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Reactivities of Dialkyl Dithiol Meseaconates in Radical Copolymerization with Styrene

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ABSTRACT

Nine novel types of dialkyldithiol meseaconates (DRTM, M_1) were synthesized and copolymerized with styrene (M_2) in tetrahydrofuran at 60°C in order to clarify the polymerization behavior of DRTM and the substituent effects on the copolymerization. From the results obtained, the monomer reactivity ratio r_1 , r_2 and Q_1 , e_1 values were determined. It was found that the relative reactivities $1/r_2$ of DRTM toward an attack by polystyryl radical were correlated only by the polar substituent constant σ^* of the alkyl group in DRTM, but not by the steric substituent constant E_s in Taft's equation: $\log (1/r_2) = \rho^* \sigma^* + \delta E_s$. It was also observed that the Q_1 and e_1 values for DRTM were correlated by Taft's σ^* constant. The number-average molecular weights of the DRTM-ST copolymer were found to be between 5.0×10^3 and 1.2×10^4 .

INTRODUCTION

In order to clarify the polymerization reactivities of unsaturated dibasic acid derivatives, especially of five-membered cyclic imides, we have investigated *N*-(4-substituted phenyl)isomaleimide [1], *N*-substituted maleimide [2], *N*-substituted citraconimide [3, 4], *N*-substituted itaconimide [5, 6], and alkyl *N*-(4-substituted phenyl)itaconamate [7]. In a previous paper [8] it was reported that the relative reactivities $1/r_2$ of dialkyl mesaconate (DRM) toward an attack by a polystyryl radical were correlated only by the polar-substituent constant σ^* of the alkyl group in DRM, not by the steric substituent constant E_s in Taft's equation (Eq. 1) [9]:

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

where ρ^* is a polar reaction constant and δ is a steric reaction constant. According to Eq. (1), it was found that a linear relation was obtained as $\rho^* = 0.66$ and $\delta = 0$.

In this article we investigate the relative reactivities $1/r_2$ of dialkyl dithiol mesaconate (DRTM) toward an attack by a polystyryl radical. Nine novel types of DRTM (M_1) were synthesized and copolymerized with styrene (ST, M_2). From the result obtained, the monomer reactivity ratio r_1 and r_2 , and Q_1 and e_1 values for DRTM were calculated. Furthermore, in order to clarify substituent effects on copolymerization, application was made of Eq. (1), and the results are discussed.

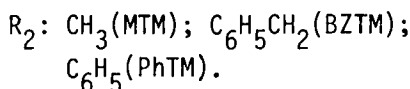
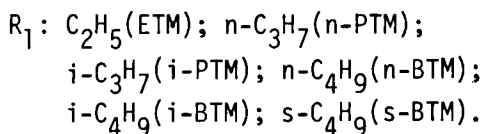
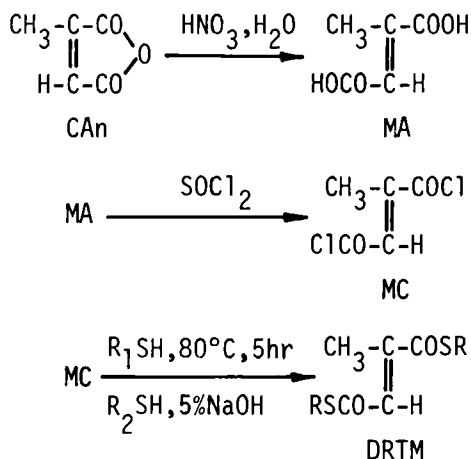
EXPERIMENTAL

Syntheses of DRTM Monomers

Nine types of DRTM monomers were prepared, following the process in Scheme 1, and by a method similar to that described by Ham et al. [10] and by Marvel et al. [11]. The DRTM monomers were identified on the basis of elemental analysis and IR and $^1\text{H-NMR}$ spectra. Table 1 gives the boiling point, yield, and refractive index of each DRTM monomer.

Materials

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



SCHEME 1.

