CO<sub>2</sub> weight ratio, monomer spectra (-CH<sub>2</sub>, -CH<sub>2</sub>CF<sub>3</sub>) 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 CO<sub>2</sub> to monomer. These represented same tendency that again increased after showing the minimum value with gradually charging CO<sub>2</sub>. This result is shown in Fig. 5 by various pressures. This reason might be the effect of high pressure of CO<sub>2</sub>. Pressure had two competing effects on heterogeneous polymerization kinetics [Charpentier et al., 2000; Wang and Kärner, 1982]. Increasing pressure decreased the free volume of the polymer through a

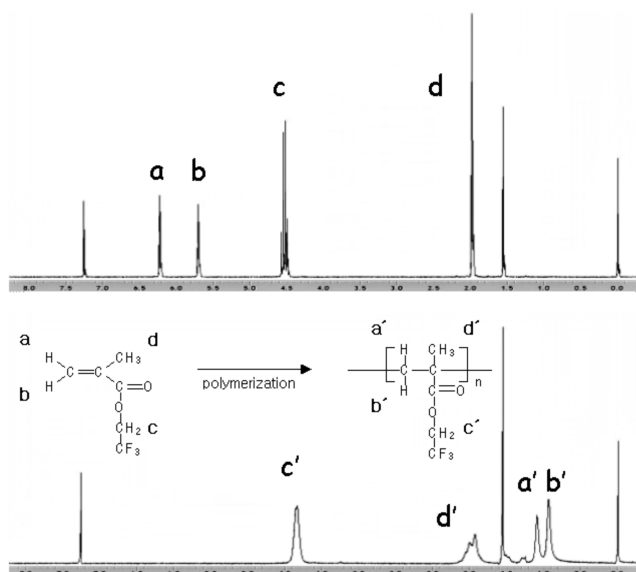


Fig. 3.  $^1\text{H-NMR}$  spectra of TFEMA and poly (TFEMA).

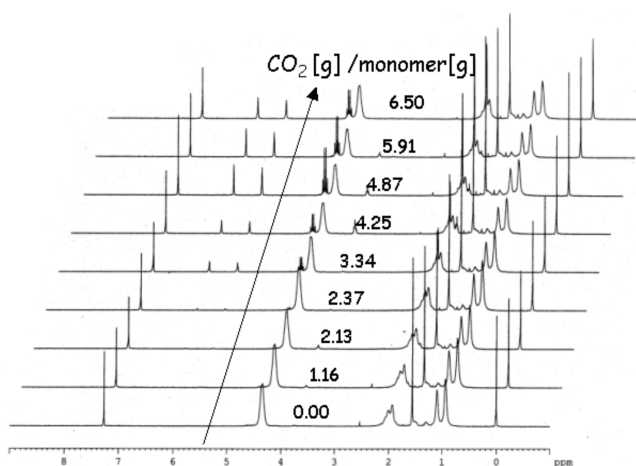


Fig. 4.  $^1\text{H-NMR}$  spectra during polymerization of TFEMA for various ratios of  $\text{CO}_2$ .

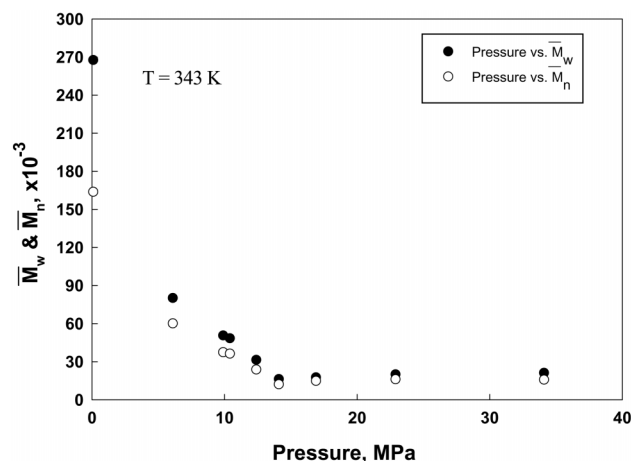


Fig. 5. Varied pressure and density of pure  $\text{CO}_2$  and molecular weight by pressure.

hydrostatic effect. On the other hand, increasing pressure increased sorption of  $\text{CO}_2$  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].

