Solubility Behavior of Copolymers of Tetrahydropyranyl Methacrylate and \(1H,1H,2H,2H\)-Perfluoroctyl Methacrylate in Carbon Dioxide: Effect of Deprotection of THP Groups

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Abstract: A series of homopolymer and copolymers, which consist of heat-cleavable tetrahydropyranyl methacrylate (THPMA) and \(\text{CO}_2\)-philic \(1H,1H,2H,2H\)-perfluoroctyl methacrylate (FOMA), were prepared by group transfer polymerization (GTP). The THPMA units of homo- and copolymers were deprotected to methacrylic acid (MAA) units by thermolysis after the polymerization. The solubilities of the copolymers in \(\text{CO}_2\) were examined; the phase behavior of block copolymers was investigated in terms of the cloud pressure. Their solubility was greatly influenced by the copolymer compositions as well as by the extent of deprotection of the THPMA units. As the mole fraction of fluorinated methacrylate in the copolymers decreases, the cloud point curves shift to higher pressures.

Keywords: semifluorinated copolymer, carbon dioxide, group transfer polymerization

Introduction

Both liquid and supercritical carbon dioxide have attracted much interest as promising alternatives for organic solvents in industrial processes because of \(\text{CO}_2\)’s environmental acceptability and easily accessible critical points (\(T_c = 31^\circ\text{C}, P_c = 73.8\) bar). \(\text{CO}_2\) is nontoxic, readily available, inexpensive, and nonflammable, and thus it offers new opportunities in chemical processes, including polymerization [1], pharmaceutical applications [2], textile processing, dyeing [3], coating [4], food extractions [5], cleaning [6], and chromatography [7].

Polymers containing fluorine atoms or siloxane units display much higher solubility in \(\text{CO}_2\) [8,9] relative to most of polymers, which are virtually insoluble. The development of fluoroacrylate and fluoroether amphiphiles has allowed successful heterogeneous polymerization to occur in \(\text{CO}_2\) [10-12], as well as the extraction of metals and proteins with \(\text{CO}_2\) [13,14]. The mechanism of solubility of the fluorine- and silicon-containing polymers in \(\text{CO}_2\) has been identified; the important parameters are the specific solute-solvent interactions between the polymers and \(\text{CO}_2\), solute-solute interactions, van der Waals interactions, the free volume, Lewis-acid-base interactions, and the cohesive energy density of the polymer [15-17].

Recently, \(\text{CO}_2\) was utilized as the spin coating and developing solvent in microlithography. Hoggan and co-workers have reported the synthesis of a \(\text{CO}_2\)-compatible photoresist comprising random copolymers of \(1H,1H,2H,2H\)-perfluoroctyl methacrylate and \(t\)-butyl methacrylate. [18]. The removal of acid-sensitive \(t\)-butyl groups renders the polymer much less soluble in \(\text{CO}_2\), which enables this polymer to form a negative resist.

More recently, block copolymers incorporating tetrahydropyranyl and fluorinated methacrylate segments have been patterned using 193-nm and e-beam imaging as negative-tone resists in \(\text{CO}_2\) [19]. Block copolymers containing more than 50 vol% of the \(1H,1H,2H,2H\)-perfluoroctyl methacrylated part were found to be soluble in supercritical \(\text{CO}_2\) under the conditions of temperatures below 80°C and pressures below 7000 psi. After exposure, the THPMA block is deprotected to form a more polar methacrylic acid, which is insoluble in \(\text{CO}_2\). The selectivity of \(\text{CO}_2\) to both polarity changes and the molecular structure of the polymer were utilized to develop an environmentally

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friendly lithographic process. A systematic study of the phase behavior of the copolymers in CO₂, however, has yet to be established.

The present article reports the solubility behavior of copolymers composed of PTHPMA units and PFOMA units in dense carbon dioxide. PTHPMA-b-PFOMA copolymers that have controlled molecular weights can be prepared by GTP. In addition, the solubility in CO₂ of the protected and deprotected copolymers of different compositions was investigated by measuring the cloud point pressure. The cloud point curve indicates the pressure or density above which the polymer is soluble and below which the polymer is insoluble.

