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New Attempt at Preparation of Fluorine-containing Poly(ether ketone)s in Supercritical Carbon Dioxide

Kunio Kimura*, Shinichi Yamazaki*, Patrick E. Cassidy**,
John W Fitch** and Sreenu R. Venumbaka**

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Fluorine-containing poly(ether ketone)s was synthesized by the nucleophilic aromatic substitution reaction of 2,2-bis(4-hydroxyphenyl)-1,1,1,3,3,3-hexafluoropropane and 4,4'-bis(2,3,4,5,6-pentafluorobenzoyl) diphenyl ether in super-critical CO_2. Polymerizations were carried out at 80°C for 6 hours under 5000 psi of CO_2 pressure, which was super-critical phase. Polymerization concentration was 0.5 g of polymer in 10 - 12 mL of CO_2. The polymer was not obtained in CO_2 due to the insolubility of both the potassium bisphenoxide and the polymer into CO_2. However, the polymer was formed by an addition of DMAc and NMP in CO_2, even though molecular weight was not so high. Very small amount of co-solvents which were immiscible with CO_2 was effective, and it was 1/20 - 1/25 amount of the solvent used in the conventional poly(ether ketone) synthesis. The polymerization mechanism was also discussed.

***Key words**: super-critical carbon dioxide, plastics, high performance, environmentally benign*

1. INTRODUCTION

Carbon dioxide has become an attractive solvent for a variety of polymerization due to its environmentally benign nature and chemical inertness. Properties of CO_2 such as dielectric constant and density are sensitive to both the temperature and pressure, and are tunable with temperature and pressure. [1-5]

Although CO_2 dissolves many small compounds readily, it is a very poor solvent for most high molecular weight polymers. Currently, only amorphous or low melting fluorine-containing vinyl polymers and silicon polymers are known to be soluble in CO_2 or CO_2-philic, while many important polar polymers are relatively insoluble. Recently, homogeneous free radical polymerizations of a CO_2-philic fluorinated acrylate have been reported. [5,6] However, homogeneous polymer synthesis in CO_2 is fundamentally limited by the extremely low solubility of the most polymers at readily accessible conditions.

In order for CO_2 to be an effective phase for polymerizations, heterogeneous reaction systems must necessarily be developed analogous to classical emulsion, inverse emulsion, dispersion, suspension and precipitation polymerization processes. With some highly reactive monomers such as acrylic acid [7] and tetrafluoroethylene, [8] free-radical precipitation polymerization can afford polymers with high yields and high molecular weight. It has been reported that the surfactants consisting of covalently bound CO_2-philic and

*Graduate School of Environmental Science, Okayama University,
** Institute for Environmental and Industrial Science, Texas State University at San Marcos

CO_2-phobic segments in the dispersion polymerization of various CO_2-insoluble polymers is stabilized polymer colloid in CO_2 and dry, free flowing powders after isolation.

With respect to polycondensation, a few studies have been reported so far, and CO_2 was used as a melt viscosity reducer for polyester and crystallization medium for solid-state polymerization of polycarbonate. [9,10] Many condensation type polymers are insoluble in non-polar CO_2 due to their polar structures. Furthermore, many condensation reaction are reversible reactions and elimination of by-product is necessary to move an equilibrium to polymer formation site. This is also of disadvantage for making polymers in CO_2.

We have been reported the synthesis of novel fluorine-containing poly(ether ketone)s (F-PEK) derived from 2,3,4,5,6-pentafluorobenzoic acid by nucleophilic aromatic substitution reaction (SnAr) and some of these F-PEKs show very outstanding solubility into less polar aprotic solvents such as toluene and tetrahydrofuran. [11] This excellent solubility is of great advantage for the homogeneous polymerization in CO_2. This article provides our initial trial on the preparation of F-PEK in super critical CO_2.

2. Experimental

Materials

2,2-Bis(4-hydroxyphenyl)-1,1,1,3,3,3-hexafluoropropane (6FBA) was purchased from Aldrich Co. Ltd. and used after sublimation purification. 4,4'-Bis(2,3,4,5,6-pentafluorobenzoyl)diphenyl ether (BPDE) was synthesized according to the previous procedure. [11] *N,N*-Dimethylacetamide (DMAc), 1-methyl-2-pyrrolidinone (NMP), tri-*n*-butylamine (TBA), THF, methanol were purchased from Aldrich Co. Ltd. and used after distillation.

