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# Free Radical Copolymerization of Maleic Anhydride with Cyclohexene

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*Free radical copolymerization of maleic anhydride ( $M_1$ ) with cyclohexene ( $M_2$ ) was carried out with 2,2'-azobis(isobutyronitrile) as an initiator in various solvents. The copolymerization of maleic anhydride with cyclohexene in benzene and toluene proceeded in a heterogeneous system to give an alternating copolymer independent of the monomer composition in the feed. The powerful alternation tendency cannot be explained by the participation of charge-transfer complex in the propagation due to the absence of charge-transfer complex formation between maleic anhydride and cyclohexene in the copolymerization system. Furthermore, the initial rate of copolymerization ( $R_p$ ) was found depend on the monomer composition and was a maximum of about 60 mol% of maleic anhydride in the feed. A solvent effect on the copolymerization system was also investigated, i. e., copolymerization in benzene produced a higher  $R_p$  than that in toluene or in chloroform. The copolymer was characterized by <sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectra.*

**Keywords** maleic anhydride, cyclohexene, radical copolymerization, alternating copolymer

## Introduction

In recent years, there has been considerable interest in the research of alternating copolymerization systems in which electron donor-acceptor complexes are formed between pairs of electron-rich and electron-deficient comonomers. A link has been found to exist between the alternating tendency of the comonomer units in a number of systems containing cyclic anhydride units by using <sup>13</sup>C-NMR spectroscopy (1). An electron donor monomer and maleic anhydride as electron acceptor is a classical comonomer pair, which forms alternating copolymers with radical initiators (2). The powerful alternating tendency in the copolymerization system has been explained by the addition of a charge-transfer complex (CTC), which was formed between the electron acceptor (maleic anhydride) and the electron donor such as styrene, dimethylbutadiene, vinyl ethers, and ethylene (3–7). On the other hand, the results (8) obtained by many authors for alternating copolymerization of MA with benzofuran, indol and benzothiophene

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indicated that the reactivity of the comonomer to form alternating copolymers was governed by the resonance stabilization of the monomer and to a lesser extent by complex formation, and the formation of CTCs is not the most important factor in determining the reactivity in copolymerization of MA with the above-mentioned heterocyclic monomers. Furthermore, much evidence has been proposed to query the mechanism of CTC and against the participation of a CTC in the propagation of styrene-maleic anhydride (9).

However, until now, no references to copolymerization of maleic anhydride with cyclohexene have been found. We recently became interested in this system, for cyclohexene is a barely homopolymerized monomer by using any kind of initiators. In this paper, we deal with the free radical copolymerization of maleic anhydride with cyclohexene, the effects of reaction condition on the copolymerization were discussed. The copolymer was characterized from  $^1\text{H-NMR}$  and  $^{13}\text{C-NMR}$  spectra.

## Experimental

### Materials

Cyclohexene (CH) was from Aldrich and distilled before use. Maleic anhydride (MA) was recrystallized from benzene and sublimed in vacuum before use, the melting point of purified MA was  $52.7^\circ\text{C}$ . 2,2'-Azobis(isobutyronitrile) (AIBN) was purified by recrystallization from methanol. Solvents were purified by distillation.

### Polymerization Procedures

Copolymerization reactions were carried out in glass tubes, which contained a magnetic stirrer. A solution of MA, CH and AIBN was placed into the tube. Then, the tube was degassed, swept with nitrogen three times, and finally, the tube was sealed. After polymerization for a given time at  $60^\circ\text{C}$  with stirring, the polymerization mixture was poured into a large amount of methanol to precipitate the polymer. The yield of polymers was determined gravimetrically.

The composition of the copolymers was determined from the anhydride concentration presented in the copolymer. A typical measurement procedure was as follows: 0.5 g of copolymer was dissolved in 200 mL of chloroform at ambient temperature and 0.1 mL of water was added. The solution was stirred for two days in order to fully hydrolyze the anhydride groups. The anhydride concentration presented in the copolymer was determined by titration of the solution to a phenolphthalein end point using potassium hydroxide in methanol.

