# Mutual Solubility and Bulk Copolymerization of Vinyl Monomers with *N*-Substituted Maleimide

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ABSTRACT: On the basis of the structure and melting parameters of *N*-substituted maleimide and vinyl monomer, the saturated molar solubility fraction of *N*-substituted maleimide in vinyl monomer or their mixtures was predicted. The predicted value was consistent with the experimental data. The effects of reaction temperature, initiator concentration, molar fraction of monomer, and monomer feed mode on the copolymerization rate of styrene (St)/*N*-phenylmaleimide (PMI) were studied. The bulk copolymerization kinetics of methyl methacrylate (MMA)/*N*-cyclohexylmaleimide, St/PMI/MMA, and St/PMI/acrylonitrile were also investigated. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 2641–2647, 1999

**Key words:** bulk copolymerization; vinyl monomer; N-substituted maleimide; saturated molar solubility fraction

# **INTRODUCTION**

N-substituted maleimide polymers usually have high heat resistance,<sup>1</sup> but they cannot be used as engineering plastics because their high glass transition temperatures lead to difficulty in processing. However, the properties of *N*-substituted maleimide/vinyl monomer copolymers could be altered by adjusting the comonomer feed ratio and comonomer pair<sup>2,3</sup> so as to overcome these shortcomings.

All radical copolymerizations of *N*-substituted maleimide with vinyl monomers have been studied so far in solvents, in which the *N*-substituted maleimide completely dissolves.<sup>4-6</sup> The solubility of *N*-substituted maleimide in vinyl monomer used as a solvent is important for bulk copolymerization. Under these conditions, the quantity of

*N*-substituted maleimide copolymerized with a vinyl monomer cannot exceed the saturated solubility at the reaction temperature.

The kinetics of bulk polymerization is of considerable interest in preparing commodity polymers by bulk or suspension polymerization. But unfortunately, research work on kinetics for vinyl monomer/N-substituted maleimide copolymerization will be somewhat difficult.

In this paper, the saturated solubility of *N*substituted maleimide in vinyl monomer was investigated. The kinetics of St/PMI copolymerization was studied in detail, and those of styrene (St)/*N*-phenylmaleimide (PMI)/methyl methacrylate (MMA), St/PMI/acrylonitrile (AN), and MMA/ *N*-cyclohexylmaleimide (ChMI) copolymerization were also investigated.

# **EXPERIMENTAL**

#### Materials

St, MMA, and AN were distilled under reduced pressure after removal of the inhibitor by the usual method. They were kept cold before use.

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PMI and ChMI were prepared by the method of Searle<sup>7</sup> and recrystallized several times from the ethanol/water mixture (volume ratio 1 : 2). They were characterized by NMR and IR spectra in order to make sure that they were free from unreacted maleic anhydride and uncyclized maleamic acid. The purity of PMI and ChMI were measured by elemental analysis.

The initiator, benzoyl peroxide (BPO), was recrystallized from the chloroform solution with absolute methanol.

#### Saturated Solubility Measurement

Accurately weighed N-substituted maleimide and vinyl monomer or their mixture were added into a large glass tube with condenser and agitator. The tube was placed in a double-jacketed water bath. The temperature was increased at a rate of 0.1°C per minute until N-substituted maleimide dissolved; at this point the temperature was noted. Then the mixture was cooled and the temperature recorded at which the N-substituted maleimide precipitated out again. The experiment was repeated until the dissolution temperature was identical with the precipitation temperature. The saturated molar solubility fraction of N-substituted maleimide  $(S_2)$  is

$$S_2 = n_2 / (n_1 + n_2) \tag{1}$$

where  $n_1$  and  $n_2$  are the mole of vinyl monomer and N-substituted maleimide at the solid-liquid equilibrium.

#### Copolymerization

Accurately weighed vinyl monomer, N-substituted maleimide, and BPO were mixed and placed in a long, fine, glass tube. The tube was connected to a vacuum and nitrogen system, and after being swept of oxygen, the tube was sealed. Copolymerization was carried out in a water bath at various temperatures. The glass tube was remove at a definite time interval and cooled down immediately to stop the reaction; then the product was dissolved in tetrahydrofuran, precipitated from a large amount of ethanol, washed with ethanol, and dried under vacuum at 60°C. The weight conversion of copolymerization was obtained. The molar conversion of copolymerization was calculated using the data of weight conversion and copolymer composition.