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

This model suggests that the glass transition temperature ( $T_g$ ) reaches a limiting value ( $T_g^\infty$ ) as the number average molecular weight ( $M_n$ ) 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<sup>a</sup>

No	$\text{CO}_2$ (g)	Relative ratio <sup>b</sup>	Pressure (MPa)	Conversion (%) <sup>c</sup>	$\overline{M}_w$ <sup>d</sup>	PDI <sup>d</sup>	$T_g$ (K) <sup>e</sup>
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

<sup>a</sup>TFEMA=4.0 g and AIBN=0.04 g in all reactions.

<sup>b</sup>Relative ratio= $\text{CO}_2$  (g)/ monomer (4.0 g).

<sup>c</sup>Determined as the ratio of residual mass after ethanol-washing to initially charged monomer mass.

<sup>d</sup>Determined by GPC (PMMA standards).

<sup>e</sup>Determined by DSC.

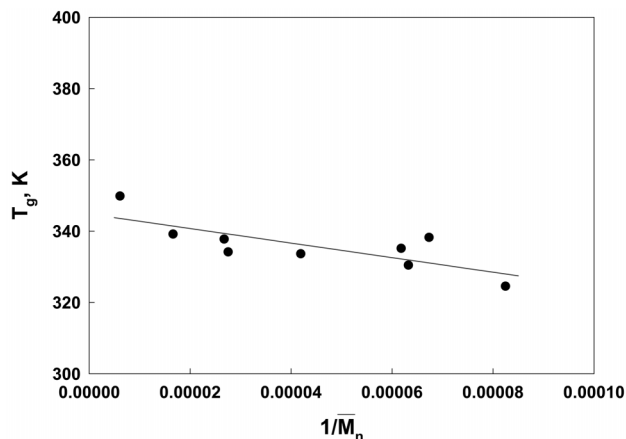


Fig. 6.  $T_g$  as a function of the number-average molecular weight ( $\bar{M}_n$ ).

$T_g$  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 CO<sub>2</sub> are useful advantages to polymer reactions and processes. 17.00 g of CO<sub>2</sub> (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 CO<sub>2</sub> 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 <sub>2</sub>	17.00	87.1	16,000	1.4
None	0	92.8	268,000	1.6

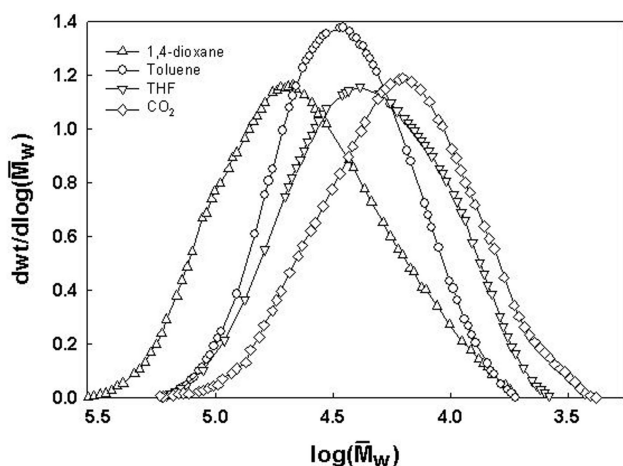


Fig. 7. Effect of solvents on the MWD of polymerization.

molecular weight and molecular weight distribution are the lowest when CO<sub>2</sub> is used as a solvent. The larger sorption of CO<sub>2</sub> 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 CO<sub>2</sub> to monomer heterogeneously. Weight changes of CO<sub>2</sub> 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 CO<sub>2</sub> under same reaction conditions. Molecular weight was the lowest and molecular weight distribution was the most narrow in CO<sub>2</sub>. It can be described by the largest free volume of polymer in CO<sub>2</sub> and special interaction between perfluorine group and CO<sub>2</sub>.

The future research is to understand polymerization of perfluoro methacrylate polymerization in CO<sub>2</sub> as a solvent. Through this further research, we may assimilate unknown interactions between perfluorine group and CO<sub>2</sub> in radical polymerization.

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