**Experimental**

**Materials**

Tetrahydrofuran (THF) (J. T. Baker) was freshly distilled from benzophenone/sodium under nitrogen before polymerization. THPMA was synthesized by the acid-catalyzed esterification of methacrylic acid with 3,4-dihydro-2H-pyran using a modification of the method described by Hertler [20]. THPMA and FOMA (SynQuest Lab) were purified by passing them through an alumina column, and then distilling them over CaH₂. The catalyst, tetra-n-butylammonium benzozate (TBABB) was prepared by the method reported by Dicker and coworkers [21]. Methyl trimethylsilyl dimethyl ketene acetal (MTSDA) (Aldrich) was distilled in the presence of CaH₂. 2,2-Azobisisobutyronitrile (AIBN; Junsei Chemical) was recrystallized twice from methanol.

**Synthesis of THPMA Homopolymer and Deprotection of PTHPMA**

For the synthesis of THPMA homopolymer by GTP, the catalyst (4 mg of TBABB) was placed in a 50 mL round-bottom flask under nitrogen. THF (8 mL) was transferred into the flask through a double-tipped needle followed by the addition of MTSDA (0.07 mL). This solution was stirred for 5 min and then THPMA monomer was added over 1 min. After 1 hr, the reaction mixture was quenched by the addition of methanol (2 mL) and then the product was precipitated into hexane. The polymer was filtered and washed with methanol prior to drying under vacuum for 1 day. The product weighed 1.9 g.

The THP protecting groups were removed by thermolysis: the polymer samples were heated in a vacuum oven at 140°C for 60 h.

**Synthesis of Copolymers of THPMA and FOMA**

A general procedure for preparing PTHPMA-b-PFOMA by GTP follows: The solid catalyst, TBABB (0.04 g), was added into a 50 mL round-bottom flask under a nitrogen purge. THF (8 mL) was then transferred into the flask through a double-tipped needle before the addition of MTSDA (0.047 mL). This solution was stirred for 5 min and then the THPMA monomer was added over 1 min. The mixture was then stirred for an additional 20 min before predistilled FOMA (1.52 mL) was added rapidly. After another 1 hr of stirring, the reaction mixture was quenched by the addition of methanol (2 mL) and then the product was precipitated into hexane. The product of (2.51 g, 91%) was collected. The molecular weights of block copolymers were determined by ¹H NMR spectroscopic analysis. The THP protecting groups of the block copolymers were removed by thermolysis.

**Synthesis of PTHPMA-ran-PFOMA**

Radical polymerization of PTHPMA-ran-PFOMA, using AIBN as an initiator, was carried out in a sealed tube under nitrogen at 65°C. The product was isolated by precipitation in hexane. The copolymer was filtered, dried, and weighed. The THP protecting groups of the random copolymer were removed by thermolysis.

**Phase Behavior of Copolymers in CO₂**

A 28-mL stainless-steel, high-pressure variable-volume view cell was used for the phase behavior investigations. One end of the cell was equipped with a sapphire window, which permitted visual observation. The cell was charged with 0.02 g of the copolymer, followed by the addition of CO₂, from 1500 to 5000 psi, by a syringe pump (ISCO model 260D). The view cell was then placed on a magnetic plate and heated within the temperature range 25–60°C in a water bath maintained to within ±0.2°C. When an optically transparent single-phase solution was obtained, the pump was stopped. The cell was slowly depressurized by means of a piston in the cell until the cloud point was reached.

**Instrumentation**

¹H NMR spectra were obtained in CDCl₃, FC-113/DMSO mixed solvent, or methanol-d₄ using a JNM ECP-400 (JEOL) spectrometer. FT-IR spectra were taken on a B-100 (BOMEN) spectrometer. GPC was performed using a Hewlett-Packard 1100 series apparatus equipped with four columns (guard, 100 Å, 1000 Å, 10,000 Å). Molecular weight calculations were based on a calibration curve obtained using polymethylmethacrylate (PMMA) standards (Mₙ = 1660, 5090, 10,900, 31,600, 93,300, and 29,600).

