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# Reactivities of Dialkyl Citraconates in Radical Copolymerization with Styrene

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## ABSTRACT

The radical copolymerization of dialkyl citraconate (DRC, R = $CH_3$, $C_2H_5$, n-$C_3H_7$, i-$C_3H_7$, n-$C_4H_9$, i-$C_4H_9$, s-$C_4H_9$, $C_6H_{11}$, $C_6H_5CH_2$) ($M_1$) with styrene (ST, $M_2$) was performed at 60°C, using azobisisobutyronitrile as the initiator in tetrahydrofuran in order to clarify the polymerization behavior of DRC and the substituent effects on copolymerization. The monomer reactivity ratios $r_1$ and $r_2$ and the $Q_1$ and $e_1$ values were determined from the results obtained. It was found that the relative reactivities $1/r_2$ of DRC toward an attack by a polystyryl radical could be correlated not by the steric-substituent constant $E_s$ of the alkyl group in DRC, but by the polar-substituent constants $\sigma^*$ in Taft's equation: $\log(1/r_2) = \rho^*\sigma^* + \delta E_s$. It was also observed that the $e_1$ values are associated with Taft's $\sigma^*$ constant. It was found that the weight-average molecular weights of the copolymers are between $8.5 \times 10^3$ and $1.4 \times 10^4$.

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## INTRODUCTION

In order to obtain additional detailed information on the polymerization behavior of an unsaturated dibasic acid and its derivatives, we have investigated the reactivities of N-(4-substituted phenyl)isomaleimide [1], N-substituted maleimide [2], N-substituted citraconimide [3, 4], N-substituted itaconimide [5, 6], alkyl N-(4-substituted phenyl) itaconamate [7], dialkyl mesaconate [8], and dialkyl dithiol mesaconate [9]. The present article describes the results of the relative reactivities $1/r_2$ of dialkyl citraconate (DRC) toward an attack by a polystyryl radical. Some of the DRC monomers have been synthesized by Brown et al. [10] and Coulson et al. [11]. However, no attempts to investigate the polymerization reactivities of DRC have been made so far. Nine types of DRC ($M_1$) were synthesized and copolymerized with styrene (ST, $M_2$). From the result obtained, the monomer reactivity ratios $r_1$ and $r_2$ and the $Q_1$ and $e_1$ values for DRC were calculated. Furthermore, in order to clarify substituent effects on the copolymerization, Eq. (1) was applied, and the results are discussed:

$$\log (1/r_2) = \rho^*\sigma^* + \delta E_s \qquad (1)$$

where $\rho^*$ is the polar reaction constant, $\sigma^*$ is the polar substituent constant, $\delta$ is the steric reaction constant, and $E_s$ is the steric substituent constant.

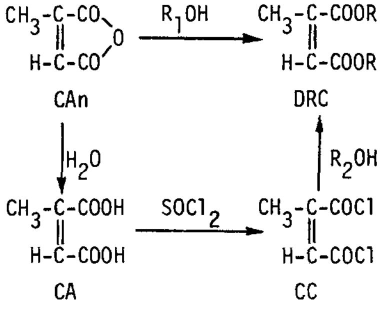
## EXPERIMENTAL

### Syntheses of DRC Monomers

Nine types of DRC monomers were prepared, following the process in Scheme 1, and by a method described by Brown et al. [10] and Coulson et al. [11], with some modification. The DRC monomers were identified on the basis of elemental analysis and IR and $^1$H-NMR spectra. The boiling point, yield, and refractive index of each DRC monomer are shown in Table 1.

### Materials

ST, $\alpha,\alpha'$-azobisisobutyronitrile (AIBN), tetrahydrofuran (THF), benzene, toluene, and methanol were purified by the usual methods.



$R_1$: $CH_3$(MC), $C_2H_5$(EC), n-$C_3H_7$ (n-PC), $C_4H_9$(n-BC).

$R_2$: i-$C_3H_7$(i-PC), i-$C_4H_9$(i-BC), s-$C_4H_9$(s-BC), $C_6H_{11}$(CHC), $C_6H_5CH_2$(BZC).

SCHEME 1.

