Macromolecules 1992, 25, 102–107

Radical Copolymerization of Citraconic Anhydride with Styrene and Terpolymerization of Citraconic Anhydride and Maleic Anhydride with Styrene

Jian-Zhong Yang[†] and Takayuki Otsu*

Department of Applied Chemistry, Faculty of Engineering, Osaka City University, Sugimoto, Sumiyoshi-ku, Osaka 558, Japan

Received February 5, 1991; Revised Manuscript Received September 12, 1991

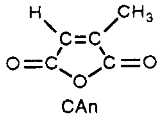
ABSTRACT: Radical copolymerization of citraconic anhydride (CAn) with styrene (St) and terpolymerization of CAn, St, and maleic anhydride (MAn) were carried out in bulk at 60 °C and in benzene at 50 °C, respectively. Existence of a 1:1 charge-transfer complex between CAn and St in the copolymerization system was confirmed by means of UV spectroscopies. The equilibrium constant of the complex formation was determined as 0.098 L/mol in $CHCl_3$ at 15 °C. The copolymerization of CAn with St was evaluated by using either the terminal or the penultimate model, and the complex participation model. As a result, the penultimate model was demonstrated to be the relatively adequate description of the mechanism of the copolymerization. The relative reactivity of MAn toward a poly(St) radical was found to be about 6.8 times higher than that of CAn. The alternating copolymer of dialkyl citraconate (DRC) with St, having a relatively high thermal stability, was prepared by esterification of the copolymer of CAn and St.

Introduction

Much interest has been shown in the radical copolymerization of maleic anhydride (MAn) with styrene (St),[1–10] which gives an alternating copolymer, probably via formation of a donor–acceptor complex between both monomers. From this system, high molecular weight alternating copolymer was obtained even in the absence of the initiator.[2,3] The existence of a 1:1 charge-transfer complex has been firmly established for the copolymerization system.[4,5] However, Ebdon and Towns proposed recently that such complexes play only a very small part in leading to alternation in this system.[1] Moreover, the kinetics and mechanism of these copolymerizations have been widely investigated by using various models.[1,6–8]

Recently, we studied radical polymerization reactivities of citraconic (α-methylmaleic) acid derivatives. The radical homopolymerization of *N*-alkylcitraconimides was attempted and found to give the polymers consisting of 1,1,2-trisubstituted ethylenic structure.[11] The copolymerizations of dialkyl citraconates (DRC) and the isomeric mesaconates with vinyl acetate, as well as isobutyl vinyl ether, have been performed and found to give alternating copolymers.[12,13]

Next, our attention is focused on the reactivity and behavior of citraconic anhydride (CAn) as an electron-accepting monomer in radical copolymerization. Although there have been a few publications on copolymerization parameters of CAn with St,[14] no systematical study has been done.



CAn

In the present study, radical copolymerization of CAn with St was carried out and studied spectroscopically. The mechanism of the copolymerization was evaluated by three types of models, i.e. the classical terminal model, the penultimate model, and the complex participation model. Moreover, radical terpolymerization of CAn, St, and MAn was also investigated to compare the relative reactivities of CAn and MAn toward the poly(St) radical. Furthermore, the esterification of the anhydride moiety in the copolymer of CAn with St was attempted to obtain the copolymer involving DRC. The results obtained are described and discussed in this paper.

Experimental Section

Materials. CAn was obtained by isomerization–dehydration of itaconic acid at 200 °C and purified by distillation under reduced pressure. St and MAn were distilled from their commercial materials before use. 2,2′-Azobis(isobutyronitrile) (AIBN) was recrystallized from methanol. Other reagents were purified by ordinary methods.

Polymerizations. Copolymerization and terpolymerization 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 copolymers obtained were then reprecipitated from acetone solution into diethyl ether to obtain pure copolymers for the composition analysis. The copolymer compositions were determined by elementary analyses. The terpolymer compositions were determined by measuring the intensity of the specific absorption for the respective monomer units in ^1H NMR spectra: St, C_6H_5 protons (6.8–7.2 ppm); CAn, CH_3 protons (1.3 ppm); MAn, CH proton (3.0 ppm) and CH_2 protons (2.0–3.0 ppm).

Esterification of the Copolymer. Methylation of poly(CAn-*co*-St) was performed by refluxing the copolymers with an excess amount of methanol in the presence of sulfuric acid as a catalyst. After reaction for 20 h, unchanged methanol was removed, and the copolymers obtained were purified by reprecipitation from the THF–hexane system.

Measurements. UV spectra were measured by a Shimadzu UV-160 ultraviolet spectrometer in $CHCl_3$ at 15 °C using 1-cm quartz cells. IR spectra were recorded on a JASCO A-202 spectrometer. NMR spectra (400 MHz) were taken on a JEOL-GX 400 FT NMR spectrometer in deuterium acetone at 27 °C. Number-average molecular weight ($\bar{M}_n$) was determined by Tosoh 8000 series gel-permeation chromatography (GPC) at 38 °C using THF as an eluent. Thermogravimetric analysis (TGA) was carried out in an atmosphere of nitrogen at a heating rate of 10 °C/min.