**Results and Discussion**

**Synthesis of Polymers**

The THPMA homopolymer was prepared with high conversion (> 90%) by GTP. The molecular weight was
Table 1. GTP of THPMA

<table>
<thead>
<tr>
<th>Exp. No.</th>
<th>Initiator (^b) (mmol)</th>
<th>Cat. (^c) (mmol)</th>
<th>Theor. (M_n)</th>
<th>Obsd. (M_n) (^d)</th>
<th>Conversion (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.5</td>
<td>4</td>
<td>2000</td>
<td>2100</td>
<td>92</td>
</tr>
<tr>
<td>2</td>
<td>0.33</td>
<td>3</td>
<td>3000</td>
<td>3500</td>
<td>95</td>
</tr>
<tr>
<td>3</td>
<td>0.25</td>
<td>2</td>
<td>4000</td>
<td>4500</td>
<td>93</td>
</tr>
</tbody>
</table>

\(^a\) [THPMA] = 5.747 mmol, \(^b\) MTSAD, \(^c\) TBABB, \(^d\) calculated by GPC

Figure 1. Time-dependent \(^1\)H-NMR spectra (CDCl\(_3\)) of a protected THPMA homopolymer and its deprotected forms, which we prepared by thermolysis. The completion of the deprotection is manifested by the disappearance of the acetal peak at 5.9 ppm.

easily controlled by varying the ratio of monomer to initiator, and the molecular weight distribution was quite narrow (1.13 ~ 1.23). Table 1 summarizes the theoretical and observed number-average molecular weights (\(M_n\)) of the polymers; these values agree well with each other.

There are two kinds of methods for deprotection of THP groups reported in the literature; thermolysis [22] and acid hydrolysis [23]. In our study, quantitative removal of 2-tetrahydropyranyl groups was achieved by thermolysis reactions. The deprotection of THPMA was confirmed by FT-IR spectroscopy. The appearance of a characteristic band at 3400 cm\(^{-1}\), due to the O-H stretching vibration of the carboxylic group of MAA, provided evidence for the successful conversion of THPMA to MAA. Also, a weak band representing an anhydride unit appeared at around 1800 cm\(^{-1}\) [24].

The degree of deprotection was determined using \(^1\)H NMR spectroscopy (Figure 1). Quantitative deprotection was confirmed by the complete disappearance of the signal representing the acetal hydrogen atom (A in Figure 1) of the THPMA ring (at 5.9 ppm) in the \(^1\)H NMR spectra. Conversely, a new peak for a carboxylic acid proton (D in Figure 1) appeared increasingly at 12.3 ppm upon increasing the thermolysis time.

PTHHPMA-b-PFOMA copolymers were prepared by sequential addition of THPMA and FOMA using GTP. Block copolymers of various block lengths were prepared by varying the ratio of monomer to initiator in the polymerization. THPMA was polymerized first in all cases because of the bad solubility of PFOMA homo-
Table 2. GTP of THPMA and FOMA via Sequential Monomer Addition

<table>
<thead>
<tr>
<th>Block copolymer</th>
<th>Theor. $M_n$ (g mol$^{-1}$)</th>
<th>Obsd. $M_n$ (g mol$^{-1}$)</th>
<th>Theor. Molar Composition (%)</th>
<th>Obsd. Molar Composition (%)</th>
<th>Conversion (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PTHPMA1.5k-b-PFOMA31k</td>
<td>12000</td>
<td>12500</td>
<td>32:68</td>
<td>26:74</td>
<td>91</td>
</tr>
<tr>
<td>PTHPMA6.5k-b-PFOMA31k</td>
<td>16500</td>
<td>16500</td>
<td>63:37</td>
<td>63:37</td>
<td>92</td>
</tr>
<tr>
<td>PTHPMA5.6k-b-PFOMA31k</td>
<td>11000</td>
<td>11300</td>
<td>72:28</td>
<td>71:29</td>
<td>95</td>
</tr>
</tbody>
</table>

*Calculated from $^1$H NMR spectra

![Chemical structure](image)

Figure 2. Chemical structure of the (a) THPMA monomer, (b) PTHPMA-PFOMA, (c) PMAA-PFOMA.