## Copolymerization Procedure

DRC ($M_1$, 0.69 to 2.72 mol/L) was copolymerized with ST ($M_2$, 0.12 to 2.29 mol/L) in THF at 60°C in a sealed glass tube in the presence of $3.0 \times 10^{-2}$ mol/L of AIBN. After copolymerization for a given time (3 to 48 h), the content of the tube was poured into a large amount of methanol to precipitate the copolymer. The resulting copolymer was purified by precipitating it from a benzene-THF (50 vol%) solution into a large amount of methanol. The copolymer obtained was filtered, thoroughly washed with methanol, and dried under reduced pressure to obtain the copolymer.

The composition of the copolymer was determined from carbon analysis. The monomer reactivity ratios $r_1$ and $r_2$ were determined according to the methods reported by Fineman-Ross [12] and by Mayo-Lewis [13].

## Measurement

The molecular weights of the copolymers were measured by gel permeation chromatographic (GPC) analysis by using the same technique as described in an earlier article [8]. IR and $^1$H-NMR spectra

TABLE 1. Boiling Points, Yields, Refractive Indices of DRC, and Monomer Reactivity Ratios ($r_1$, $r_2$) for DRC ($M_1$) and ST ($M_2$), and $Q_1$, $e_1$ Values

| DRC,[a] $M_1$ | bp, °C/mmHg | Yield,[b] % | $n_D^{22}$ | Monomer reactivity ratio $r_1$ | ± | $r_2$ | ± | $Q_1$[f] | $e_1$[f] |
|---|---|---|---|---|---|---|---|---|---|
| MC | 108-109(23)<br>112-120(29)[d] | 49[c]<br>- | 1.4478<br>1.4453[d] | 0.049 | 0.05 | 1.58 | 0.05 | 0.18 | 0.80 |
| EC | 112-114(15)<br>122(21)[e] | 62[c]<br>- | 1.4429<br>1.4442[e] | 0.029 | 0.04 | 2.48 | 0.04 | 0.11 | 0.83 |
| n-PC | 94-95(3) | 58[c] | 1.4466 | 0.027 | 0.03 | 2.19 | 0.03 | 0.12 | 0.88 |
| i-PC | 80-82(3) | 51 | 1.4402 | 0.076 | 0.03 | 1.62 | 0.03 | 0.19 | 0.65 |
| n-BC | 142-146(9) | 22[c] | 1.4459 | 0.054 | 0.06 | 2.74 | 0.06 | 0.12 | 0.58 |
| i-BC | 147-149(15) | 45 | 1.4443 | 0.030 | 0.04 | 1.80 | 0.04 | 0.14 | 0.91 |
| s-BC | 117-120(3) | 41 | 1.4455 | 0.13 | 0.03 | 2.00 | 0.03 | 0.20 | 0.36 |
| CHC | 160-162(3) | 35 | 1.4903 | 0.030 | 0.04 | 1.88 | 0.04 | 0.14 | 0.90 |
| BZC | 242-243(10) | 26 | 1.5519 | 0.047 | 0.03 | 1.55 | 0.03 | 0.18 | 0.80 |

[a] MC: dimethyl citraconate; EC: diethyl citraconate; n-PC: di-n-propyl citraconate; i-PC: di-i-propyl citraconate; n-BC: di-n-butyl citraconate; i-BC: di-i-butyl citraconate; s-BC: di-s-butyl citraconate, CHC: dicyclohexylcitraconate; BZC: dibenzyl citraconate.

[b] Based on citraconyl chloride.

[c] Based on citraconic anhydride.

[d] See Ref. 10.

[e] See Ref. 11.

[f] Calculated by assuming that $Q_2$ and $e_2$ values for ST were 1.0 and -0.8, respectively.

were obtained, and thermal and elemental analyses were done by using the same instruments as reported previously [14].

## RESULTS AND DISCUSSION

All bulk homopolymerizations of DRC (1.0 g; 3.2 to 6.3 mmol) were carried out with AIBN (1 wt% of DRC; $6.1 \times 10^{-2}$ mmol) at various temperatures (50, 70, 90, 110°C) for 48 h, and gave no appreciable amount of homopolymer. All solution homopolymerizations of DRC were achieved with AIBN in THF (2 mL), benzene (2 mL), and toluene (2 mL) at 40 and 60°C under the same conditions as described above. However, no homopolymers could be obtained. This may be attributable to steric hindrance due to the 1,1,2-trisubstituted ethylene structure. Similar behavior occurred in the homopolymerizations of dialkyl mesaconate [8] and dialkyl dithiol mesaconate [9].