Results and Discussion

Copolymerization of CAn with St. The results of the copolymerizations of CAn (M_1) with St (M_2) in bulk at 60 °C with 0.02 mol/L of AIBN are shown in Table I.

[†] Present address: Department of Chemistry, Virginia Commonwealth University, Richmond, VA 23284.

0024-9297/92/2225-0102$03.00/0

Table I
Radical Copolymerization of CAn (M_1) with St (M_2) in Bulk at 60 °C: [AIBN] = 0.02 mol/L

$[M_1]$ in comonomer/ (mol %)	polymn time/ min	copolymer yield/%	10^4R_p/ (mol/ (L·s))	$10^{-4}\bar{M}_n$	$[M_1]$ in copolymer/ (mol %)
5.0	60	4.5	1.1		21.9
10.0	30	2.6	1.3	8.1[a]	28.7
20.0	30	2.8	1.4	7.4	34.0
30.0	45	5.5	1.9	9.7	36.4
40.0	30	3.6	1.9	12.3	40.3
50.0	60	7.8	2.1	12.4[a]	43.1
50.0[b]	300	1.5	0.1	53.9[a]	45.4
60.0	30	4.0	2.3	15.0	45.4
70.0	45	8.5	3.2	12.5	48.0
80.0	30	4.1	2.4	8.4	48.9
90.0	60	10.4	3.1	11.5[a]	49.8

[a] The samples methylated were used. [b] Spontaneous thermal copolymerization.

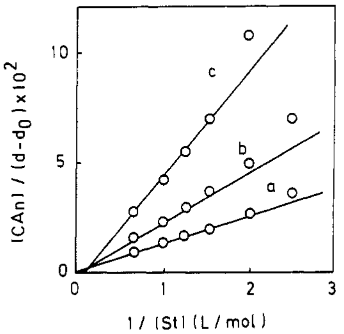


Figure 1. Continuous variations for the chloroform solutions of CAn with St: [CAn] + [St] = 1.0 mol/L.

The copolymerizations proceeded rapidly to give the copolymers having $\bar{M}_n$ in the range of (7.4–15.0) × 10^4. The rate of copolymerization (R_p) was found to increase with an increase in the molar fraction of M_1 in the monomer mixture, and the $\bar{M}_n$ of the copolymers have a maximum $[M_1]$ value at about 60 mol %. In addition, it was observed that the copolymerization proceeded slowly even in the absence of AIBN, to give a high molecular weight (>500 000) copolymer.

Confirmation of a Charge-Transfer Complex in the CAn–St System. It has been confirmed that the charge-transfer complex is formed in the MAn–St copolymerization system.[4,5] In order to examine whether or not such a complex exists in the presence of the CAn–St copolymerization system, a UV spectroscopic study was attempted. From the UV spectra obtained, a new absorption band due to complex formation was observed in the range of 300–350 nm. Figure 1 depicts the plots by a continuous variation technique of Garrett and Guile[15] to determine the compositions of the complex of CAn with St. From this figure, it is clear that CAn formed a 1:1 charge-transfer complex with St in $CHCl_3$ at 15 °C.

The formation of the complex (C) between St and CAn is expressed as follows:

$$\mathrm{St} + \mathrm{CAn} \overset{K}{\rightleftharpoons} \mathrm{C} \tag{1}$$

where K is an equilibrium constant of complex formation.

If the concentration of St is much larger than that of CAn and the molar extinction coefficient (ϵ_{St}) of St at a given wave length is zero, the following equation can be derived:[16,17]

$$\frac{[\mathrm{CAn}]}{d - d_0} = \frac{1}{K(\epsilon_C - \epsilon_{CAn})[\mathrm{St}]} + \frac{1}{\epsilon_C - \epsilon_{CAn}} \tag{2}$$

where [CAn] and [St] are the initial concentrations of CAn and St, respectively. d_0 and d are the optical densities per unit cell length of CAn and the mixed solution, and ϵ_{CAn} and ϵ_C are molar extinction coefficients of CAn and the complex, respectively.

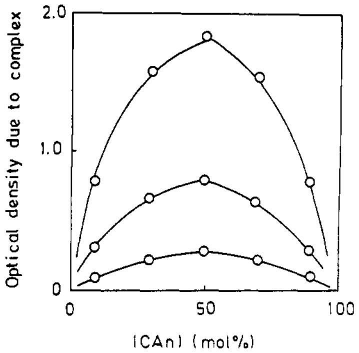


Figure 2. Plots by eq 2 for the CAn–St system in chloroform: (a) 310, (b) 320, and (c) 330 nm.

