Chinese Chemical Letters Vol. 11, No. 10, pp. 933–934, 2000

Controlling the Molecular Weight and Molecular Weight Distribution using Compressed CO_2 Antisolvent

Jun LIU[1], Zhi Min LIU[1], Bu Xing HAN[1]*, Jian WANG[2], Qing HUO[2], Fang Fang LIU[3]

1. Center For Molecular Sciences, Institute of Chemistry, Chinese Academy of Sciences,
2. Beijing 100080
3. Chemical Engineering College of Beijing United University, Beijing 100023
4. Department of Chemical Engineering, University of Science and Technology of Hebei, Shijiazhuang 050018

Abstract: Effect of CO_2 dissolved in tetrahydrofuran (THF) on the polymerization of styrene in THF was studied at 333.2 K and different pressures. It was found that the molecular weight (MW) and MW distribution of the polystyrene (PS) could be controlled by pressure.

Keywords: CO_2, antisolvent, styrene, polymerization

High-pressure gases are quite soluble in organic solvents and expand them largely[1], which can reduce the solvent strength of a solvent to such an extent that a solid dissolved in the solvent is precipitated. This process is called gas antisolvent process (GAS). GAS process has been used in recrystallization of organic solids[2], preparation of ultrafine particles[5, 4.] The applications of GAS are based on the fact that the composition of a gas-liquid solution changes with pressure of the gas, *i.e.*, properties of the solvent can be tuned continuously by pressure. Polymerization in liquid solvents has been studied for many years, and it is well known that the properties of the solvents affect the properties of products. In this work we studied the effect of CO_2 in THF on the MW and MW distribution of the polystyrene polymerized in the THF. This kind of work was not found in a literature survey.

Materials. CO_2 with a purity of 99.95% was supplied by Beijing Analytical Instrument Factory. THF, styrene, and 2,2'-Azobis (isobutyronitrile) (AIBN) were A.R. grade, which were supplied by Beijing Chemical Factory.

The apparatus was mainly composed of a gas cylinder, a high-pressure syringe pump, an optical cell of 35 cc, a pressure gauge, a constant temperature water bath. There were graduations on the optical cell so that the volume of the liquid in the cell could be known easily. In a typical reaction, the cell was purged with CO_2 for about 15 minutes. Then suitable amount of THF and Styrene (V:V=1:1) and 0.30 grams of AIBN were charged into the optical cell at room temperature. The cell was then transferred into the water bath of 336.2 K. As the cell was heated to the set temperature, suitable amount of CO_2 was charged into the cell until the volume of the liquid phase got to 30cc. The mixture in the cell was stirred using a magnetic stirrer. The polymerization reaction lasted for 16 hours. At the end of the reaction the cell was cooled, the CO_2 was slowly released and the liquid with polystyrene was collected. The polystyrene in the liquid was precipitated by methanol, and the product was collected. The molecular weight distribution of the product was determined by GPC.

The solubility of CO_2 in THF-styrene solution depends on pressure at fixed temperature. The solution is expanded after CO_2 is dissolved. **Table 1** show the effect of pressure on the volume expansion, yields, the weight average molecular weight (Mw), the numerical average molecular weight (Mn) and Mw/Mn. V_0 and V in **Table 1** stand for the volume of the liquid before and after dissolution of CO_2. The data in **Table 1** indicate that the molecular weight decrease with increasing pressure and the molecular weight distribution becomes narrower at the higher pressures. Thus the molecular weight and molecular weight distribution can be controlled by pressure. However, the yield becomes too low at larger $(V-V_0)/V_0$. This problem needs to be studied further.

Table 1. Effect of pressure on the $(V-V_0)/V_0$, yields, Mn, Mw, Mw/Mn

P/MPa	0	5.76	7.84	9.14	10.08
$(V-V_0)/V_0$	0.0	0.5	1.0	2.0	4.0
Yields/%	59	41	35	24	11
$Mw\times10^4$	8.08	4.21	2.26	1.89	1.27
$Mn\times10^4$	3.63	2.30	1.44	1.42	1.00
Mw/Mn	2.22	1.81	1.57	1.33	1.27

Acknowledgment

The authors are grateful to the National Natural Science Foundation of China for financial support (29725308, 29633020).

References

1. A. Kordikowski, A. P. Schenk, R. M. van Nielen, C. J. Peters, *J Supercrit. Fluids*, **1995**, *8*, 205.
2. P. M. Gallagher, M. P. Coffey, and V. J. K rukonis, *J. Supercrit. Fluids*, **1992**, *5*, 130.
3. E. Reverchon, G. Della Porta, D. Sannino, P. Ciambelli, *Powder Technology*, **1999**, *102*, 127.
4. E. Reverchon, *J. Supercrit. Fluids*, **1999,** *15*, 1.

Received 10 April 2000