Copolymerization Procedure

The copolymerization of DRTM (M_1 , 0.66 to 2.20 mol/L) with ST (M_2 , 0.35 to 3.75 mol/L) was carried out in THF at 60°C in a sealed glass tube in the presence of 3.0×10^{-2} mol/L of AIBN. After copolymerization for a given time (3 to 6 h), which gave a conversion lower than 10%, the tube was opened and its contents were poured into a large amount of methanol to precipitate the copolymer. The resulting copolymer was purified by reprecipitating it from the THF-benzene (50 vol%) solution into a large amount of methanol. The precipitate 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 calculated according to a method by Fineman-Ross [12].

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

DRTM ^a M_1	bp [mp] [°C(mmHg)]	Yield ^b (%)	n_D^{20}	Monomer reactivity ratio					
				r_1	r_2	Q_1^d	e_1^d		
MTM	90-92(2)	44 ^c	1.5747	0.068	0.03	0.35	0.03	0.60	1.13
ETM	161-162(18)	29	1.5564	0.027	0.04	0.40	0.04	0.46	1.33
n-PTM	142-143(2)	41	1.5411	0.055	0.05	0.39	0.05	0.54	1.16
i-PTM	158-161(16)	26	1.5364	0.049	0.03	0.44	0.03	0.48	1.16
n-BTM	203-205(15)	40	1.5338	0.050	0.04	0.41	0.04	0.50	1.17
i-BTM	194-197(16)	22	1.5291	0.026	0.02	0.41	0.03	0.42	1.39
s-BTM	189-191(16)	17	1.5311	0.020	0.02	0.45	0.03	0.39	1.37
BZTM	93-95(2)	40 ^c	1.6284	0.057	0.05	0.28	0.05	0.70	1.23
PhTM	mp 74-75	81 ^c	-	0.15	0.06	0.16	0.05	1.30	1.13

^aMTM: dimethyldithiolmesaconate; ETM: diethyldithiolmesaconate; n-PTM: di-n-propyldithiolmesaconate; i-PTM: di-i-propyldithiolmesaconate; n-BTM: di-n-butyldithiolmesaconate; i-BTM: di-i-butyldithiolmesaconate; s-BTM: di-s-butyldithiolmesaconate; BZTM: dibenzoyldithiolmesaconate; PhTM: diphenyldithiolmesaconate.

^bBased on mesaconyl chloride.

^cRSNa.

^dCalculated by assuming that Q_2 and e_2 values for ST were 1.0 and -0.8, respectively.

Measurement

The molecular weights of the copolymers were measured by gel permeation chromatographic (GPC) analysis using the same procedure as described in an earlier paper [8].

RESULTS AND DISCUSSION

The radical homopolymerization of DRTM was carried out in THF in the presence of AIBN (3.0×10^{-2} mol/L) at 60°C for 240 h, giving no appreciable amount of homopolymer. This may arise from the steric hindrance due to the 1,1,2-trisubstituted ethylene structure. A similar tendency was also recognized in the homopolymerization of DRM [8].

The composition curves of the diphenyldithiolmesaconate (PhTM)-St and di-*s*-butyldithiolmesaconate (*s*-BTM)-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 increasing concentration of DRTM in a monomer mixture. Figure 1 indicates that the mole fraction of DRTM in the copolymer tends to increase with an increase in the mole fraction of

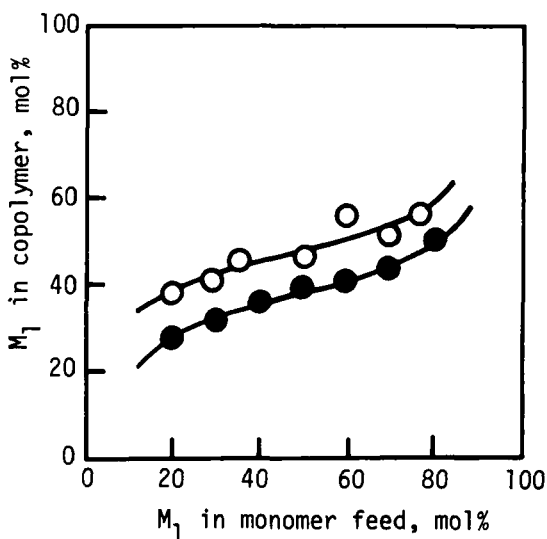


FIG. 1. Copolymer-composition curves for DRTM (M_1) and ST (M_2) systems: (○) PhTM-ST, (●) *s*-BTM-ST.