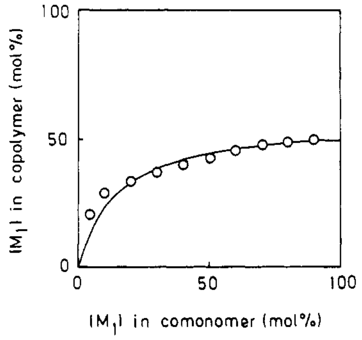


Figure 3. Copolymer composition curve for copolymerization of CAn (M_1) with St (M_2) in bulk at 60 °C.

Accordingly, the equilibrium constant, K, can be determined from the plots of $[\mathrm{CAn}]/(d - d_0)$ vs $1/[\mathrm{St}]$. The plots by eq 2 are shown in Figure 2, in which straight lines whose slopes are equal to $1/K(\epsilon_C - \epsilon_{CAn})$ and whose intercept is $1/(\epsilon_C - \epsilon_{CAn})$ are obtained. An average value of K for the complex formation was calculated as 0.098 L/mol in $CHCl_3$ at 15 °C from Figure 2, which is smaller than that reported for the MAn–St system (0.24 L/mol in $CHCl_3$ at 25 °C).[4]

Evaluation of the Mechanism for the Copolymerization of CAn with St. On the basis of the terminal copolymerization model by Mayo and Lewis,[18] which involves four propagation reactions (eqs 3–6), the monomer reactivity ratios for CAn ($r_1 = k_{11}/k_{12}$) and St ($r_2 = k_{22}/k_{21}$) can be determined.

$$\sim\sim\sim M_1^{\bullet} + M_2 \xrightarrow{k_{11}} \sim\sim\sim M_1^{\bullet} \tag{3}$$

$$\sim\sim\sim M_1^{\bullet} + M_2 \xrightarrow{k_{12}} \sim\sim\sim M_2^{\bullet} \tag{4}$$

$$\sim\sim\sim M_2^{\bullet} + M_2 \xrightarrow{k_{22}} \sim\sim\sim M_2^{\bullet} \tag{5}$$

$$\sim\sim\sim M_2^{\bullet} + M_1 \xrightarrow{k_{21}} \sim\sim\sim M_1^{\bullet} \tag{6}$$

Figure 3 shows the copolymer composition curve, where the open circles represent the experimental points and the solid line is calculated by using a nonlinear least-squares procedure,[19] from which r_1 and r_2 are evaluated and summarized in Table II, together with those from the penultimate model, as will be described in the following section. Comparing these values with those reported for MAn–St copolymerization (r_1 = 0.018 and r_2 = 0.074),[1]

Table II
Reactivity Ratios Calculated by the Terminal Model or Penultimate Model for the Copolymerization of CAn (M_1) with St (M_2)

parameter	value	parameter	value
	Terminal Model		
r_1	0.00	r_2	0.25
	Penultimate Model		
r_{12}	0.59	r_{12}/r_{22}	6.6
r_{22}	0.090		

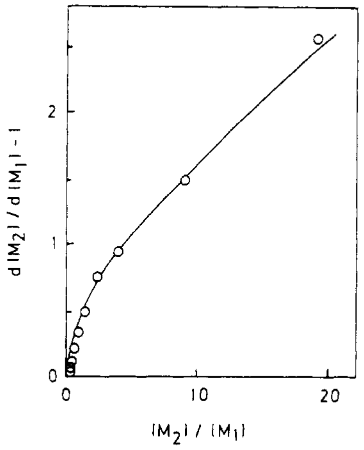


Figure 4. Plot by eq 12 for copolymerization of CAn (M_1) with St (M_2) in bulk at 60 °C.

one can conclude that the alternating tendency of the CAn–St system is somewhat lower than that of the MAn–St system.

It has been demonstrated that MAn–St copolymerization exhibits a deviation from the terminal copolymerization model shown above.[20] Such a deviation has been considered also, presumably, to occur for CAn (M_1)–St (M_2) copolymerization. Therefore, the data obtained in the present study were also analyzed with the penultimate model as represented by equations 7–11 in which it is assumed that CAn-ended radicals are incapable of adding to the CAn monomer.

$$\sim\sim\sim M_2M_2^{\bullet} + M_2 \xrightarrow{k_{222}} \sim\sim\sim M_2M_2^{\bullet} \tag{7}$$

$$\sim\sim\sim M_2M_2^{\bullet} + M_1 \xrightarrow{k_{221}} \sim\sim\sim M_2M_1^{\bullet} \tag{8}$$

$$\sim\sim\sim M_1M_2^{\bullet} + M_2 \xrightarrow{k_{122}} \sim\sim\sim M_2M_2^{\bullet} \tag{9}$$

$$\sim\sim\sim M_1M_2^{\bullet} + M_1 \xrightarrow{k_{121}} \sim\sim\sim M_2M_1^{\bullet} \tag{10}$$

$$\sim\sim\sim M_2M_1^{\bullet} + M_2 \xrightarrow{k_{212}} \sim\sim\sim M_1M_2^{\bullet} \tag{11}$$

From these equations, eq 12 was obtained, in which $r_{22} = k_{222}/k_{221}$ and $r_{12} = k_{122}/k_{121}$.

