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Terpolymerization behaviour of citraconic anhydride, styrene, and isobutyl vinyl ether

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Summary

Radical terpolymerizations of citraconic anhydride (CAn), styrene (St), and isobutyl vinyl ether (IBVE) have been investigated in benzene at 60°C. St monomer shows higher reactivity toward a poly(CAn) radical compared with IBVE. The complex of St-CAn is observed to be also more reactive than the CAn- IBVE complex.

Introduction

Recently, we have been studying on reactivity of citraconic (α-methylmaleic) anhydride (CAn) as an electron-accepting monomer in radical copolymerizations. In the course of our studies, it has been found that CAn underwent radical alternating copolymerization with some unconjugated electron-donating vinyl monomers such as isobutyl vinyl ether (IBVE) and vinyl acetate [1,2], similar to maleic anhydride (MAn). The copolymerization of CAn with styrene (St) was also found to show a relatively high alternating tendency [3].

A 1:1 charge-transfer complex has been confirmed to exist in the copolymerization systems of CAn with St and with IBVE, and to participate in the propagation reactions of these copolymerizations. The equilibrium constant of the complex formation was determined to be 0.098 and 0.162 L/mol for CAn-St and CAn-IBVE system, respectively. Radical terpolymerization of CAn, St, and MAn has also been investigated to compare the reactivities of CAn and MAn as an electron-accepting monomer [3]. As a result, MAn was found to be about 6.5 times more reactive than CAn toward a polystyryl radical.

On the other hand, radical terpolymerizations of MAn with two kinds of electron-donating monomers including St, vinyl sulfide, and vinyl ether have been reported to give terpolymers in which the contents of MAn unit was always constant at about 50 mol %, independent of the feed monomer compositions [4,5]. In order to clarify whether or not such a composition-controlled terpolymer can be obtained from terpolymerizations incorporating CAn, and to compare the reactivities of CAn-St and CAn-IBVE complexes, radical terpolymerization of CAn, St, and IBVE was studied. The results obtained are described in this paper.

Experimental

CAn was obtained by isomerization-dehydration of itaconic

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*To whom offprint requests should be sent acid at 200°C, and then purified by distillation under reduced pressure. St and IBVE were distilled from their commercial materials before use. 2,2'-Azobisisobutyronitrile (AIBN) was recrystallized from methanol. Other reagents including solvents were used after purification by ordinary methods.

Terpolymerizations were carried out in a sealed glass tube in the presence of AIBN. After polymerization for a given time, the content of the tubes was poured into a large amount of dried diethyl ether to isolate the copolymer. The terpolymers obtained were then reprecipitated from acetone solution into the precipitant to obtain pure terpolymer for the composition analysis. The terpolymer compositions were determined by elementary analysis along with measuring the intensity of the specific absorption for the respective monomer units in their ^{1}H NMR spectra.

^{1}H NMR spectra (400 MHz) were taken on a JEOL-GX 400 FT NMR spectrometer in deuterium acetone at 27°C. Number-average molecular weight ($\bar{M}_n$) relative to polystyrene standards was determined by TOSO 8000 series gel-permeation chromatography (GPC) at 38°C using THF as an eluent.

Results and discussion

The results of terpolymerization of CAn (M_1), St (M_2), and IBVE (M_3) in benzene at 60°C are shown in Table 1. It is noted that the terpolymerizations proceeded readily but the content of CAn in terpolymer is always somewhat lower than 50 mol %.

Table 1 Radical terpolymerization of CAn (M_1), St (M_2), and MAn (M_3) in benzene at 60°C; $[M]_{Total}$ = 3.0 mol/L , [AIBN] = 0.02 mol/L

Run No.	Composition of monomers (mol%)			Time (h)	Yield (%)	$\bar{M}_n \cdot 10^{-4}$	Composition of terpolymer (mol%)		
	M_1	M_2	M_3				M_1	M_2	M_3
1	33.3	33.3	33.3	1	3.4	2.5	46.3	48.1	5.6
2	33.3	40.7	26.0	2	7.0	2.6	39.1	55.5	5.5
3	33.3	20.0	46.7	3	9.8	2.0	39.0	40.0	21.0
4	15.0	30.0	55.0	2	4.2	1.7	38.8	50.0	11.3
5	15.0	40.0	45.0	2	4.7	1.7	39.8	52.7	7.5
6	45.0	15.0	40.0	4	14.9	3.3	46.6	32.9	20.6
7	45.0	40.0	15.0	2	8.3	3.0	45.0	50.2	4.8

The free propagation and the complex propagation models were checked for the terpolymerization system.

Among the three monomers in the terpolymerization systems, CAn and IBVE can not homopolymerize, and the copolymerization of IBVE with St seems to be negligible under the present terpolymerization conditions. This sassumption is supported by the results that the contents of CAn and IBVE in the terpolymers are always lower than 50 mol % (see Table 1).