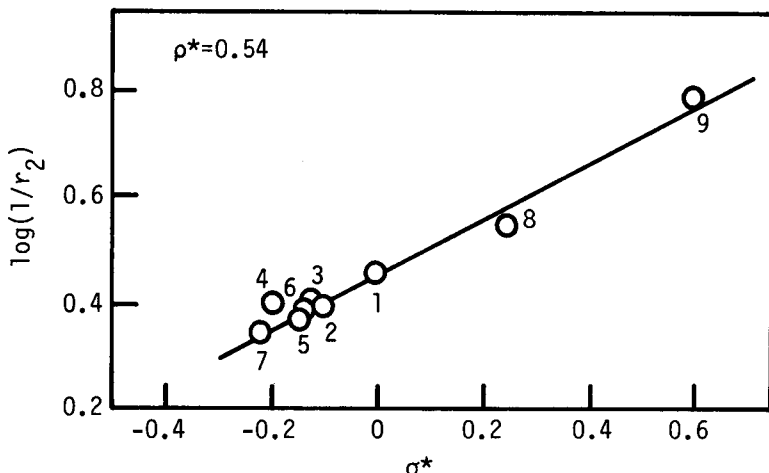


FIG. 2. Correlation between the relative reactivities ($1/r_2$) of DRTM toward an attack by a polystyryl radical and σ^* constants of alkyl groups: (1) CH₃, (2) C₂H₅, (3) n-C₃H₇, (4) i-C₃H₇, (5) n-C₄H₉, (6) i-C₄H₉, (7) s-C₄H₉, (8) C₆H₅CH₂, (9) C₆H₅.

DRTM in the monomer mixture. This tendency could be detected in the copolymerization of DRM with ST [8].

The monomer reactivity ratio r_1 and r_2 and the Alfrey-Price [13] Q_1 and e_1 values for DRTM are summarized in Table 1. It was found that these parameters changed regularly with the ester alkyl groups in DRTM.

The relative reactivities ($1/r_2$) of the DRTM monomers toward an attack by a polystyryl radical increased with an increase in the electron-withdrawing nature of their ester alkyl groups. When $\log(1/r_2)$ was plotted against the Taft σ^* constants according to Eq. (1), a straight-line relationship with $\rho^* = 0.54$, with 0.11 standard deviation, was obtained, as Fig. 2 shows. However, the plot of $\log(1/r_2) - \rho^*\sigma^*$ (where $\rho^* = 0.54$) against the E_s constants also gave a straight line with $\delta = 0$ as is also shown in Fig. 3. This result strongly indicates that the radical reactivities of DRTM monomers depend on the polar character of their alkyl substituents, but not on their steric character. A similar correlation was also observed for the relative reactivities of DRM ($\rho^* = 0.66$, $\delta = 0$) [8].

Table 1 indicates that the e_1 values for DRTM are slightly larger than those for DRM (0.57-1.12). From Table 1, however, the Q_1 values for DRTM are quite a bit larger than those for DRM (0.19-0.50) [8], indicating that the 3d orbital conjugation by the sulfur atom in DRTM may play a significant role in the stabilization of the transition state structure of their reaction.