Figure 4 shows the plot of $d[M_2]/d[M_1] - 1$ vs $[M_2]/[M_1]$, where the open circles represent the experimental points and the solid line is calculated by using the nonlinear least-squares procedure. The reactivity ratios obtained, r_{22} and r_{12}, are indicated in Table II.

$$\frac{d[M_2]}{d[M_1]} - 1 = r_{12}\frac{[M_2]}{[M_1]}\left[\left(1 + r_{22}\frac{[M_2]}{[M_1]}\right)\Big/\left(1 + r_{12}\frac{[M_2]}{[M_1]}\right)\right] \tag{12}$$

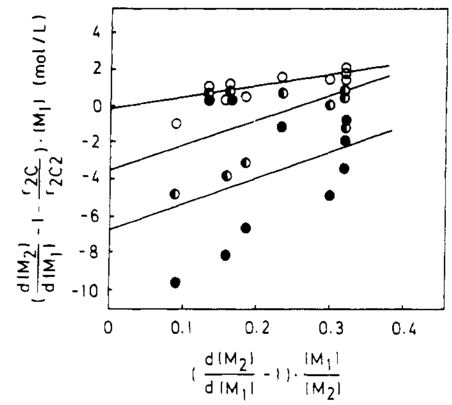


Figure 5. Litt plots (eq 20) for copolymerization of CAn (M_1) with St (M_2) in bulk at 60 °C: (○) $r_{2C}/r_{2C2} = 0$; (◐) $r_{2C}/r_{2C2} = 0.5$; (●), $r_{2C}/r_{2C2} = 1.0$.

The value of r_{12}/r_{22} in Table II indicates that M_1 is about 6.6 times more reactive toward the $\sim\sim\sim M_2M_2^{\bullet}$ radical than toward the $\sim\sim\sim M_1M_2^{\bullet}$ radical. This tendency is observed to be stronger than that for MAn–St copolymerization when the value of r_{12}/r_{22} is compared with that reported for the MAn–St system (3.7).[1] The relatively low reactivity of CAn toward the poly(St) radical with a penultimate CAn unit seems to be attributed to steric and dipolar repulsion.

Because the existence of the CAn (M_1)–St (M_2) complex was confirmed, as described above, the compositions against the predictions of a simple terminal complex participation model proposed by Seiner and Litt[21] were also tested. In this model, six equations in which CAn is assumed not to be self-propagating again are included.

$$\sim\sim\sim M_2^{\bullet} + M_2 \xrightarrow{k_{22}} \sim\sim\sim M_2^{\bullet} \tag{13}$$

$$\sim\sim\sim M_2^{\bullet} + M_1 \xrightarrow{k_{21}} \sim\sim\sim M_1^{\bullet} \tag{14}$$

$$\sim\sim\sim M_1^{\bullet} + M_2 \xrightarrow{k_{12}} \sim\sim\sim M_2^{\bullet} \tag{15}$$

$$\sim\sim\sim M_2^{\bullet} + M_2M_1 \xrightarrow{k_{221}} \sim\sim\sim M_1^{\bullet} \tag{16}$$

$$\sim\sim\sim M_2^{\bullet} + M_1M_2 \xrightarrow{k_{212}} \sim\sim\sim M_2^{\bullet} \tag{17}$$

$$\sim\sim\sim M_1^{\bullet} + M_2M_1 \xrightarrow{k_{121}} \sim\sim\sim M_1^{\bullet} \tag{18}$$

From these reactions is derived

$$\frac{d[M_2]}{d[M_1]} = 1 + \frac{r_2([M_2]/[M_1]) + r_2K[M_2]/r_{2C2}}{1 + r_2[M_2]/Kr_{2C}} \tag{19}$$

where $r_{2C2} = k_{22}/k_{221}$ and $r_{2C} = k_{22}/(k_{221} + k_{212})$.

Equation 19 can be rearranged to a form given by

$$\left(\frac{d[M_2]}{d[M_1]} - 1 - \frac{r_{2C}}{r_{2C2}}\right)[M_1] = \frac{r_{2C}}{K} - \frac{r_{2C}}{Kr_2}\left(\frac{d[M_2]}{d[M_1]} - 1\right)\frac{[M_1]}{[M_2]} \tag{20}$$

Here, if a value is postulated for r_{2C}/r_{2C2}, a plot of the left side of eq 20 vs $(d[M_2]/d[M_1] - 1)/([M_2]/[M_1])$ yields a straight line whose intercept is r_{2C}/K and whose slope is r_{2C}/Kr_2. The plot for several values of r_{2C}/r_{2C2} is shown in Figure 5. It can be seen that the closeness of fit is better

Table III
Reactivity Ratios Calculated by the Complex Participation Model for the Copolymerization of CAn (M_1) with St (M_2)

r_{2C}/r_{2C2}	r_{2C}/K	r_{2C}[a]	r_2
0	0.15	0.015	0.026
0.5	3.45	0.34	0.31
1.0	6.76	0.66	0.42

[a] By using K = 0.098 L/mol.