Polymerization

Into a round bottom flask were placed KOH (0.334 g, 5.95 mmol) and 20 ml of methanol. 6FBA (2.000 g, 5.95 mmol) was then added into the solution and stirred for 6 hours at room temperature. Methanol and by-produced water were evaporated, and the obtained white solid was dried at 25°C under reduced pressure for 12 hours. Into a cylinder of CO_2 apparatus, as illustrated in Figure 1, were placed ground 6FBA potassium bisphenoxide (0.241 g, 0.585 mmol) and BPDE (0.327 g, 0.585 mmol), and cylinder was put on the lid very tightly. A small amount of co-solvent was added into the reaction cylinder, and then CO_2 was purged into the cylinder from the CO_2 gas pump. After checking no leak of gas, cylinder was heated at 80°C in water bath for 6 hours. The CO_2 gas was leaked and polymer was poured into water containing 5% of acetic acid. The precipitated polymers were collected by filtration, washed with water and dried. Product characteristics were as follows. Tg: 174°C, FT-IR(KBr)(cm^{-1}):1680 (C=O stretching), 1497 (aromatic C=C stretching), 1239 (ether C-O-C antisymmetric stretching). ^{1}H-NMR(ppm): 8.1 (4H at *ortho* position to carbonyl group), 7.5 – 7.1 (12H). ^{19}F-NMR (ppm): -63.8(6 aliphatic F), -141.5 (4 aromatic F at *ortho* position to carbonyl group), -152.9 (4 aromatic F at *meta* position to carbonyl group). ηsp/c was 0.12 $dL \cdot g^{-1}$.

Measurement

NMR spectra were recorded on an Varian Unity-500 operating at 500 MHz (^{1}H) and 470 MHz

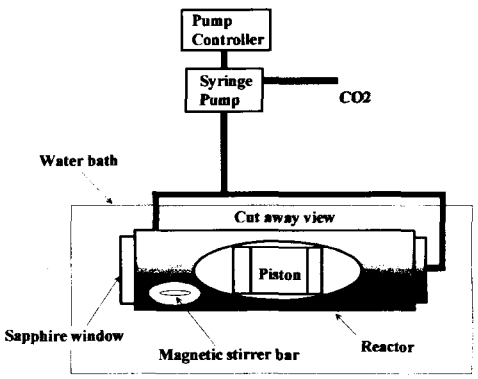
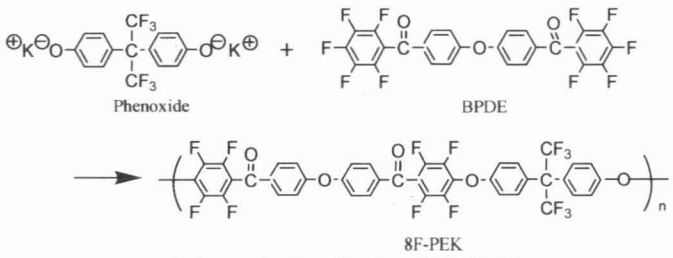


Figure 1. Apparatus for polymerization in super critical carbon dioxide.

(^{19}F). $CDCl_3$ and DMSO-*d*6 were used as the measuring solvents for monomers and polymers. 4,4'-Difluorobenzophenone was used as an internal standard for ^{19}F-NMR measurements. FT-IR spectra were measured on JASCO FT/IR-410 spectrometer. Glass transition temperatures (Tg) was measured by differential scanning calorimetry on Perkin-Elmer DSC 7 at a scanning rate of 20°C·min^{-1}. Reduced viscosity (ηsp/c) of obtained polymers was measured with an Ostwald-Fenske viscometer at a concentration of 0.5 g·dL^{-1} in DMAc at 25°C.

3. Results and Discussion

Among F-PEKs, F-PEK(6FBA) illustrated in Scheme 1 is selected in this study because it exhibits the most excellent solubility into organic solvents [11] and many fluorine atoms may enhance CO_2-philicity. The SnAr polymerization of bisphenol with aromatic fluoride is usually performed in the presence of base to form bisphenoxide *in-situ* such as potassium carbonate and potassium hydroxide. However, these bases have no solubility into CO_2, and therefore bisphenoxide cannot be *in-situ* prepared. The reaction of potassim bisphenoxide, which is



Scheme 1. Synthesis of 8F-PEK

preformed with potassium hydroxide in methanol, and aromatic fluoride is chosen in this study as shown in Scheme 1.