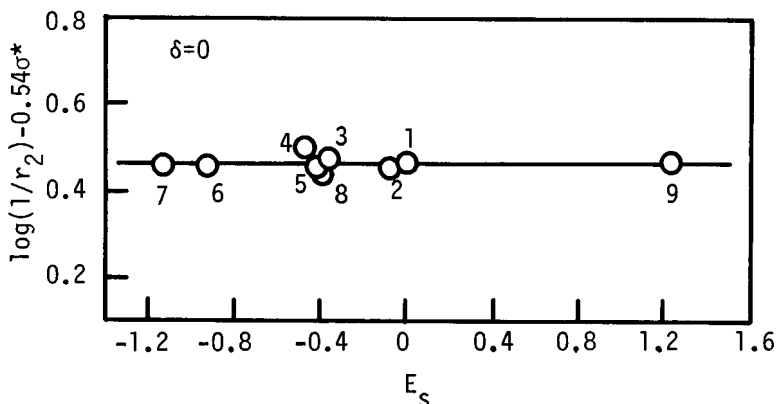


FIG. 3. Correlation between the relative reactivities ($1/r_2$) of DRTM toward an attack by a polystyryl radical and E_s constants of alkyl groups: (1) CH_3 , (2) C_2H_5 , (3) $n\text{-C}_3\text{H}_7$, (4) $i\text{-C}_3\text{H}_7$, (5) $n\text{-C}_4\text{H}_9$, (6) $i\text{-C}_4\text{H}_9$, (7) $s\text{-C}_4\text{H}_9$, (8) $\text{C}_6\text{H}_5\text{CH}_2$, (9) C_6H_5 .

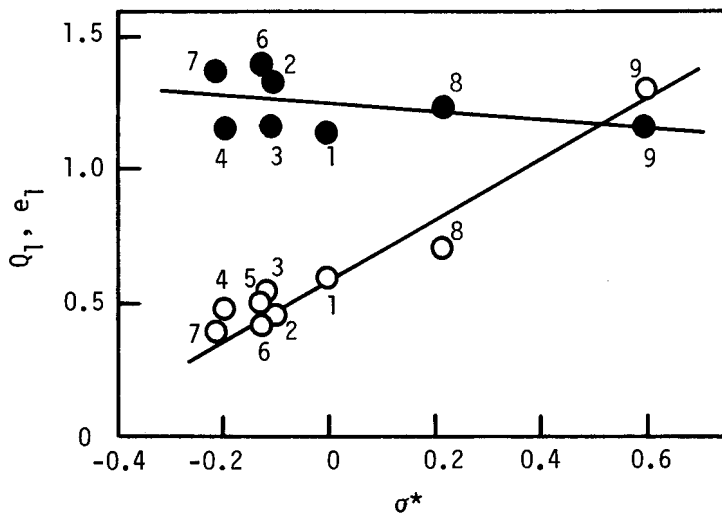


FIG. 4. Correlations between the Q_1 (\circ) or e_1 (\bullet) values of DRTM and σ^* constants of alkyl groups: (1) CH_3 , (2) C_2H_5 , (3) $n\text{-C}_3\text{H}_7$, (4) $i\text{-C}_3\text{H}_7$, (5) $n\text{-C}_4\text{H}_9$, (6) $i\text{-C}_4\text{H}_9$, (7) $s\text{-C}_4\text{H}_9$, (8) $\text{C}_6\text{H}_5\text{CH}_2$, (9) C_6H_5 .

It can be seen from Fig. 4 that e_1 values for DRTM are slightly correlated with the σ^* constant, i.e., the polar character of the alkyl substituent in DRTM, and that the Q_1 values increase with an increase in the electron-withdrawing nature of the alkyl group in DRTM. In the case of DRM, similar tendencies were observed [8].

In DRTM, since the alkyl group in question is not attached directly to the reacting vinyl group and is considerably remote from the reacting double bond, the δ value appears to be nearly zero. Similar correlations were observed for the relative reactivities of alkyl methacrylate ($\rho^* = 0.33$, $\delta = 0$) [14], alkyl acrylate ($\rho^* = 0.56$, $\delta = 0$) [15], and alkyl thiolacrylate ($\rho^* = 0.28$, $\delta = 0$) [16].

The number-average molecular weight \bar{M}_n was calculated as 5.0×10^3 to 12.1×10^3 in the DRTM-ST copolymers. In addition, the polydispersity M_w/M_n was between 1.3 and 1.9.

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