Table IV
Comparison of Experimental and Calculated Copolymer Compositions for Different Copolymerization Models

	$F = d[M_2]/d[M_1]$			
feed data $[M_2]/[M_1]$	exptl data	terminal model	penultimate model	complex model[a]
19.00	3.57	5.67	3.49	3.19
9.00	2.48	3.22	2.52	2.27
4.00	1.94	1.98	1.96	1.86
2.33	1.75	1.57	1.70	1.75
1.50	1.48	1.37	1.53	1.54
1.00	1.32	1.25	1.40	1.43
0.67	1.20	1.16	1.30	1.33
0.43	1.08	1.11	1.21	1.18
0.25	1.04	1.06	1.13	1.13
0.11	1.01	1.03	1.06	1.07
S_F[b]		0.75	0.080	0.17

[a] By using $r_{2C}/r_{2C2} = 0$. [b] Standard error, determined according to the equation $S_F = [\Sigma(F_{exp} - F_{cal})^2/(n-1)]^{1/2}$, where F_{exp} is the experimental molar fraction in the copolymer, F_{cal} is the calculated molar fraction in the copolymer, and n is the number of experimental points.

Table V
Terpolymerization of CAn (M_1), St (M_2), and MAn (M_3) in Benzene at 50 °C: $[M]_{total}$ = 3.0 mol/L, [AIBN] = 0.01 mol/L

monomer composition/(mol %)			polymn time/ min	ter-polymer yield/%	terpolymer composition/(mol %)		
M_1	M_2	M_3			M_1	M_2	M_3
33.3	33.3	33.3	10	3.1	6.9	48.7	44.4
33.3	15.0	51.7	5	1.4	6.7	46.0	47.3
33.3	51.7	15.0	10	1.5	11.8	53.1	35.1
53.0	29.1	17.9	20	2.4	12.3	35.5	52.2
15.0	30.0	55.0	5	2.6	2.8	40.4	56.7
15.0	55.0	30.0	5	1.6	4.0	46.1	49.9
65.0	25.0	10.0	30	1.5	20.8	40.5	38.7
65.0	5.0	30.0	25	1.9	10.4	33.6	56.0

for the case $r_{2C}/r_{2C2} = 0$, and these values are therefore used. Table III shows the parameters obtained from the complex model. The fact that $r_{2C}/r_{2C2} = 0$ ($r_{2C2} \gg r_{2C}$) indicates that the complex is not equally reactive on both sides toward the poly(St) radical; that is, M_1M_2 is more reactive than M_2M_1 toward the $\sim\sim\sim M_2^{\bullet}$ radical.

A comparison of experimental and calculated $d[M_2]/d[M_1]$ from different copolymerization models is summarized in Table IV. The comparison of the standard error for each model leads to the following conclusion: a significant deviation from the classical terminal model of Mayo and Lewis arises in the present copolymerization system, as has been reported for the MAn–St system. The penultimate model gives a better fit for the experimental data than the terminal and the complex models, indicating that the penultimate group effect is very important in this copolymerization. The complex model provides a somewhat better fit to the composition data than the terminal model, indicating presumably that complexes also play a certain but small part in the copolymerization. This observation is in agreement with that reported for the MAn–St copolymerization.[1]

Terpolymerization of CAn, St, and MAn. Although the difference in reactivity between MAn and CAn toward poly(St) radical might be evaluated from the copolymerization parameters, as shown above, it is not the surest way because both systems showed considerably high alternating tendency. In order to compare the reactivity of CAn with that of MAn toward poly(St) radical, and also to compare the reactivity of the CAn–St complex with that of the MAn–St complex if it is possible, a terpolymerization technique[22,23] was adopted.

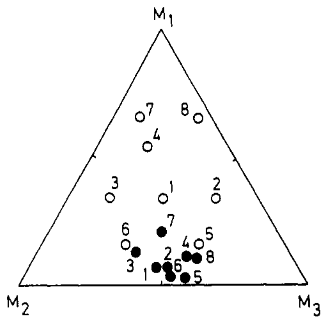


Figure 6. Monomer–terpolymer composition diagrams for terpolymerization of CAn (M_1), St (M_2), and MAn (M_3) in benzene at 50 °C: (○) monomer composition; (●) terpolymer composition.

Table VI
TGA Data of Poly(DMC-*co*-St) and Poly(CAn-*co*-St)

copolymer	decomposition temp/°C T_{init}	T_{max}	residue at 500 °C/%
poly(DMC-*co*-St)	325	377	2.3
poly(CAn-*co*-St)	264	373	11.5

The terpolymerizations of CAn (M_1), St (M_2), and MAn (M_3) in benzene at 50 °C with 0.01 mol/L of AIBN were performed. The results of the terpolymerizations are shown in Table V. From these results, the monomer–terpolymer composition diagram is obtained, as is shown in Figure 6.