### Measurements

The molecular weight of the resulting polymer was determined by gel permeation chromatography (GPC) calibrated with polystyrene standards using Waters-1515 with tetrahydrofuran (THF) as an eluent. NMR spectra were taken by means of a Varian Unity-200.

## Results and Discussion

### Charge-Transfer Complex

Copolymerization of MA and CH was carried out with AIBN as initiator in benzene and an alternating copolymer was obtained (Table 1). This result is better understood since both

**Table 1**  
Radical copolymerization of MA ( $M_1$ ) with CH ( $M_2$ ) in benzene, chloroform,  
and toluene at 60°C

Solvent	MA in feed mol% <sup>a</sup>	Polymer yield wt%	$M_n \times 10^{-3}$	$M_w/M_n$	MA in copolymer mol% <sup>b</sup>
Benzene	10	3.6	1.7	2.7	45.9
	20	6.0	1.4	2.5	48.6
	30	6.4	1.5	2.3	49.3
	40	8.1	1.6	2.6	49.8
	50	9.1	1.5	2.5	50.0
	60	9.9	1.3	2.7	50.1
	70	8.6	1.4	2.0	49.9
	80	7.5	1.5	2.6	50.0
	90	7.0	1.3	2.7	50.1
Toluene	50	7.3	1.1	2.4	49.8
Chloroform	50	6.8	0.9	2.8	50.1

<sup>a</sup>[CH] + [MA] = 1.0 mol/L, [AIBN] =  $1.0 \times 10^{-2}$  mol/L, the reaction time is 75 h.

<sup>b</sup>Determined by the titration method.

MA and CH are scarcely homopolymerized. In the literature, the powerful alternating tendency in the copolymerization of MA with vinyl monomers has often been discussed in connection with the participation of CTC. Rzaev and Cowie et al. (10, 11) has proposed that the radical alternating copolymerization of MA with styrene probably finished through formation of a CTC between initial monomers. From this monomer system, high molecular weight copolymer with an alternating structure was prepared even in the absence of the initiator (12). Rzaeva et al. (13) investigated the radical copolymerization of dicyclopentadiene with maleic anhydride. A quantitative kinetic analysis shows reactions that involve the complexed monomers prevail in the elementary propagation steps and a "complex" mechanism of chain growth has been proposed for alternating copolymerization of dicyclopentadiene with maleic anhydride. However, evidence against the participation of CTC in the propagation has also been reported. Seymour and Gamer studied the effect of temperature on the CTC equilibrium of styrene-MA and the copolymerization, they found that the CTC of styrene-MA was not detectable in decalin at a temperature above 120°C. Dong has reported that the random copolymer of styrene and MA had a yield above 140°C, the maximum copolymerization rate for some acceptor-donor electron monomer system did not appear in the monomer ratio of 1:1 (9, 14).

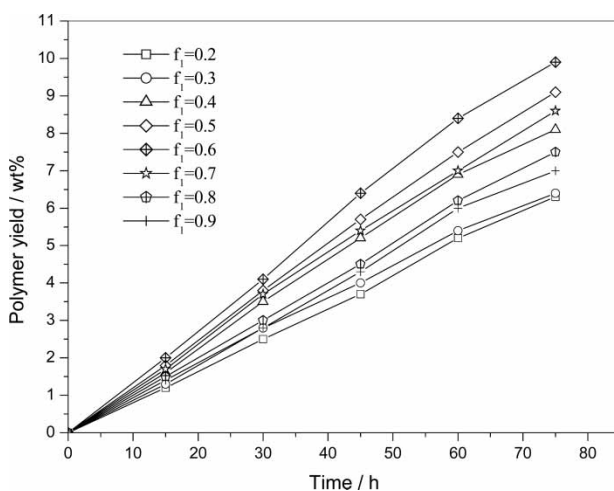
In this work, the <sup>1</sup>H-NMR method, with use of the Hana-Ashbaugh equation, was applied to determine whether or not the CTC between MA and CH existed in this system. The value of complex formation constant K for MA-CH CTC in benzene at 25°C is found to be zero (results are not shown) which indicates that the CTC between monomers does not exist in this polymerization system. The result may be explained that the interaction between MA and CH is very weak due to the weak electron donation of CH. CTC equilibrium constant is related with the donor/acceptor strengths of comonomer systems. A comparison of alternating copolymerization systems results revealed that for a series of related copolymers prepared under identical conditions,

