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Experimental measurement of solubility curves for poly(methyl methacrylate-co-pentafluorophenyl methacrylate) in supercritical solvents

Chang-Ryong Kim, Hun-Soo Byun *

Department of Chemical and Biomolecular Engineering, Chonnam National University, Yeosu, Jeonnam 59626, South Korea

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ABSTRACT

The seven poly(methyl methacrylate-co-pentafluorophenyl methacrylate) [P(MMA-co-PnFPMA)] copolymers were prepared by dispersion polymerization under supercritical carbon dioxide. The physicochemical characterisation for the P(MMA-co-PnFPMA) was investigated with varied mole ratios of MMA vs PnFPMA (30:1, 25:1 and 20:1), AIBN amounts (1.0, 2.0 and 4.0 wt%) and the weight average molar mass (M_w).

Experimental values at temperatures from (333 to 453) K and pressures up to 229 MPa are reported for binary and ternary mixtures of P(MMA-co-PnFPMA) in supercritical CO_2, CH_2F_2, CHF_3 and $CHClF_2$. Phase behaviour of binary systems for the P(MMA-co-PnFPMA) (mole ratio = 25:1, 1.0 wt%, 2.0 wt%, and 4 wt% AIBN) + supercritical fluoric solvents (CH_2F_2, CHF_3 and $CHClF_2$) mixtures at temperature range from (333 to 434) K and pressure up to 168 MPa are measured for the upper critical solution temperature (UCST) type behaviour with negative slope for the {P(MMA-co-PnFPMA) + CH_2F_2} as well as for the lower critical solution temperature (LCST) type curve with positive slope for the {P(MMA-co-PnFPMA) + CHF_3} and {P(MMA-co-PnFPMA) + $CHClF_2$} mixtures. Cloud-point curves for the {P(MMA-co-PnFPMA) [mole ratio = 30:1 (M_w = 157,000), 25:1 (M_w = 149,000), and 20:1 (M_w = 142,000): 1.0 wt% AIBN; 30:1 (M_w = 109,000), 25:1 (M_w = 94,000), and 20:1 (M_w = 88,000): 2.0 wt% AIBN] + supercritical (CH_2F_2, CHF_3 and $CHClF_2$)} mixtures show a negative slope for the P(MMA-co-PnFPMA) + CH_2F_2, and a positive slope for the {P(MMA-co-PnFPMA) + CHF_3} and {P(MMA-co-PnFPMA) + $CHClF_2$} mixtures at temperatures to 435 K and pressures up to 150 MPa. Also, the impact of MMA on phase behaviour for the P(MMA-co-PnFPMA) (mole ratio = 25:1; AIBN: 1.0 wt% and 2.0 wt%) + CH_2F_2 mixtures are measured in changes of the (pressure + temperature) (p, T) slope from UCST behaviour to LCST behaviour, and with MMA co-solvent concentrations of (0.0 to 39.0) wt%. Phase behaviour for the {P(MMA-co-PnFPMA) + (14.7 to 96.4) wt% CHF_3 [or (27.9 to 97.1) wt% $CHClF_2$]} mixture in supercritical CO_2 show favourably better (fluorocopolymer + solvents) interaction than (solvents + solvents) interaction, changing from a negative slope to a positive slope.

1. Introduction

There has been an increasing interest in process design and operation of advanced copolymer materials and industrial application, such as chemical inertness, electrical materials, coating, fibres, optics, and bio-materials. These copolymer materials demand the powerful physicochemical properties such as tensile strength and elongation at break, the high thermal properties, and the resistance to solvents. Fluorocopolymers have excellent properties that show a high chemical resistance, thermal resistance and water resistance [1–3]. In addition, copolymers with long chains fluoroalkyl side have gained a great deal of attention. The fluorinated side chains are transferred to the surface of the prepared polymers though heat treatment, which decreases the surface energy [4]. Thomas *et al.* [5] have reported that water resistance is improved with the increase of fluorinated concentration. However, the expensive prices of fluorinated monomers that possess the high physical properties have limited its applications. Therefore, it is important to control the fluorinated contents as a solution to this problem. It is desirable that the fluorinated concentration should be minimised to impart attractive properties like low surface tension.

* Corresponding author. Tel.: +82 61 659 7296; fax: +82 61 653 3659.
E-mail address: hsbyun@jnu.ac.kr (H.-S. Byun).

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Generally, fluoropolymers and their copolymers were synthesized using suspension and emulsion polymerization. In these methods, the fluoric fine particles are easily gained. However, it is very difficult to select dispersion mediums because of solubility problem. When polymerization is carried out, the careful control of pressure and temperature is also required for the preparation of resultant polymers. The preparation of fluorocopolymers by bulk polymerization method is not suitable for applications of various fields due to a high polymerization heat [6]. In addition, solution polymerization is easy to occur via a chain transfer reaction. Therefore, this method is not used because it is hard to obtain resultant polymers with high molar mass. Recently, various industries have been moving away from the use of polymerization solvents due to environmental regulations on safety hazards associated with the use of organic solvents. To minimise the consumption of organic solvent, numerous studies have been carried out using supercritical carbon dioxide as a reaction medium or supercritical solvent. Supercritical carbon dioxide has many properties that emerge as the most extensively studied supercritical fluid for polymerization reactions to synthesized fluoric fine particles in a heterogeneous reaction system [7–10].