Accordingly, by using the free propagation assumption, the propagation reactions in this case can be expressed as follows:

$$M_1\cdot \quad + \quad M_2 \quad \xrightarrow{K_{12}} \quad M_2\cdot \qquad (1)$$

$$M_1\cdot \quad + \quad M_3 \quad \xrightarrow{K_{13}} \quad M_3\cdot \qquad (2)$$

$$M_2\cdot \quad + \quad M_1 \quad \xrightarrow{K_{21}} \quad M_1\cdot \qquad (3)$$

$$M_2\cdot \quad + \quad M_2 \quad \xrightarrow{K_{22}} \quad M_2\cdot \qquad (4)$$

$$M_3\cdot \quad + \quad M_1 \quad \xrightarrow{K_{31}} \quad M_1\cdot \qquad (5)$$

By using stationary state assumption, the following equations (6)-(8) are derived:

$$\frac{d[M_1]}{d[M_2]} = \frac{1 + (K_{13}/K_{12})\cdot([M_3]/[M_2])}{(K_{22}/K_{21})\cdot([M_2]/[M_1]) + 1} \qquad (6)$$

$$\frac{d[M_1]}{d[M_3]} = 1 + \frac{K_{12}\cdot[M_2]}{K_{13}\cdot[M_3]} \qquad (7)$$

$$\frac{d[M_2]}{d[M_3]} = \frac{K_{12}\cdot[M_2]}{K_{13}\cdot[M_3]}\cdot\left(1 + \frac{K_{22}}{K_{21}}\cdot\frac{[M_2]}{[M_1]}\right) \qquad (8)$$

Equation (7) was used to determine the ratio of rate constants, K_{12}/K_{13}, which indicates the difference in reactivities between St and IBVE toward the poly(CAn) radical. The plots by equation (7) is shown in Figure 1. The value of K_{12}/K_{13} are

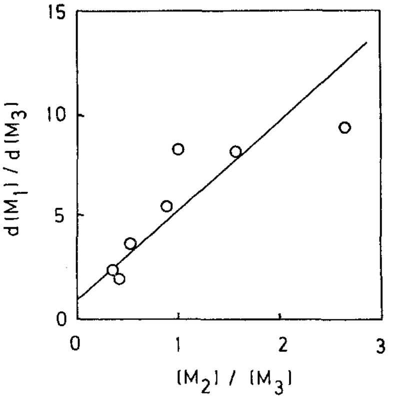

Figure 1 Plot by equation (7) for terpolymerization of CAn (M_1), St (M_2), and IBVE (M_3).

calculated as 4.4, indicating that St is 4.4 times more reactive than IBVE. This can be understood from the difference in conjugation ability between St and IBVE.

On the other hand, by using the complex propagation model, the apparent reactivity ratios, $C_{12}\cdot$(CAn-St) and $C_{13}\cdot$(CAn-IBVE), can be determined in the forms of $r_{12}\cdot(k_{12}/k_{13})$ and $r_{12}\cdot(k_{12}/k_{13})$, respectively, as described below.

If only two complexed monomers, C_{21} and C_{23}, participate in the propagation step, the present terpolymerization can be treated simply as binary copolymerization between the complexed monomer [equations (9),(10)].

$$M_2 + M_1 \xrightleftharpoons{K_{21}} C_{21} \qquad (9)$$

$$M_2 + M_3 \xrightleftharpoons{K_{23}} C_{23} \qquad (10)$$

In this case, the following equation (11) can be derived:

$$\frac{d[M_2]}{d[M_3]} = \frac{[M_2]}{[M_3]} \cdot \frac{r_{12}\cdot(K12/K13)\cdot[M_2] + [M_3]}{[M_2] + r_{12}\cdot(K_{12}/K_{13})\cdot[M_3]} \qquad (11)$$

The composition curve between $[M_2]/([M_2]+[M_3])$ and $d[M_2]/(d[M_2]+d[M_3])$ obtained by the least-square procedure [6] is shown in Figure 2, from which a relatively good fit of the calculated curve for the experimental data is observed. The values of $r_{12}\cdot(K_{12}/K_{13})$ and $r_{13}\cdot(K_{13}/K_{12})$ were calculated to be 9.14 and 0.48, respectively. Although the K values in the terpolymerization systems should be slightly different from those determined in $CHCl_3$ at 15 °C [1,3], r_{12} and r_{13} were calculated approximately to be 5.53 and 0.77, respectively, by using K = 0.098 L/mol for CAn-St system and K = 0.162 L/mol for CAn-IBVE system. Therefore, the CAn-St complex is observed to be more reactive than that of CAn-IBVE complex.

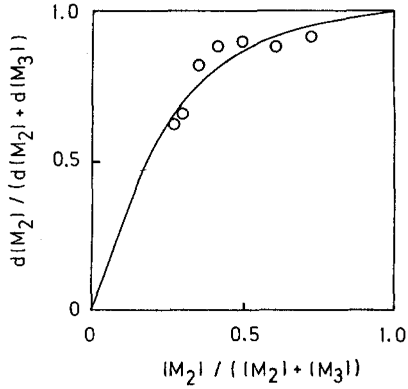

Figure 2 Composition curve determined as copolymerization between CAn-St and CAn-IBVE complexes for terpolymerization of CAn (M_1), St (M_2), and IBVE (M_3).

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