comonomer systems with greater donor/acceptor strengths, and hence higher values of the equilibrium constant for a 1:1 electron donor-acceptor complexes formation (1).

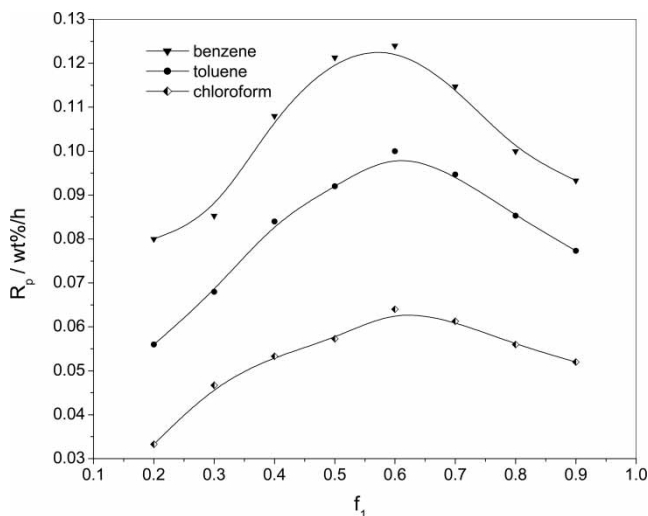
### Copolymerization of MA and CH

Radical copolymerization of MA ( $M_1$ ) and CH ( $M_2$ ) was carried out with AIBN in benzene under a series of comonomer composition ( $f_1$ ) at a constant total monomer concentration at 60°C. Figure 1 shows the relationships between the copolymer yield and reaction time under various initial comonomer molar fraction ( $f_1$ ). The copolymerization proceeded heterogeneously in all cases. The results of Figure 1 showed that the copolymerization of MA with CH at a very low rate, e.g., very low yields, and low molecular weight copolymer (Table 1). This indicates that the steric hinderance is more important in the copolymerization system because MA and CH are both 1,2-disubstituted monomers. Figure 2 shows the relationship between the initial rate of copolymerization ( $R_p$ ) and comonomer composition ( $f_1$ ) for radical copolymerization of MA with CH in several solvents at 60°C. The  $R_p$  values with units of wt%/h were determined from the initial slope of the polymer yield-time curves in consideration of the copolymers obtained with. A variation in the  $R_p$  values depending on the comonomer composition was observed for the copolymerization system in benzene, toluene and chloroform, i. e., in benzene, the  $R_p$  value increased quickly with increasing the molar fraction of MA in the feed until it reached a maximum value when  $f_1$  was 0.6. As the  $f_1$  value increased further, the  $R_p$  value decreased. The  $R_p$  value in benzene was higher than that in toluene and chloroform. However, the value of  $f_1$  at the maximum  $R_p$  value was almost the same. A similar result has been found by Li (15) in their studies of the copolymerization of N-phenylmaleimide with cyclohexene.

Table 1 presented the comonomer-copolymer composition for the copolymerization of MA and CH in benzene, toluene, and chloroform, an alternating copolymer was obtained regardless of the comonomer composition. The monomer reactivity ratio were



**Figure 1.** Relationships between polymer yield and reaction time for the radical copolymerization of maleic anhydride with cyclohexene in benzene at 60°C under various comonomer composition ( $f_1$ ),  $[CH] + [MA] = 1.0 \text{ mol/L}$ ,  $[AIBN] = 1.0 \times 10^{-2} \text{ mol/L}$ .