The composition curves of the dibenzyl citraconate (BZC)-ST and di-n-butylcitraconate (n-BC)-ST copolymers are shown in Fig. 1. The composition curves of other copolymers are between these two curves. It was observed that the rate of copolymerization decreased with an increase in the concentration of DRC in the monomer mixture. As can be seen from Fig. 1, the DRC content in the copolymer increases with increasing DRC in the monomer mixture.

The monomer reactivity ratios $r_1$ and $r_2$ and the Alfrey-Price [15]

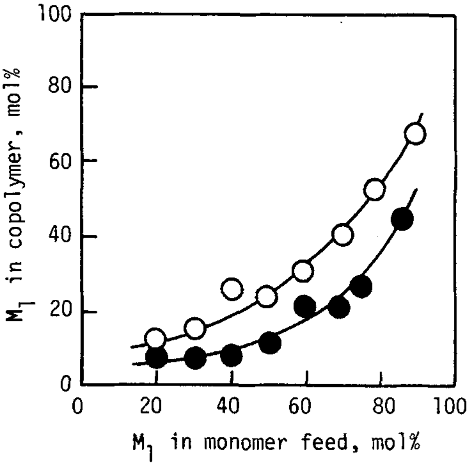


FIG. 1. Copolymer composition curves for DRC ($M_1$) and ST ($M_2$) systems: (○) BZC-ST, (●) n-BC-ST.

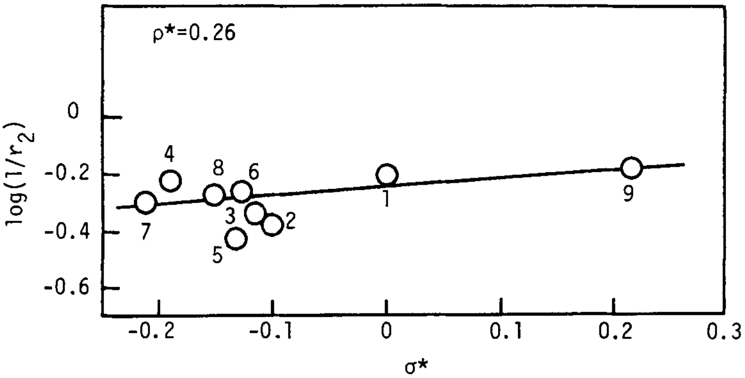


FIG. 2. Correlation between the relative reactivities ($1/r_2$) of DRC toward an attack by a polystyryl radical and σ* constants of alkyl groups: (1) $CH_3$, (2) $C_2H_5$, (3) n-$C_3H_7$, (4) i-$C_3H_7$, (5) n-$C_4H_9$, (6) i-$C_4H_9$, (7) s-$C_4H_9$, (8) $C_6H_{11}$, (9) $C_6H_5CH_2$.

$Q_1$ and $e_1$ values for DRC monomers are shown in Table 1. These parameters were found to vary with the ester alkyl groups in DRC.

The relative reactivities $1/r_2$ of the DRC monomers toward an attack by a polystyryl radical increased with an increase in the electron-withdrawing nature of the ester alkyl groups. Figure 2 indicates that an approximately linear relationship with $\rho^* = 0.26$ in Eq (1), with 0.14 standard deviation, exists between log ($1/r_2$) and the Taft σ* constant. However, plots of log $(1/r_2)-\rho^*\sigma^*$ (where $\rho^* = 0.26$) against the $E_s$ constants also gave a straight line with $\delta = 0$, as shown in Fig. 3. This result strongly suggests that the radical reactivities of DRC monomer depend on the polar character of the alkyl substituents, but not on the steric character. These phenomena are not characteristic of DRC. Similar correlations are also observed for dialkyl mesaconate ($\rho^* = 0.66$, $\delta = 0$) [8], dialkyl dithiol mesaconate ($\rho^* = 0.54$, $\delta = 0$) [9], N-alkyl itaconimide ($\rho^* = 0.55$, $\delta = 0$) [6], and N-alkyl citraconimide ($\rho^* = 0.34$, $\delta = 0$) [4].

