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Effect of Dissolved CO_2 and Tetrahydrofuran on the Polymerization of Acrylic Acid

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Abstract: The polymerization of acrylic acid (AA) with dissolved carbon dioxide and tetrahydrofuran (THF) in the monomer is studied. Viscosity measurement, differential scanning calorimetry (DSC), and scanning electron microscopy (SEM) indicate that the concentration of tetrahydrofuran has pronounced effect on the molecular weight (Mη), glass transition temperature (Tg), and the morphology of the product.

Keywords: Polymerization, acrylic acid, tetrahydrofuran, supercritical, carbon dioxide.

Recently, compressed gases have been used in some gas antisolvent processes, such as fractionation of natural products, recrystallization of organic and inorganic materials, and polymer processing[1,2]. We studied the effect of the dissovled supercritical CO_2 and THF on the polymerization of AA. It was not found in theliterature.

Experimental

One ml acrylic acid monomer, 0.020 g initiator 2,2'-azobis (isobutyronitrile) (AIBN), and desired amount of THF were added into an optical cell of 10 ml. CO_2 was charged, stirred until vapor-liquid equilibrium was reached at about 300 K and 5 MPa. The temperature of the cell was then increased and controlled to be 333.2 K. The pressure in the cell was increased to 6.5 MPa by charging CO_2 again, the polymerization was unnoticeable at this stage. The reaction was allowed to last for 4 hours. The product was collected and yields were determined gravimetrically. The Mη, Tg, and morphology of the products were characterized by viscosity measurement, DSC, and SEM, respectively.

Results and Discussion

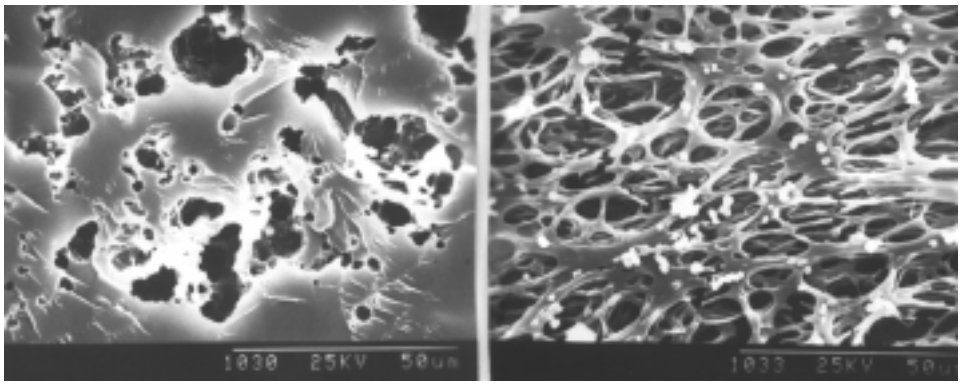
The properties of the polymer samples synthesized are listed in **Table** 1. THF/AA in the **Table** stands for the volume ratio of THF to AA in the feed. It can be seen from **Table** 1 that the concentration of THF has pronounced effect on the molecular weight and glass transition temperatures. As usual, the Tg increases with Mη.

Table 1. Properties of the polymers

Sample	THF/AA	Mη	Tg (K)	Yield (%)
1	0.09	1.946E5	390.0	84
2	0.27	2.141E5	395.6	85

Electron micrographs of the products prepared at different THF concentrations are shown in **Figure 1**. THF/AA affects the morphology of the product significantly. There may be two main reasons. First, some of the CO_2 and most of the THF in the cell is dissolved into AA monomer before the reaction occurs. The viscosity, diffusivity and other physical properties of the AA monomer is directly related with the amount of the dissolved CO_2 and THF, which affects the reaction process. Second, CO_2 -THF solution is trapped in the product and occupies some space in the product and they are vaporized after the pressure is released. It was found that in the absence of THF, the effect of dissolved CO_2 on the properties of the product is unnoticeable, which is not discussed in this short paper.

Figure 1 Scanning electron micrographs of the products. Left: THF/AA=0.09; right: THF/AA=0.27.



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