**Figure 2.** Relationships between  $R_p$  and several solvents under different molar fraction of MA in the feed ( $f_1$ ) for the radical copolymerization of maleic anhydride with cyclohexene at 60°C,  $[CH] + [MA] = 1.0 \text{ mol/L}$ ,  $[AIBN] = 1.0 \times 10^{-2} \text{ mol/L}$ , the reaction time is 75 h.

determined by the Kelen-Tüdös method, and the overall procedure began with conducting MA and CH copolymerization at a variety of  $M_1/M_2$  feed ratios. Copolymerization at low conversions (10 wt%) were performed and copolymer composition was analyzed by a titration method. The monomer reactivity ratios were found to be  $r_1 = 0$  and  $r_2 = 0$  in either of the solvents. The results are easy to understand because CH cannot be homopolymerized with a radical initiator, while MA is not homopolymerized under the selected conditions.

### Solvent Effects

The experimental results suggested that copolymerization of MA with CH was influenced by the solvents. Table 2 listed the results of the copolymerization of MA with CH in different solvents. The copolymer of MA and CH can be obtained only when benzene, toluene and chloroform are used as solvents. No copolymer is obtained in a solvent with a high dielectric constant such as dimethylformamide (DMF), tetrahydrofuran (THF), and dimethylsulfoxide (DMSO). This result is similar to the radical homopolymerization of N-cyclohexylmaleimide (CHMI), N-hexylmaleimide (HMI), and N-phenylmaleimide (PHMI) in THF reported by D.J.T. Hill and his coworkers (16). The mechanism of radical homopolymerization of CHMI, HMI and PHMI in THF indicates that the AIBN free radicals undergo transfer to THF and the resulting THF radicals initiated the polymerization. In the termination step, the polymer chain radical undergoes chain transfer to THF. In addition, the solvent retardation theory developed by Burnett and Loan suggests that a radical of low reactivity can be produced by transfer to solvent. Therefore, the chain transfer to solvent i.e., THF, may be the main reason for the absence of MA-CH copolymer formation in such solvent. On the other hand, the strong solvation effect of the solvents could be the explanation for the phenomenon of no polymer formation in DMSO and DMF. When copolymerization of MA with CH proceeded in such solvents,

**Table 2**  
Radical copolymerization of MA ( $M_1$ ) and CH ( $M_2$ ) in serious solvents<sup>a</sup>

Solvents <sup>b</sup>	Dielectric constant ( $\epsilon$ )	CH in feed mol%	Yield wt%	$M_n \times 10^{-3}$	$M_w/M_n$	CH in copolymer mol%
Dioxane	2.09	50	Trace	—	—	—
Benzene	2.3	50	9.1	1.5	2.5	50.0
Toluene	2.4	50	7.3	1.1	2.4	49.7
Chloroform	4.9	50	6.8	0.9	2.8	50.1
THF	7.6	50	0			
DMF	36.71	50	0			
DMSO	48.9	50	0			

<sup>a</sup>[CH] + [MA] = 1.0 mol/L, [AIBN] =  $1.0 \times 10^{-2}$  mol/L, the reaction time is 75 h.

<sup>b</sup>THF: tetrahydrofuran, DMF: dimethylformamide, DMSO: dimethylsulfone.

MA may be tightly solvated by solvent since MA is an extremely polar monomer. The CH radical may not be able to easily penetrate the solvent cage around the MA molecule because of polar repulsion between the approaching  $M_2$  radical and polar groups of the solvating solvent, and between the MA unit of  $M_2$  radical and the MA molecule in the cage. The MA may remain unattached by the propagating radical because it is strongly protected in the solvent cage. Thus, trace or no copolymer was obtained in these copolymerization systems. However, it is important to note that no polymer is obtained in the copolymerization of MA with CH in dioxane. The possible explanation is that dioxane, with two oxygen lone-pair electrons, can interact strongly with the electron-acceptor monomer MA and the electron-acceptor MA radical, which hinders of the reaction between CH radical and MA and a similar reaction between MA radical and CH.

