Reactivity Ratios for Microemulsion Copolymerization of N-butyl Maleimide and Styrene

You Liang ZHAO*, Hua Ming LI, Peng Sheng LIU

College of Chemistry and Chemical Engineering, Xiangtan University, Xiangtan 411105

Abstract: The oil-in-water microemulsion containing N-butyl maleimide(NBMI, M_1) and styrene(St, M_2) was prepared. The complexation properties of NBMI and St in microemulsion were investigated by means of ^{1}H-NMR. With the participation of charge-transfer complex(CTC), four reactivity ratios and the relative reactivity of free monomers and CTC were obtained. The result was compared with that measured by Mayo-Lewis method.

Keywords: N-Butyl maleimide, styrene, charge-transfer complex, O/W microemulsion, copolymerization, reactivity ratios.

Introduction

Reactivity ratios can offer the message of relative reactivity of comonomers. Two monomer reactivity ratios can be acquired from the end-group model proposed by Mayo and Lewis, however, there are only apparent reactivity ratios available from this kinetic model when charge-transfer complex (CTC) participates in the copolymerization. Therefore, the copolymerization in which CTC exists is worthy of further research. So far, there are three kinetic models of copolymerization with the participation of CTC in all, namely, Seiner and Litt model[1], Shirota model[2] and Shan Guorong model[3].

Maleimide and its derivatives possess an unsaturated imide ring and endow polymers with excellent thermal stability. They are among the most valuable comonomers. Polystyrene is widely used as a conventional plastic, but its application is considerably restricted due to its bad thermal properties. When styrene is copolymerized with maleimides, its heat-resistance properties will be greatly improved. The microemulsion polymerization has attracted wide attentions since it was firstly reported by Stoffer and Bone in 1980[4]. To date, some monomers have been successfully polymerized in microemulsion, nevertheless, there are few researches on microemulsion polymerization and copolymerization of maleimide and its derivatives[5].

Experimental

The oil-in-water microemulsion of N-butyl maleimide (M_1) and styrene (M_2) was prepared with sodium dodecyl sulfate (SDS) and pentanol (PTL) as the emulsifier. The chemical shifts of a series of microemulsions were measured by means of ^{1}H-NMR when

the NBMI concentration was constant. The microemulsion copolymerization was carried out in sealed ampoules at 60^0C with potassium persulfate (KPS) as an initiator. The composition of copolymers was determined by elemental analysis.

Results and discussion

From the ^{1}H-NMR spectra, it is found that when the St concentration increases, the peak height and chemical shift of NBMI vinylene protons become smaller, however the peak height of St vinyl protons increases and the chemical shift does not change, which suggests that there is CTC in microemulsion systems. The complexation equilibrium constant at 60^0C was calculated to be 0.124 L/mol by Hanna-Ashbaugh equation, and the overall activation energy of complexation reaction determined by Arrhenius plots was 34.72KJ/mol(25-60^0C).

In the course of copolymerization, by controlling the monomer conversion less than 10% and changing monomer feeds, four reactivity ratios and the relative reactivity of free monomers and CTC were obtained on the basis of kinetic model proposed by Shan Guorong. They were r_{12}=0.0420, r_{21}=0.0644, r_{1C}=0.00576, r_{2C}=0.00785, k_{1C}/k_{12}=7.29 and k_{2C}/k_{21}=8.22, respectively.

In order to compare the values of cross-propagation rate constants with homopropagation rate constants, the ratios of the cross-propagation to homopropagation constants are listed in **Table 1**.

Table 1. Reactivity ratios and ratios of cross to homo-propagation rate constants at 60^0C ([M]$_0$=0.30mol/L, [KPS]=0.5$\times10^{-3}$mol/L, [SDS]=0.21mol/L, [PTL]=0.28mol/L)

r_{12}	r_{21}	r_{1C}	r_{2C}	k_{12}/k_{11}	k_{21}/k_{22}	k_{1C}/k_{11}	k_{2C}/k_{22}
0.0420	0.0644	0.00576	0.00785	23.8	15.5	173.6	127.4

The results showed that the propagation of radical reacting with CTC was much faster than that reacting with free monomers, and the rate constant of cross-propagation was much greater than that of homopropagation.

By using Mayo-Lewis equation, two monomer reactivity ratios were calculated to be r_1=0.0512 and r_2=0.0804 at various monomer feeds. It was obvious that there was only apparent reactivity ratios available from the end-group model, it could not provide such messages as the reactivity ratios and relative reactivity of free monomers and CTC.

References

1.   J. A. Seiner, M. Litt, *Macromolecules*, **1971**, *4*, 308.
2.   M. Yshimura, T. Nogami, M. Yokoyama, *Macromolecules*, **1976**, *9*, 211.
3.   G. R. Shan, Z. M. Huang, Z. X. Weng, Z. R. Pan, *Macromolecules*, **1997**, *30*, 1279.
4.   J. O. Stoffer, T. Bone, *J. Polym. Sci.: Polym. Chem.*, **1980**, *18*, 2641.
5.   Y. L. Zhao, P. S. Liu, H. M. Li, J. Y. Ai, Q. Cao, *Preprints of 6th Pacific Polymer Conference, Guangzhou*, **1999**, 115.