In this terpolymerization, as CAn has been confirmed not to homopolymerize and the copolymerization between CAn and MAn seems to be negligible, there are six elementary reactions to be considered (eqs 21–26).

$$\sim\sim\sim M_1^{\bullet} + M_2 \xrightarrow{k_{12}} \sim\sim\sim M_2^{\bullet} \tag{21}$$

$$\sim\sim\sim M_2^{\bullet} + M_1 \xrightarrow{k_{21}} \sim\sim\sim M_1^{\bullet} \tag{22}$$

$$\sim\sim\sim M_2^{\bullet} + M_2 \xrightarrow{k_{22}} \sim\sim\sim M_2^{\bullet} \tag{23}$$

$$\sim\sim\sim M_2^{\bullet} + M_3 \xrightarrow{k_{23}} \sim\sim\sim M_3^{\bullet} \tag{24}$$

$$\sim\sim\sim M_3^{\bullet} + M_2 \xrightarrow{k_{32}} \sim\sim\sim M_3^{\bullet} \tag{25}$$

$$\sim\sim\sim M_3^{\bullet} + M_3 \xrightarrow{k_{33}} \sim\sim\sim M_3^{\bullet} \tag{26}$$

Accordingly, the eqs 27–29 are derived by using the ordinary stationary-state assumption, where $r_{MS(MAn)}$ (=0.018) and $r_{MS(St)}$ (=0.074) are the monomer reactivity ratio for MAn and St, respectively, in the copolymerization of MAn with St. $r_{CS(St)}$ (=0.25) is the monomer reactivity ratio for St in the copolymerization of CAn with St.

By using eqs 27–29 for the results of Table VI, the average value of k_{23}/k_{21} is calculated as 6.8, indicating that MAn is about 6.8 times more reactive than CAn toward

$$\frac{d[M_3]}{d[M_1]} = \frac{k_{23}[M_3]}{k_{21}[M_1]}\left(1 + r_{MS(MAn)}\frac{[M_3]}{[M_2]}\right) \tag{27}$$

$$\frac{d[M_3]}{d[M_2]} = \frac{(r_{MS(MAn)}[M_3]/[M_2]) + 1}{1 + (k_{21}/k_{23})[M_1]/[M_3] + r_{MS(St)}[M_2]/[M_3]} \tag{28}$$

$$\frac{d[M_1]}{d[M_2]} = \frac{1}{(k_{23}/k_{21})[M_3]/[M_1] + r_{CS(St)}[M_2]/[M_1]} \tag{29}$$

the poly(St) radical in benzene at 50 °C. The lower reactivity of CAn compared with MAn is considered to result from the steric effect of its α-methyl group. In the propagation reactions within the copolymerization of CAn with St, the poly(St) radical should attack selectively in a limited direction to the β-position of the C–C double bond of CAn, but not the α-position, as formulated in Scheme I.

A similar result has been obtained for alternating copolymerization of CAn with ethylene.[24]

As described above, CAn has been confirmed to form a 1:1 charge-transfer complex with St, and MAn has also been known to form a similar complex with St. In such cases, the terpolymerization can usually be treated simply as binary copolymerization between the complexed monomers C_{23} and C_{21} (eqs 30 and 31) which participate in the propagation reaction. In this case, eq 32 can be derived,[25,26]

$$M_2 + M_1 \overset{K_{21}}{\rightleftharpoons} C_{21} \tag{30}$$

$$M_2 + M_3 \overset{K_{23}}{\rightleftharpoons} C_{23} \tag{31}$$

where K_{21} and K_{23} are the equilibrium constants for complex formations of M_2–M_1 and M_2–M_3, respectively.

$$\frac{d[M_3]}{d[M_1]} = \frac{[M_3]}{[M_1]}\,\frac{r_{23}(K_{23}/K_{21})[M_3] + [M_1]}{[M_3] + r_{21}(K_{21}/K_{23})[M_1]} \tag{32}$$

If the present terpolymerization is suitable for the assumption described above, the apparent reactivity ratios, $r_{23}(K_{23}/K_{21})$ and $r_{21}(K_{21}/K_{23})$, can be obtained by using eq 31. The composition curve between $[M_3]/([M_3] + [M_1])$ and $d[M_3]/(d[M_3] + d[M_1])$ obtained by the least-squares procedure is shown in Figure 7, together with that obtained from the free propagation assumption (eq 27). The values of $r_{23}(K_{23}/K_{21})$ and $r_{21}(K_{21}/K_{23})$ were calculated as 6.24 and 0, respectively. These values appear to be reasonable, at least qualitatively, indicating that the MAn–St complex is much more reactive than the CAn–St complex toward the attacking polymer radical. However, their quantitative meaning is doubtful, as discussed below. The complex propagation assumption used requires that St should always be 50 mol % in the terpolymer, but the deviations from this requirement are quite large in the terpolymerization of CAn, St, and MAn. Therefore, suitability of this assumption for the present terpolymerization is not so reliable.