# **RESULTS AND DISCUSSION**

# Mutual Solubility of N-Substituted Maleimide in Vinyl Monomer

From the view of thermodynamics, the general equation of the saturated molar solubility fraction for solid-liquid equilibrium is<sup>8</sup>

$$S_{2} = \frac{1}{\gamma_{2}} \exp\left[\frac{\Delta H_{tp}}{R} \left(\frac{1}{T_{tp}} - \frac{1}{T}\right) - \frac{\Delta C_{p}}{R} \left(\ln\frac{T_{tp}}{T} - \frac{T_{tp}}{T} + 1\right) - \frac{\Delta V}{RT}(P - P_{tp})\right]$$
(2)

Neglect the amendment of pressure and heat capacity difference, and replace the triple point data with the atmospheric melting point, melting enthalpy and entropy. Equation (2) can be simplified to

$$S_{2} = \frac{1}{\gamma_{2}} \exp\left[\frac{\Delta S_{m}}{R} \left(1 - \frac{T_{m}}{T}\right)\right]$$
(3)

The activity coefficient of solute is calculated by the Scatchard–Hildebrand equation.<sup>9–11</sup> Thus we have

$$S_2 = \exp\left[\frac{\Delta S_m}{R} \left(1 - \frac{T_m}{T}\right) - \frac{V_2 \phi_1^2 (\delta_1 - \delta_2)^2}{RT}\right] \quad (4)$$

$$\phi_1 = V_1 S_1 / (V_1 S_1 + V_2 S_2) \tag{5}$$

where S, V, and  $\delta$  are the saturated molar fraction, molar volume, and solubility parameter, respectively. Subscript 1 and 2 are the solvent (vinyl monomers) and solute (*N*-substituted maleimides).  $T_m$  and  $\Delta S_m$  are the atmospheric melting point and melting entropy of *N*-substituted maleimide. The  $\phi_1$  is the volume fraction of solvent.

For the mixed solvent,

$$\delta_1 = \sum S_i V_i \delta_i / \sum S_i V_i \tag{6}$$

$$V_1 = \sum S_i V_i / \sum S_i \tag{7}$$

The data of V,  $\delta,$   $T_m,$  and  $\Delta S_m$  are listed in Table I.

In Table I,  $T_m$  and  $\Delta H_m$  of N-substituted maleimide are measured by differential scanning calorimetry (DSC), and  $\Delta S_m = \Delta H_m/T_m$ . The V

	$T_m$ (°C)	$\begin{array}{c} \Delta {S_m} \\ \text{(J/mol/K)} \end{array}$	V (cm <sup>3</sup> /mol)	$\delta (J/cm^3)^{1/2}$
N-Phenyl maleimide	88.97	55.68	111.0	21.9
N-Cyclehexyl maleimide	87.32	63.21	148.6	17.6
Styrene			115.0	17.7
Methyl methacrylate			106.0	17.8
Acrylonitrile			66.5	21.3

Table I Calculated Parameters of Solid-Liquid Equilibrium

and  $\delta$  of *N*-substituted maleimide are calculated using the group additive method according to reference 12. The *V* and  $\delta$  of vinyl monomer are provided in ref. 13.

The modeling values of the *N*-substituted maleimide saturated molar solubility fraction in vinyl monomer are calculated from eq. (4)  $\sim$  eq. (7). The modeling values and experimental data are presented in Figures 1–6.

The modeling value of the *N*-substituted maleimide saturated molar solubility fraction in both single and mixed vinyl monomer solvents are in agreement with experimental data. So, the saturated molar solubility fraction can be predicted from the comonomer structure parameters, and the melting point and melting entropy of *N*-substituted maleimide.

#### Kinetics of St/PMI Bulk Copolymerization

The effect of reaction temperature on conversion is shown in Figure 7. Because of the glass transition effect, high conversion of St/PMI bulk co-



Figure 1 Solubility of PMI in St.

polymerization was not reached at low temperature (such as 80°C). When the reaction temperature is high enough (90°C), the final conversion of St/PMI bulk copolymerization would exceed 90%.

In order to establish the overall activation energy for St/PMI bulk copolymerization, the conversion dependence of the reaction temperature was investigated when the PMI feed  $(f_2)$  was 0.05 (see Fig. 8). The overall activation energy can be calculated from the curve of  $\ln(R_p)_0$  vs. 1/T (see Fig. 9), and it is 70 kJ/mol and less than the one in chloroform.<sup>14</sup> It is evident that the contribution of charge-transfer complex (CTC) is considerable in the bulk copolymerization.

From the curve of  $\ln(R_p)_0$  vs.  $\ln[BPO]$  (see Fig. 10), the relationship  $(R_p)_0 \propto [BPO]^{0.52}$  demonstrates the bimolecular termination of the copolymerization process. The result is similar to that in chloroform.<sup>14</sup>

In general, the copolymerization rate will increase with the increase of the highly reactive monomer fraction. Figure 11 indicates that the copolymerization rate increases rapidly with the



Figure 2 Solubility of PMI in MMA.



Figure 3 Solubility of PMI in AN.

increase of PMI fraction. When the equimole comonomer pair is added to a glass autoclave (the reaction temperature must be higher than 64°C, according to the PMI saturated molar solubility fraction in St) under the protection of nitrogen, rapid copolymerization happens without the presence of initiator after the St and PMI monomers mixed about 10 min.

In order to investigate the effect of all PMI fractions on the copolymerization rate, DSC was used to measure the copolymerization rate of St/PMI. On the basis of the relationship between time and molar copolymerization heat, the copolymerization rate was given at all PMI fractions (see Fig. 12). The initial copolymerization



Figure 5 Solubility of PMI in St/MMA.

rate does not maximize at the equimolar feed ratio but at approximately 0.6 molar fraction of PMI. This means that both the CTC and free monomers participate in the copolymerization process. The  $f_2$  is approximately 0.7 in chloroform<sup>14</sup> and 0.6 in bulk copolymerization, and it is more nearly to 0.5 in bulk copolymerization. It is obvious that the contribution of CTC is considerable in the bulk copolymerization.