As previously mentioned, the copolymerization rate in benzene was higher than that in toluene and in chloroform, which was obviously seen in Figure 2. These results are very much in agreement with results of the PHMI-CH copolymerization system. It is found that the solvent effect in the copolymerization of PHMI and CH influenced not only the copolymerization rate, but also the copolymer composition, together with the monomer reactivity ratio (15). The fact that the polymerization rate for radical copolymerization of MA with CH influenced by solvents can be discussed in connection with a chain transfer constant ( $C_s$ ) for the solvent. For example, the chain transfer constant for benzene, toluene, and chloroform in polymerization of styrene at 60°C are  $0.23 \times 10^{-5}$ ,  $1.25 \times 10^{-5}$ , and  $5 \times 10^{-5}$ , respectively (17). Benzene has the lowest  $C_s$  because of its strong bonds. On the other hand, the presence of the weaker benzyl hydrogens in toluene and weak C–H bond in chloroform leads to high  $C_s$  values relative to benzene. Even though the absolute value of the  $C_s$  for any one compound may change very significantly depending on the monomer being polymerized, the order of reactivity of a series of transfer agents usually remains the same irrespective of the monomer. Therefore, it is reasonable to assume that the  $C_s$  values for benzene, toluene, and chloroform in the copolymerization of MA with CH increase in the following order: benzene < toluene < chloroform. As previously mentioned, a radical of low reactivity can be produced from chain transfer to solvent. Thus, the effect of chain transfer in the polymerization rate may depend on the  $C_s$  value, and the  $R_p$  value may decrease with an increasing  $C_s$ .

value. The results, shown in Figure 2, may support this effect of chain transfer to solvent. Furthermore, benzene and toluene are not solvents for the copolymer of MA and CH, the acceleration effects may exist in these instances of heterogeneous copolymerization caused by a decrease in termination rate constant  $k_t$  relative to the propagation rate constant  $k_p$ . The growing polymeric radicals become coiled up, since they are essentially insoluble in such a solvent. Termination between radicals becomes progressively more difficult, while propagation may still proceed reasonably well. However, such effects do not exist in a homogeneous polymerization system, i.e., chloroform, since the copolymer of MA and CH is soluble in chloroform.

### Characterization of Copolymer

The resulting copolymers were soluble in many organic solvents including chloroform, acetone, DMF, DMSO and insoluble in benzene, toluene, and n-hexane. The  $^1\text{H-NMR}$  and  $^{13}\text{C-NMR}$  spectrum of the copolymer of MA and CH are shown in Figures 3 and 4. In the  $^1\text{H-NMR}$  spectra (chloroform-*d*), there are two major resonances in the 0.6 ~ 4.2 ppm region. The highly overlapped signals in the region of 0.6 ~ 2.8 ppm are assigned to the methylene protons and the methine protons of the CH unit, while the signals at 2.8 ~ 4.2 ppm can be attributed to the two methine protons of the MA units in the copolymer. It is important to note that the resonances of the MA unit are confined to the 2.8 ~ 4.2 ppm region, which suggests that the sequence of successive MA units may not exist in the MA-CH copolymer. Since poly(maleic anhydride) gives a broad group of resonances in the 4.0 ~ 5.0 ppm region, which is centered on 4.5' ppm. This result, in turn, indicates that the copolymers are composed of completely alternating monomer unit sequences, which is consistent with the fact that MA and CH are incapable of homopolymerizing with a radical initiator. Indeed, the copolymer composition was about MA : CH = 1.02:1.00, as estimated from the integrals associated with the CH unit of the 0.6 ~ 3.0 ppm region and the MA unit with resonances in the 3.0 ~ 4.2 ppm region in Figure 3. In addition, the weak signal at about 12.4 ppm is caused by -COOH groups formed, probably by hydrolysis during polymer work-up, while the very weak

