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Effect of Co-solvent and Pressure on the Thermal Decomposition of 2, 2′ Azobis - (isobutyronitrile) in Supercritical CO_2

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Abstract: The thermal decomposition of 2, 2′-azobis (isobutyronitrile) (AIBN) in supercritical CO_2 with cosolvent methanol or cyclohexane has been studied by using UV/Vis spectroscopic method at 335.15 K and at 12.0 MPa and 14.0 MPa. Both of the cosolvents can accelerate the decomposition rate, and the effect of methanol is more significant than that of the cyclohexane.

Keywords: Supercritical CO_2, co-solvent, 2, 2′-Azobis(isobutyronitrile), thermal decomposition, pressure effect.

Recently, researchers pay much attention to the polymerization in supercritical (SC) CO_2. 2, 2′-Azobis (isobutyronitrile) (AIBN) is a commonly used initiator in free radical polymerization in supercritical CO_2[1]. It is well known that the decomposition rate of the initiator AIBN plays an important role for a polymerization process[2]. Guan *et al*. have studied the effect of pressure on the decomposition rate of AIBN in SC CO_2[2]. A small amount of polar cosolvent can influence the properties of SC CO_2 significantly[3]. It is expected that suitable cosolvents can be used to control the polymerizations. Thus, study of the effect of cosolvents on the decomposition rate of AIBN in SC CO_2 is of importance. In this work we studied the effect of cosolvents methanol and cyclohexane on the decomposition rate of AIBN at different pressures.

Carbon dioxide (99.995% purity) was supplied by Beijing Analytical Instrument Factory. Methanol and cyclohexane (>99.5%) were provided by Beijing Chemical Reagent Plant. AIBN was A. R. grade supplied by Beijing Chemical Reagent Plant and was recrystallized twice from methanol prior to use. The experimental setup used and procedures were similar to that reported previously[4]. The only difference was that a UV/Vis spectrophotometer produced by Beijing General Instrument Company (model TU-1201, resolution: 2 nm) was used in this work and all the data were collected and processed by computer.

In the UV/Vis spectra there is a peak at 347 nm, which is assigned to AIBN[2]. lnA (absorbance of AIBN) is a linear function of reaction time at all the experimental conditions, which indicates that decomposition of AIBN is a first-order kinetic reaction, and the rate constant (K_d) can be easily calculated on the basis of the slopes of the lnA *vs* reaction time curves. **Figure 1** shows the dependence of the thermal decomposition

rate constant on pressure and cosolvent concentration. The original concentration of AIBN is 1.23×10^{-2} M. Methanol and cyclohexane are cosolvents.

Figure 1 Dependence of K_d in SC CO_2 -methanol and SC CO_2-cyclohexane on pressure and co-solvent concentration at 335.15K

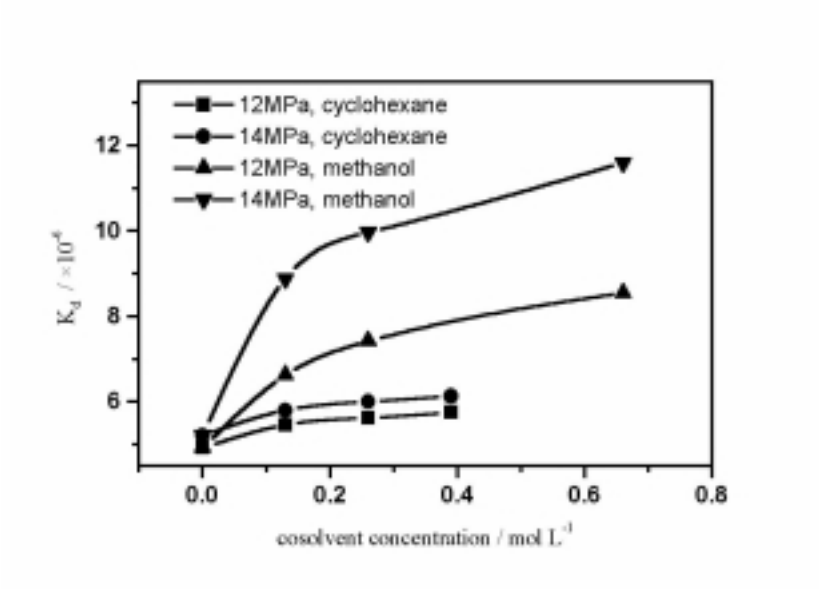

Figure 1 shows that both of the cosolvents can accelerate the decomposition of AIBN. The effect of cyclohexane is much smaller. The K_d increases with the increase of pressure. K_d is more sensitive to pressure in the presence of the polar co-solvent. It can be deduced from the results in **Figure 1** that a polymerization process in SC CO_2 can be tuned by suitable cosolvents.

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