Various advantages can be realised when CO_2 is used as the supercritical fluid. The chemical process has become increasingly aware of environmental problems for the use of organic solvents in the manufacture, processing, and preparation of commercial polymer products applicable a variety of fields. Although using water as reaction medium reduces these problems, large amounts of hazardous aqueous waste require the treatment or removal of wasted water. In order to solve these problems, it is necessary to develop a new reaction medium as an eco-friendly alternative solvent. CO_2, in particular, is the most applied supercritical fluid for polymerization reactions due to its numerous advantages: it is non-toxic, and non-flammable [11,12]. In addition, it has an easily accessible critical point with a T_c of 304.2 K and a P_c of 7.38 MPa [13,14].

The major focus of this work is to understand the fluorocopolymer preparation under supercritical carbon dioxide and phase behaviour measurement of binary and ternary systems for (fluorocopolymer + supercritical fluorine solvent + co-solvent) mixtures. Preparation of poly(methyl methacrylate-co-pentafluorophenyl methacrylate) [P(MMA-co-PnFPMA)] copolymer was performed using dispersion polymerization in $scCO_2$. The characterisation for the prepared P(MMA-co-PnFPMA) copolymer was investigated using the particle shape and the weight average molar mass (M_w). In addition, (pressure + temperature) space isotherms were measured for phase behaviour of binary and ternary systems between P(MMA-co-PnFPMA) and association liquid fluid as well as the influence of quality of association solvents, M_w, and co-solvents. The phase behaviour of fluorocopolymers in the supercritical fluids is very important in most polymerization processes, polymer production, processing technologies, material development, and industrial application [15,16].

2. Experimental

2.1. Materials

Methyl methacrylate (MMA) (>0.985 mass fraction purity, M_w = 100.12, CH_2=C(CH_3)$COOCH_3$, CAS RN 80-62-6), 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl methacrylate (HDFDMA) (>0.970 mass fraction purity, M_w = 532.19, H_2C=C(CH_3)CO_2CH_2-$CH_2(CF_2)_7CF_3$, CAS RN 1996-88-9) and pentafluorophenyl methacrylate (PnFPMA) (>0.970 mass fraction purity; M_w = 218.12, H_2C=C(CH_3)CO_2 $CH_2CF_2CF_3$, CAS RN 13642-97-2) used in this work were obtained from Sigma-Aldrich, Ltd. All components were used with further purification in the experiments. Difluoromethane (>0.999 mass fraction purity, M_w = 52.02, CH_2F_2: HFC-32, CAS RN 75-10-5), fluoroform (>0.999 mass fraction purity, M_w = 70.01, CHF_3, CAS RN 75-46-7), and chlorodifluoromethane (>0.999 mass fraction purity, M_w = 86.47, $CHClF_2$, CAS RN 76-45-6) were obtained from Dae Han Gas Ltd., carbon dioxide (CO_2) (>0.999 mass fraction purity, M_w = 44.01, CAS RN 124-38-9) was purchased from Deok Yang Co. and used as received. The specifications of all chemicals used are summarised in table 1. Also, table 2 lists physical properties of solvents and co-solvents used in this study. MMA, PnFPMA and HDFDMA were pre-treated on an alumina column to remove the inhibitor, and dissolved oxygen was removed by nitrogen purging. α,α′-Azobis(isobutyronitrile) (AIBN, >0.980 mass fraction purity, M_w = 164.21, $C_8H_{12}N_4$, CAS RN 78-67-1) was recrystallized from methanol.

2.2. Apparatus and procedure

2.2.1. Dispersion polymerization of fluorocopolymer in supercritical CO_2

Figure 1 shows the schematic diagram of experimental apparatus for the dispersion polymerization at high pressure [16]. As shown in figure 1, the dispersion polymerization of fluoric copolymer in CO_2 was conducted in a stainless steel 316 high-pressure reactor (30 ml). The pressure was measured using a Bourdon tube pressure gauge (NUOVA FIMA, model MGS44 DN100, accuracy: 1.6 of FSV). The temperature was measured using K-type thermocouple and indicator (Hanyoung Electronics Inc., model NX3, the relative standard uncertainty of 0.5%). A Teflon-coated magnetic

TABLE 1
Specifications of the chemical used.

Chemical name	Source	Mass fraction purity[a]	Purification method	Analysis method[a]
CO_2	Deok Yang Gas Co.	>0.999	None	
MMA[d]	Aldrich-Sigma Co.	>0.985	Distillation	GC[b]
HDFDMA[e]	Aldrich-Sigma Co.	>0.970	Distillation	GC[b]
PnFPMA[f]	Aldrich-Sigma Co.	>0.950	Distillation	GC[b]
CH_2F_2	Dae Han Gas Co.	>0.999	None	
CHF_3	Dae Han Gas Co	>0.999	None	
$CHClF_2$	Dae Han Gas Co	>0.999	None	
AIBN[g]	Junsei Chemical Co.	>0.980	Recrystallization	HPLC[c]

[a] Both the analysis method and the mass fraction purity were provided by the suppliers.
[b] (Gas + liquid) chromatography.
[c] High performance liquid chromatography.
[d] MMA = methyl methacrylate.
[e] HDFDMA = 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl methacrylate.
[f] PnFPMA = pentafluorophenyl methacrylate.
[g] AIBN = α,α′-Azobis(isobutyronitrile).