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The Magnetic Field Effect on the Polymerization of Styrene in Supercritical Carbon Dioxide

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Abstract: Styrene was polymerized in supercritical (sc) CO_2 with benzoyl peroxide (BPO) as initiator. It was found that the polymerization was accelerated by the external magnetic field.

Keywords: Magnetic field effect, polymerization, styrene, supercritical carbon dioxide.

Over the past decade there has been a growing interest in using supercritical fluids (SCFs) to promote reactions and to replace hazardous solvents with environmentally benign solvents, such as supercritical CO_2 and H_2O. Many reactions in SCFs have been studied[1], including polymerization in $scCO_2$[2]. It is known that a small change in the pressure near critical point of a fluid causes a significant change in density-dependent properties such as the solubility parameter, viscosity, and dielectric constant. There are some unique advantages for conducting chemical reactions in SCFs[1-2]. Magnetic field (MF) can affect the kinetics of some reactions[3-5]. However, study on the magnetic field effect (MFE) on chemical reaction in SCFs was not found in a literature survey. This paper we studied MFE on the polymerization of styrene in $scCO_2$.

Materials: CO_2 with a purity of 99.95% was supplied by Beijing Analytical Instrument Factory. THF, BPO, methanol and styrene were A.R. grade, which were supplied by Beijing Chemical Factory. Styrene was washed twice with 10% NaOH aqueous solution, and twice with water, dried over fused $CaCl_2$ for 24 h and distilled under reduced pressure. BPO was recrystallized with $CHCl_3$/MeOH. A stainless steel reactor of 10 mL was used which was placed in a constant temperature water bath. Two permanent magnets were used to obtain the MF and the intensity of the MF in the reactor was 1000 Gauss.

The polymerization of styrene, initiated with BPO (0.02 $mol.L^{-1}$), was conducted in $scCO_2$ at 343.2 K and at pressures of 13 MPa and 16 MPa. The initial concentration of the monomer was 1 $mol.L^{-1}$ and the yields were measured gravimetrically. The yields of the polymerization (PS) at different conditions were shown in **Table 1**. It can be seen that the polymerization yields with MF was higher than that without MF. In other words the application of MF accelerates the polymerization reaction noticeably. The effect of MF strength on the polymerization will be studied further.

Table 1 The yields and the relative change of the yields of styrene polymerized in $scCO_2$

Time h	13 MPa			Time h	16 MPa		
	[a]Y_{MF}	[b]Y_0	[c]R(H)		NMF	MF	R(H)
10.0	23.87	25.02	4.8	10.0	20.58	21.21	3.7
14.0	37.60	38.99	3.7	15.0	31.50	33.15	5.2
18.7	51.46	52.32	1.7	20.3	44.42	46.81	6.0

a, Y_{MF} is the yields in the presence of MF.
b, Y_0 is the yields without MF.
c, R(H) is defined as $100 \times (Y_{MF}-Y_0) / Y_0$.

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