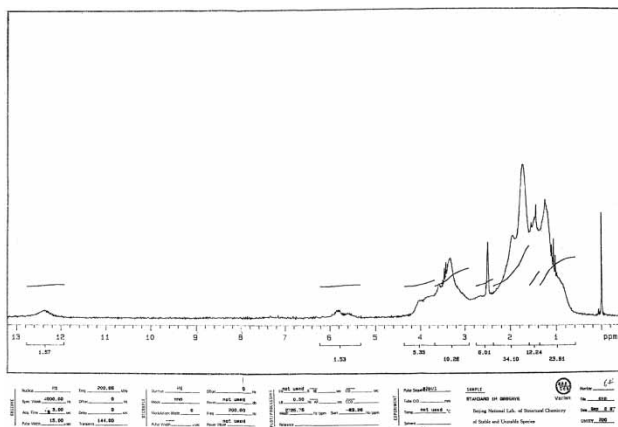


Figure 3.  $^1\text{H-NMR}$  spectrum of maleic anhydride-cyclohexene copolymer.



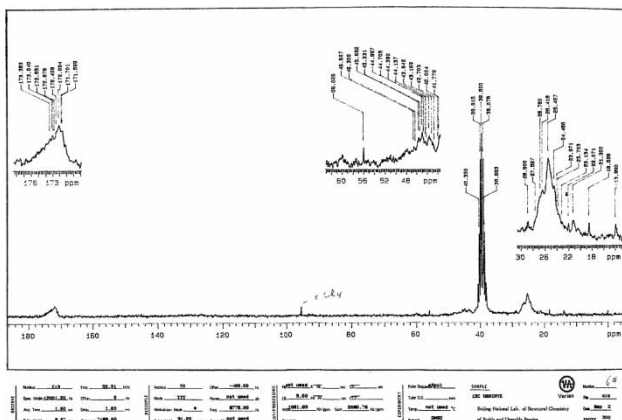


Figure 4.  $^{13}\text{C}$ -NMR spectrum of maleic anhydride-cyclohexene copolymer.

peaks at 5.4 ~ 6.0 ppm imply that the propagating radicals may be partly terminated by inconsistency.

The  $^{13}\text{C}$ -NMR spectrum of a copolymer of MA and CH is shown in Figure 4 (DMSO- $d_6$ ). It has been reported that methine carbon of MA unit resonates at 44.8 ppm in the poly(maleic anhydride), and that it resonates at 49 ~ 53 ppm and 37.5 ~ 42.5 ppm, respectively, in the alternating copolymer of MA and n-butyl vinyl ether. In Figure 4, the resonances at low field (about 172 ppm) are assigned to carboxylic groups of MA unit, whereas the resonances at 44 ~ 46 ppm are attributed to methine carbon of MA unit in copolymer of MA-CH. For CH unit, the methylene carbons resonate at 20 ~ 30 ppm, while the methine carbons resonate at 42 ~ 44 ppm.

## Conclusions

Free radical copolymerization of maleic anhydride ( $M_1$ ) with cyclohexene ( $M_2$ ) was carried out with 2,2'-azobis(isobutyronitrile) as an initiator in various solvents and an alternating copolymer was obtained independent of the monomer composition in the feed. The powerful alternation tendency can be explained by the absence of homopolymerizing ability of MA and CH under the selected conditions. The initial rates of copolymerization of MA and CH are dependent on the comonomer condition and solvents used. The copolymerization rate in benzene is higher than that in toluene and in chloroform. These results are explained by a chain transfer constant of solvent ( $C_s$ ) and low reactivity of the resulting solvent radicals. The copolymer MA and CH was characterized by  $^1\text{H}$ -NMR and  $^{13}\text{C}$ -NMR spectra.