When all the PMI monomer is added at the beginning, the initial copolymerization rate is too high to control for preparing the high PMI unit content copolymer. If PMI is added portionwise several times, the concentration of CTC will be low to decrease the copolymerization rate, the



Figure 4 Solubility of ChMI in St.



Figure 6 Solubility of PMI in St/AN.



**Figure 7** Conversion curves of St/PMI copolymerization ( $f_2 = 0.05$ , [BPO] = 0.3%).

copolymerization heat will generate slowly, and the composition of copolymer will be easy to control. So two feed modes are designed:

- Feed mode 1: all the PMI monomer is added at the beginning.
- Feed mode 2: a quarter of PMI monomer is added at the beginning, then a quarter of the PMI monomer is added once at every 100min interval.

The kinetics comparison of the two feed modes is shown in Figure 13. For feed mode 1, the initial



Figure 8 Molar conversion-time curves at different temperature ( $f_2 = 0.05$ , [BPO] = 0.3%).



Figure 9 Initial reaction rate vs temperature ( $f_2 = 0.05$ , [BPO] = 0.3%).

copolymerization rate is very high and the conversion is more than 30% after 100 min. For feed mode 2, the copolymerization rate is gentle and even. It may be expected that an even copolymerization rate can be controlled in the continuous feed mode of the PMI monomer.

### Kinetics of the Other Bulk Copolymerization

In order to prepare the transparent and heatresistant plastics, the MMA/ChMI copolymerization was investigated at 90°C with BPO as initi-



**Figure 10** Effect of BPO concentration on the initial reaction rate ( $f_2 = 0.09, T = 50$ °C).



**Figure 11** Effect of low PMI fraction on copolymerization ( $T = 90^{\circ}$ C, [BPO] = 0.3%).

ator. The copolymerization rate of MMA and ChMI is much lower than that of St and PMI since no CTC formed between MMA and ChMI.

MMA or AN is selected as the third monomer for St and PMI copolymerization. There are two aims to add the third monomer: one is to adjust the copolymer composition and decrease the glass transition temperature of the St/PMI copolymer; the another is to research the effect of the third monomer on the copolymerization rate.

The glass transition temperatures of the St/ PMI/MMA and St/PMI/AN terpolymer decrease to 180 and 120°C, but that of St/PMI copolymer is



**Figure 12** Effect of PMI fraction on copolymerization measured by DSC ( $T = 90^{\circ}$ C, [BPO] = 0.3%).



**Figure 13** Comparison the effect of feed mode on St/PMI copolymerization ( $f_2 = 0.09$ , T = 50°C, [BPO] = 0.3%).

over 200°C at the same PMI feed ratio (20 wt %). The lower glass transition temperature will do well for processing.

The 20 wt % St in the St/PMI copolymerization system was replaced by the same weight ratio of MMA or AN; the reaction rates of the three systems are similar before 30% conversion, but different after 30% conversion. The final conversions of St/PMI, St/PMI/MMA, and St/PMI/AN are approximately 35, 60, and 90% at 60°C (see Fig. 14). St/PMI copolymerization is nearly alternating,<sup>14</sup>



**Figure 14** Conversion curves of MMA/ChMI (80 : 20), St/PMI (80 : 20), St/PMI/MMA (60 : 20 : 20), and St/PMI/AN (60 : 20 : 20) copolymerization in bulk process ( $T = 60^{\circ}$ C, [BPO] = 0.3%).

the reaction rates of these three systems are mainly contributed by the St/PMI alternating copolymerization, so they are similar. When the alternating comonomer was over, the remaining monomers homopolymerized or copolymerized. It is obviously that the St homopolymerization rate is much lower than that of St/AN or St/MMA copolymerization.

# CONCLUSION

Using the nonideal solid-liquid equilibrium equation, the saturated molar solubility fraction of N-substituted maleimide in vinyl monomer could be calculated. The calculated results were in agreement with the experimental data in both single and mixed vinyl monomer solvents. The bulk copolymerization of St/PMI was investigated in detail. The higher reaction temperature was necessary to prepare high conversion St/PMI copolymer. The overall activation energy for St/PMI bulk copolymerization was 70 kJ/mol and less than that one in chloroform. The bimolecular termination was proven. The maximum of initial copolymerization rate was at approximately 0.6 molar fraction of PMI. The kinetics results of St/PMI bulk copolymerization provided evidence that the contribution of CTC was more in the bulk copolymerization than in chloroform. The copolymerization rate could be controlled in feed mode. The kinetics of other vinyl monomer/N-substituted maleimide bulk copolymerization indicated that there was no charge-transfer complex formation between MMA and ChMI, but the third

monomer of MMA or AN could decrease the glass transition temperature of the copolymers and enhance the later reaction rate.

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