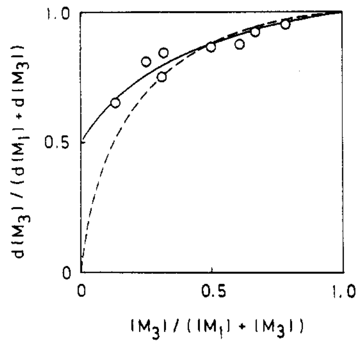


Figure 7. Composition curves determined for copolymerization between CAn–St and MAn–St complexes (—) and from eq 27 (- -) for terpolymerization of CAn (M_1), St (M_2), and MAn (M_3) in benzene at 50 °C.

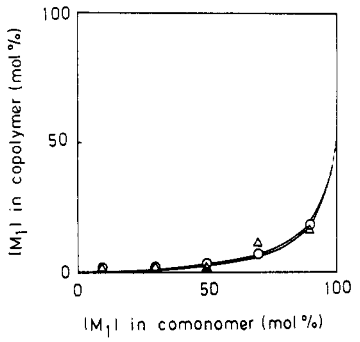


Figure 8. Copolymer composition curves for copolymerization of DMC (△) and DEC (○) (M_1) with St (M_2) in bulk at 60 °C.

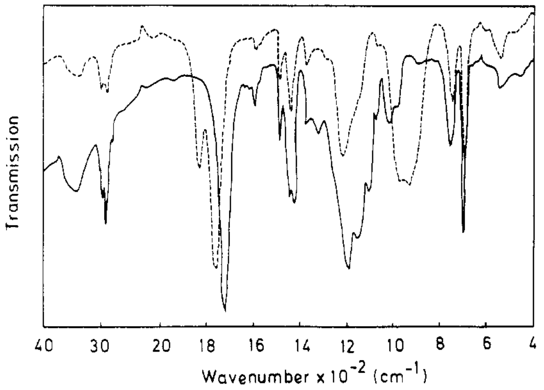
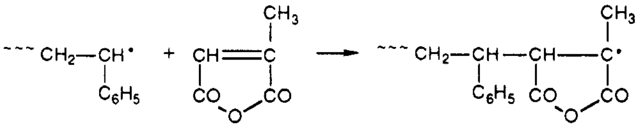


Figure 9. IR spectra of poly(CAn-*co*-St) (- -) and poly(DMC-*co*-St) from poly(CAn-*co*-St) (—).

Scheme I



Esterification of Poly(CAn-*co*-St). As described above, the copolymers with considerably high alternating tendency have been obtained easily by radical copolymerization of CAn with St. On the other hand, DRC is a low reactive in copolymerizations with St, as can be seen from Figure 8 in which the copolymer composition curves for copolymerization of dimethyl citraconate (DMC) and diethyl citraconate (DEC) with St are shown.

Therefore, alternating poly(DRC-*co*-St) has been expected to be obtained by the esterification of the anhydride moiety in poly(CAn-*co*-St). In order to clarify this point, poly(CAn-*co*-St) was allowed to react with methanol.

IR spectra of poly(CAn-*co*-St) and the methylated polymer are shown in Figure 9. In the spectrum of the methylated poly(CAn-*co*-St), evidence for the presence of anhydride and acid groups was not found, but strong absorption bands centered at 1730 and 1200 cm^{-1} attributed to carboxylic ester groups were observed. It is clear, therefore, that poly(CAn-*co*-St) was completely meth-

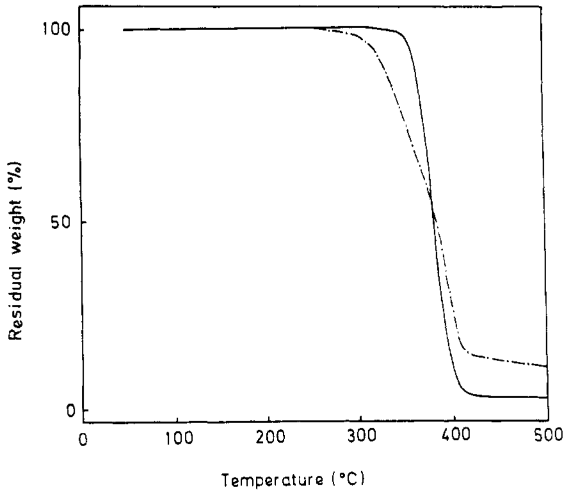


Figure 10. TGA curves of poly(DMC-*co*-St) (—) and poly(CAn-*co*-St) (– · · –).

ylated. That is, the esterification of poly(CAn-*co*-St) is a useful route for preparing the alternating copolymers of DRC with St.

The thermal stability of the resulting poly(DMC-*co*-St) was evaluated by means of TGA measurement. The TGA curve obtained is indicated in Figure 10, together with that of poly(CAn-*co*-St). The TGA data for the copolymers are summarized in Table VI, from which it is noted that the poly(DMC-*co*-St) thus obtained shows a higher thermal stability than the initial poly(CAn-*co*-St). This leads to a conclusion that the thermal stability of poly(CAn-*co*-St) can be improved by its esterification.