Polymerizations were carried out at 80°C for 6 hours under 5000 psi of CO_2 pressure, which was

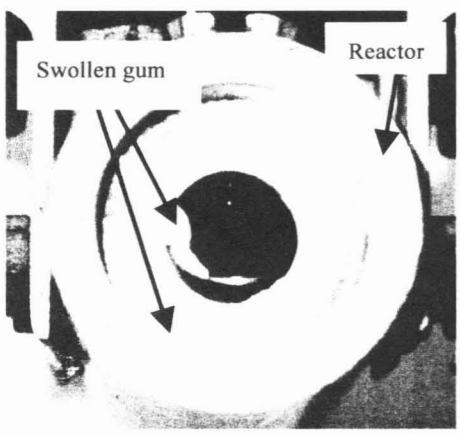


Figure 2. Polymers as prepared in super critical carbon dioxide with DMAc at γcs of 0.2.

Table 1 Results of polymerization in supercritical CO_2 [a]

Run No.	Solvent [b]	Co-solvent	Co-colvent ratio (γcs) [c]	Yield (%)	ηsp/c [d] (dL·g^{-1})	Remarks
1	$SCCO_2$	none	-	70	<0.01	Powder
2	$SCCO_2$	Methanol	2.0	59	0.01	Powder
3	$SCCO_2$	THF	2.0	22	- [e]	Powder
4	$SCCO_2$	TBA	2.0	54	0.03	Swollen gum
5	$SCCO_2$	DMF	2.0	85	0.03	Swollen gum
6	$SCCO_2$	DMAc	2.0	74	0.03	Swollen gum
7	$SCCO_2$	DMAc	1.0	70	0.03	Swollen gum
8	$SCCO_2$	DMAc	0.5	91	0.07	Swollen gum
9	$SCCO_2$	DMAc	0.2	86	0.13	Swollen gum
10	$SCCO_2$	NMP	0.5	83	0.09	Swollen gum
11	$SCCO_2$	NMP	0.2	83	0.03	Swollen gum
12	$SCCO_2$	NMP	0.1	88	0.03	Swollen gum, powder
13 [f]	DMAc	-	-	87	0.58	-

a)Polymerizations were carried out at 80°C for 6 hours in the volume of CO_2 of 10 -12 ml under 5000 psi.
b) $SCCO_2$: Supercritical carbon dioxide
c)γ = [solvent volume (ml) / calculated polymer weight (g)]
d) measured in DMAc at a concentration of 0.5 g·dL^{-1} and 25°C.
e) not measured because of the contamination of insoluble parts.
f) cited from ref. 11.

supercritical CO_2 phase, and polymerization concentration was 0.5 g of polymer in 10 - 12 mL of supercritical CO_2. Polymer was not obtained in CO_2 and monomers were recovered because of the insolubility of potassium bisphenoxide into CO_2. In order to dissolve potassium bisphenoxide, several co-solvents were added into the polymerization solution. Table 1 summarized the polymerization results. Among the co-solvents, only methanol and THF are miscible into CO_2 under this condition, and other polar aprotic solvents such as TBA, DMF, DMAc and NMP are immiscible with CO_2. Methanol dissolves the potassium bisphenoxide very well but polymer cannot be obtained. Methanol is very poor solvent to polymer, and therefore polymerization is terminated due to the precipitation of oligomers. THF slightly dissolves the potassium bisphenoxide at 80°C. White powders were formed with an addition of THF. They contain insoluble part due to the crosslinking reaction at *orth* and *para* position to carbonyl group in BPDE. On the other hand, polar aprotic solvents are better co-solvent for making polymers. The polymers were obtained as white gums swollen by CO_2 as shown in Figure 2. Although the polymers prepared in polar aprotic solvents are low molecular weights, they are much higher than those prepared with methanol. Especially, DMAc and NMP gave higher molecular weight polymers than DMF and TBA. These polar aprotic solvents are immiscible with CO_2, but they can dissolve both the potassium bisphenoxide and the polymers. This is different from methanol and THF. The polymerization with polar aprotic co-solvents seems to proceed in partially miscible phases as discussed later.