Table 3. Solubility of Block and Random Copolymers of THPMA-FOMA in CO$_2$*^*

<table>
<thead>
<tr>
<th>Composition$^a$ [PFOMA] in polymer</th>
<th>Protected PTHPMA-PFOMA</th>
<th>Partially deprotected$^c$ PMAA-PFOMA (&lt; 40 mol %)$^f$</th>
<th>Completely deprotected$^d$ PMAA-PFOMA (&gt; 90 mol %)$^f$</th>
</tr>
</thead>
<tbody>
<tr>
<td>74.4</td>
<td>Soluble</td>
<td>Cloudy (38 %)</td>
<td>Insoluble</td>
</tr>
<tr>
<td>37.5</td>
<td>Soluble</td>
<td>Insoluble (36 %)</td>
<td>Insoluble</td>
</tr>
<tr>
<td>41.2$^f$</td>
<td>Insoluble</td>
<td>Insoluble (37 %)</td>
<td>Insoluble</td>
</tr>
<tr>
<td>28.6</td>
<td>Cloudy</td>
<td>Insoluble (33 %)</td>
<td>Insoluble</td>
</tr>
</tbody>
</table>

*Conditions: 50°C, 4000 psi, 0.25 wt%,$^c$ molar ratio based on $^1$H NMR spectra, $^f$ thermolysis reaction for 1 hr, $^f$ thermolysis reaction for 48 hrs, $^f$ calculated from $^1$H NMR spectra,$^f$ random copolymer

polymer in THF.

Table 2 summarizes the theoretical and observed number-average molecular weights ($M_n$) and compositions of the copolymers. Good yields (above 90%) were obtained for all copolymerizations, with excellent control being achieved over both the molecular weight and the block copolymer composition. Furthermore, generally good agreement was observed between the theoretical molecular weights and the values from the $^1$H NMR spectroscopic analysis. The compositions and the molecular weights of the THPMA-FOMA block and random copolymers (b in Figure 2) were calculated by $^1$H NMR spectroscopy by comparing the integrations of the methylene groups (2H) attached to the fluoroalkyl chain of FOMA block at 4.2-4.6 and 2.4-2.7 ppm (–CH$_2$– and –CH$_3$–, respectively) and the acetal proton (1H) of the THPMA ring at 5.7-6.1 ppm. The THPMA-containing copolymers were deprotected by thermolysis to give PMMA-PFOMA copolymers (c in Figure 2). Similarly, deprotection was identified by the disappearance of the signals due to the acetal hydrogen atom at 5.9 ppm.

Solubility of Copolymers in CO$_2$

The solubility of the block and random copolymers in CO$_2$ was investigated using 0.25 wt% polymer at 50°C and 4000 psi. Table 2 summarizes the solubility behavior of the block and random copolymers in their protected and deprotected forms at different block ratios. Most of the PTHPMA-PFOMA block copolymers having > 28.6 mol% PFOMA were soluble in CO$_2$. For random copolymers, however, the polymer having 41.2 mol% PFOMA did not dissolve in CO$_2$. This result is probably due to the block copolymer forming micelles in CO$_2$ with the THPMA block as a core and the FOMA block as a corona [19].

PMAA-PFOMA copolymers obtained from the thermolysis were generally insoluble in CO$_2$. Only the highest PFOMA block copolymer (74.4 mol%) is slightly soluble.
block polymers of THPMA and FOMA were synthesized by group transfer polymerization. Control over molecular weight and copolymer composition was achieved by changing the ratio of monomers to initiator. The THPMA units were converted to polar PMAA units by thermolysis. The solubility of the copolymers composed of a CO$_2$-phobic PTHPMA or PMMA and a CO$_2$-philic PFOMA was examined in CO$_2$. The PTHPMA-PFOMA block copolymers having PFOMA content above 28.6 mol% were soluble in CO$_2$ at 50°C and 4000 psi. The deprotected forms of the PMAA copolymers showed very low solubility in CO$_2$. The block copolymer having 74.4 mol% PFOMA became insoluble under these conditions when the THPMA groups were deprotected above 40 mol%. The cloud point pressure of PTHPMA-b-PFOMA increased upon decreasing the mol% of the PFOMA block.

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References


Conclusions

A series of THPMA homopolymer and semifluorinated