Conclusion

The radical copolymerization of CAn with St shows a considerably high alternating tendency. However, the relative reactivity of CAn is lower when compared with that of MAn. From the terpolymerization of CAn, St, and MAn, it is clear that MAn is about 6.8 times more reactive than CAn toward the poly(St) radical. This difference is considered to come from the steric effect of the α-methyl group in CAn. However, the copolymerization behavior of CAn with St was almost similar to that of MAn with St. A 1:1 charge-transfer complex between St and CAn exists in the copolymerization system, although it is somewhat weaker than that of St–MAn and takes a certain but small part in the propagation reaction of the copolymerization. The kinetic model considering the penultimate group effect has been demonstrated to be a relatively adequate description of the copolymerization mechanism in preference to the classical terminal model or the complex participation model. The alternating copolymer of DMC with St was prepared by the methylation of the anhydride moiety in the copolymer of CAn with St and was found to be more thermally stable than the initial copolymer.

Acknowledgment. We thank Mr. Shigeki Mori for the elementary analyses and TGA measurements, Dr. Bunichiro Yamada for helpful discussions, and Ms. Min Wang for her assistance on the calculations. This work was partially supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science, and Culture of Japan. J.-Z.Y. thanks the Ichikawa International Scholarships Foundation for granting him a scholarship for the pursuit of his doctorate at the Osaka City University.

References and Notes

(1) Ebdon, J. R.; Towns, C. R. *J. Macromol. Sci., Rev. Macromol. Chem. Phys.* **1986**, *C26* (4), 523.
(2) Shirota, Y. In *Encyclopedia of Polymer Science and Engineering*; Kroschriss, J. T., Ed.; Wiley: New York, 1985; Vol. 2, p 337.
(3) Iwatsuki, S.; Yamashita, Y. In *Progress in Polymer Science of Japan*; Kodansha: Tokyo, 1971; Vol. 2.
(4) Arita, K.; Ohtomo, T.; Tsurumi, Y. *J. Polym. Sci., Polym. Lett. Ed.* **1981**, *19*, 211.
(5) Tsuchida, E.; Tomono, T.; Sano, H. *Makromol. Chem.* **1972**, *151*, 242.
(6) Cowie, J. M. G., Ed. *Alternating Copolymers*; Plenum: New York, 1985.
(7) Sato, T.; Abe, M.; Otsu, T. *Makromol. Chem.* **1977**, *178*, 1061.
(8) Hill, D. J. T.; O'Donnell, J. H.; O'Sullivan, P. W. *Macromolecules* **1982**, *15*, 960.
(9) Bevington, J. C.; Ebdon, J. R.; Huckerby, T. N. *Eur. Polym. J.* **1985**, *21*, 685.
(10) Hill, D. J. T.; O'Donnell, J. H.; O'Sullivan, P. W. *Macromolecules* **1985**, *18*, 9.
(11) Otsu, T.; Yang, J. Z. *Polym. Bull.* **1990**, *24*, 475.
(12) Yang, J. Z.; Otsu, T. *Makromol. Chem., Rapid Commun.* **1990**, *11*, 549.
(13) Yang, J. Z.; Otsu, T. *Polym. Int.*, in press.
(14) Chapin, E. C.; Ham, G. E.; Mills, C. L. *J. Polym. Sci.* **1961**, *55*, S-6.
(15) Garrett, E. R.; Guile, R. L. *J. Am. Chem. Soc.* **1953**, *75*, 3958.
(16) Ketelaar, J. A. A.; Stolpe, Van de; Goudsmit, A.; Dzcubas, W. *Recl. Trav. Chim. Pays-Bas* **1952**, *71*, 1104.
(17) Iwatsuki, S.; Yamashita, Y. *Kogyo Kagaku Zasshi* **1966**, *69*, 1467.
(18) Mayo, F. R.; Lewis, F. M. *J. Am. Chem. Soc.* **1944**, *66*, 1594.
(19) Yamada, B.; Itahashi, M.; Otsu, T. *J. Polym. Sci., Polym. Chem. Ed.* **1978**, *16*, 1718.
(20) Barb, W. G. *J. Polym. Sci.* **1953**, *11*, 117.
(21) Seiner, J. A.; Litt, M. *Macromolecules* **1971**, *4*, 308, 312, 314, 316.
(22) Walling, C.; Seimour, D.; Wolfstrin, K. *J. Am. Chem. Soc.* **1948**, *70*, 1544.
(23) Inoue, H.; Otsu, T. *Makromol. Chem.* **1972**, *153*, 37.
(24) Quach, L.; Otsu, T. *J. Polym. Sci., Polym. Chem. Ed.* **1981**, *19*, 2405.
(25) Iwatsuki, S.; Yamashita, Y. *Makromol. Chem.* **1967**, *104*, 267.
(26) Kokubo, T.; Iwatsuki, S.; Yamashita, Y. *Macromolecules* **1968**, *1*, 482.