## References

1. Paul, G.B. and Kiyohisa, F. (1995) Solvent Effects on the Copolymerization of p-Methoxystyrene with Maleic Anhydride: An Investigation into the Mechanism of Alternating Copolymerization. *Polymer*, 36 (5): 1053–1059.
2. Takashi, K., Shouji, I., and Yuya, T. (1968) Studies on the Charge-Transfer Complex Polymerization. XVII. The Reactivity of the Charge-Transfer Complex in Alternating Radical Copolymerization of Vinyl Ethers Maleic Anhydride. *Macromolecules*, 1 (6): 482–488.

3. Spirin, Yu.L. and Yatsimirskaya, T.S. (1976) The Kinetics Mechanism of Alternating Copolymerization of Styrene with Maleic Anhydride. *Polymer Science U.S.S.R.*, 18 (4): 857–862.
4. Stoyachenko, I.L., Georgiev, G.S., Golubev, V.B., Zubov, V.P., and Kabanov, V.A. (1973) Study of the Mechanism of “Alternating” Copolymerization of Maleic Anhydride with Dimethylbutadiene. *Polymer Science U.S.S.R.*, 15 (8): 2142–2149.
5. Deryabina, G.I., Kalabina, V., Petrova, T.L., Stoyachenko, I.L., Golubev, V.B., and Zubov, V.P. (1978) The Alternating Copolymerization Mechanism of Vinyl Esters with Maleic Acid Derivatives. *Polymer Science U.S.S.R.*, 20 (8): 2014–2023.
6. Terteryan, R.A. and Khrapov, V.S. (1983) Synthesis of Alternating Random Copolymers of Ethylene with Maleic Anhydride. *Polymer Science U.S.S.R.*, 25 (9): 2151–2160.
7. Petrova, T.L., Smirnova, A.I., Ratovskii, G.V., Mantsivoda, V.B., and Zubov, V.P. (1986) Influence of the Structure of the Donor Acceptor Complex of Vinylbenzyl Ether with Maleic Anhydride on Reactivity in Alternating Copolymerization. *Polymer Science U.S.S.R.*, 28 (12): 2905–2912.
8. Rzaev, Z.M.O. (2000) Complex-radical Alternating Copolymerization. *Prog. Polym. Sci.*, 25: 163–217.
9. Dong, Y.P., Feng, L.X., and Yang, S.L. (1998) The Free Radical Copolymerization of Styrene Maleic Anhydride (II), The Copolymerization Mechanism Between Styrene Maleic Anhydride. *Polymer Bulletin*, 3: 51–58.
10. Rzaev, Z.M.O. (1984) *Polymers Copolymers of Maleic Anhydride*. Elm: Baku (Russian).
11. Cowie, J.M.G. (1985) *Alternating Copolymers*; Plenum: New York.
12. Shirota, Y. (1985) *Encyclopedia of Polymer Science Engineering*; Kroschriss, J.T., Ed.; Wiley: New York; Vol. 2, 337.
13. Rzaeva, Z.I., Medyakova, L.V., and Agayev, U.Kh. (1986) Complex-radical Copolymerization of Dicyclopentadiene with Maleic Anhydride. *Polymer Science U.S.S.R.*, 28 (5): 1215–1221.
14. Dong, Y.P., Feng, L.X., and Yang, S.L. (1997) The Bulk Free Radical Copolymerization of Styrene Maleic Anhydride. *Chemical Journal of Chinese Universities*, 18 (9): 1537–1540.
15. Li, H.M. and Lin, S.A. (2000) Free Radical Copolymerization of N-Phenylmaleimide with Cyclohexene. *Journ. Mac. Sci.-Pure Appl. Chem.*, A37 (11): 1475–1486.
16. Hill, D.J.T., Shao, L.Y., Pomery, P.J., and Whittaker, A.K. (2001) The Radical Homopolymerization of N-Phenylmaleimide, N-n-Hexylmaleimide N-Cyclohexylmaleimide in Tetrahydrofuran. *Polymer*, 42: 4791–4802.
17. Pan, Z.R. (1997) *Polymer Chemistry*; Chemical Industry Press: 50. Beijing.