Table 1 reveals that the $Q_1$ values for DRC are slightly smaller than those for dialkyl mesaconate (0.19 to 0.50) [8]. However, the $e_1$ values for DRC were found to be similar to those for dialkyl mesaconate (0.57 to 1.12). Figure 4 indicates that the $Q_1$ values for DRC are almost independent of the σ* constant, and that the $e_1$

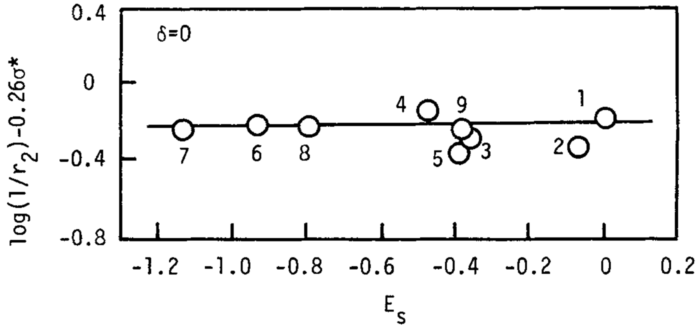


FIG. 3. Correlation between the relative reactivities ($1/r_2$) of DRC toward an attack by a polystyryl radical and $E_s$ constants of alkyl groups: (1) $CH_3$, (2) $C_2H_5$, (3) n-$C_3H_7$, (4) i-$C_3H_7$, (5) n-$C_4H_9$, (6) i-$C_4H_9$, (6) i-$C_4H_9$, (7) s-$C_4H_9$, (8) $C_6H_{11}$, (9) $C_6H_5CH_2$.

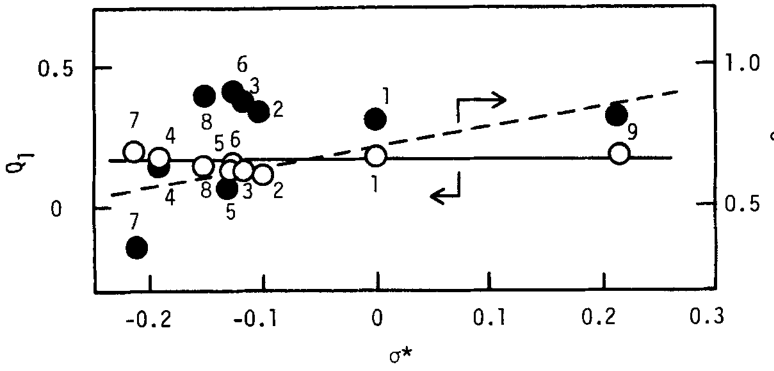


FIG. 4. Correlations between the $Q_1$ (○) or $e_1$ (●) values of DRC and σ* constants of alkyl groups: (1) $CH_3$, (2) $C_2H_5$, (3) n-$C_3H_7$, (4) i-$C_3H_7$, (5) n-$C_4H_9$, (6) i-$C_4H_9$, (7) s-$C_4H_9$, (8) $C_6H_{11}$, (9) $C_6H_5CH_2$.

values becomes larger with an increase in the electron-withdrawing nature of the alkyl group in DRC.

These tendencies were more or less detected in many reports on the reactivities of dialkyl mesaconate [8], dialkyl dithiol mesaconate

[9], N-alkyl itaconimide [6], N-alkyl citraconimide [4], alkyl methacrylate [16], alkyl acrylate [17], and alkyl thiolacrylate [18].

The number average molecular weight $\overline{M}_n$ was calculated as $5.5 \times 10^3$ to $10.3 \times 10^3$. The polydispersity $\overline{M}_w/\overline{M}_n$ was between 1.3 and 2.5. In addition, the softening point was found to be between 105 and 188°C. The initial degradation temperature was determined as 214 to 285°C using DSC (at a heating rate of 10°C/min in helium).

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