Concentration effect of co-solvent was examined with DMAc and NMP. It is very worth noting that very small amount of solvent affords the higher molecular weight polymers. The co-solvent ratio (γcs) is defined as the ratio of co-solvent volume and polymer weight. In the case of DMAc, the polymer with ηsp/c of 0.13 $dL \cdot g^{-1}$ is formed at γcs of 0.2. In the case of NMP, the polymer with ηsp/c of 0.09 $dL \cdot g^{-1}$ is formed at γcs of 0.5. The SnAr polymerization is normally carried out at a concentration of around 25% corresponding to 4 of γcs. Higher concentration makes the polymers precipitate or the solution viscous, and inhibits increasing molecular weight. In the case of this study, 20 - 25 fold smaller amount of polar solvent to that for conventional SnAr polymerization is effective for polymerization, and this result shows a strong benefit to reduce the consumption of solvents for making polymers. Figure 3 shows the plot of reduced viscosity of polymers as a function of γcs in the system of DMAc-CO_2, and 0.2 of γcs gives the maximum ηsp/c. This fact indicates that the bisphenoxide is not dissolved at less than γcs of 0.2, and the polymerization may proceed in two immiscible phases at higher γcs than 1.0. At γcs of 0.2, polymerization phase becomes partially miscible because the formed oligomers may act as surfactants, and the polymerization proceeds more smoothly.

The polymerization time dependency of reduced viscosity was also examined as shown in Figure 4. Polymerizations were carried out with an addition of NMP at γcs of 0.2 for 40 hours. The reduced viscosity of the polymers increases until 6 hours and then it becomes almost constant until 40 hours.

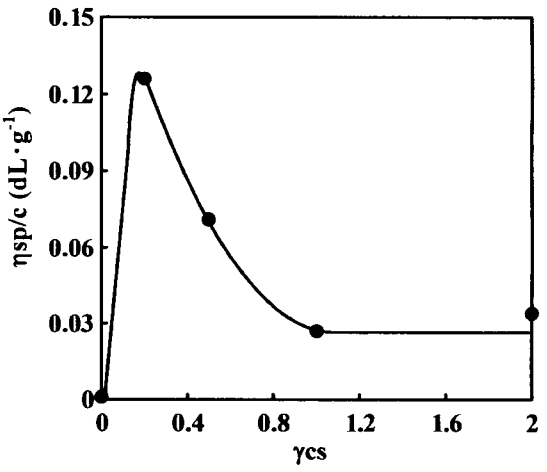


Figure 3. Plot of reduced viscosity of polymers as a function of γcs in super critical carbon dioxide with an addition of DMAc.

Even though the reduced viscosity is low, very small amount of co-solvent is effective to yield the polymers. The mechanism of polycondensation can be speculated as follows; potassium bisphenoxide is soluble only in co-solvent phase, and BPDE is soluble into both co-solvent and CO_2 phases. The SnAr reaction is taken place in co-solvent phase between bisphenoxide and BPDE, and then oligomers are formed at the early stage of polymerization. When the molecular weight of the oligomers exceed a critical value, they become soluble into CO_2 phase because fluorine atoms enhance CO_2-philicity of oligomers and it becomes stronger than CO_2-phobicity derived from potassium bisphenoxide end-group. Then, polycondensation solution might be changed from two immiscible phase to partially miscible phase because the *in-situ* formed oligomers act as surfactants. Small amount of co-solvent is enough to dissolve the potassium bisphenoxide.

4. Conclusion

F-PEK(6FBA) is synthesized by the SnAr reaction with an addition of a small amount of DMAc and NMP in CO_2, even though molecular weight is not so high. Co-solvents are immiscible with OC_2 and the miscibility with CO_2 is not so important. Polycondensation seems likely to proceed in aplotic polar co-solvent phase at an early stage, and then in partially miscible phase after the middle stage which is caused by the formation of oligomers acting like surfactants.

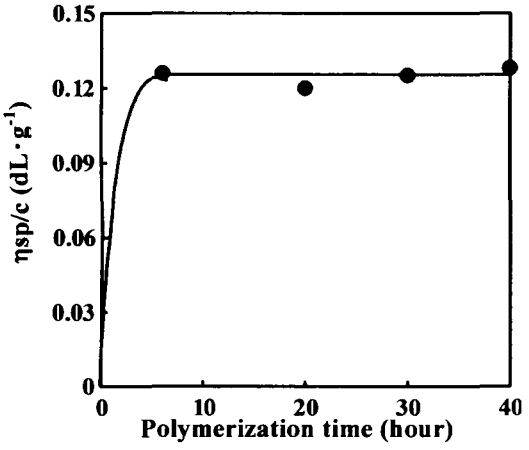


Figure 4. Polymerization time dependency of reduced viscosity of polymer prepared in super critical carbon dioxide with an addition of NMP at γcs of 0.2.

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