Copolymerization Reactivities of α-Substituted Crotonyl Monomers

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ABSTRACT

The radical copolymerizations of various α-substituted crotonyl monomers with styrene (St) and acrylonitrile (AN) were investigated, and the copolymerization parameters were determined by a least-squares procedure reported previously. The relative reactivities of the α-substituted crotonyl monomers toward polymer radicals of St and AN were found to correlate with the equation: log (relative reactivity of $CH_3CH{=}CXY$) = ρ ($\sigma_X + \sigma_Y$) + A($\Delta\log Q_X + \Delta\log Q_Y$), where σ and $\Delta\log Q$ are the polar Hammett and resonance substituent constants, respectively, and ρ and A are reaction constants. From the observed straight line relationships, the values of ρ and A were obtained to be as follows: $\rho = 0.66$, A = 0.75 for attack of poly-St radical, and $\rho = -3.20$, A = 1.3 for attack of poly-AN radical.

INTRODUCTION

Data on the reactivities of vinyl monomers in radical copolymerization have been accumulated [1]. It is claimed that the factors affecting the reactivity of addition of free radical to ethylenic double bond are controlled by the relative importance of polar, resonance, and steric contributions of the substituents.

In oure previous papers [2, 3], the reactivities of α-substituted acrylic monomers toward polystyryl radical were proposed to be expressed in terms of polar and resonance contributions of the α-substituents (X) [Eq. (1)].

$$\log \text{(relative reactivity)} = 0.83\sigma_X + \Delta\log Q_X \tag{1}$$

where σ_X is Hammett's polar substituent constant obtained for the para-substituent and $\Delta\log Q_X$ is a resonance substituent constant which is defined as follows [Eq. (2)].

$$\Delta\log Q_X = \log Q_{CH_2=CXY} - \log Q_{CH_2=CHY} \tag{2}$$

In Eq. (2), Q is defined by Alfrey-Price's Q-e scheme and calculated from the copolymerization with styrene. The $\Delta\log Q_X$ values can also be determined empirically by Eq. (3):

$$\Delta\log Q_X = \log Q_{CH_2=CXH} + 2.01 \tag{3}$$

Thus the $\Delta\log Q$ obtained were found to closely be related with the other resonance substituent constants determined by the results of the mutual copolymerizations of nuclear-substituted styrenes [4] and of the hydrogen abstraction by polymer radicals from nuclear-substituted cumenes [5, 6].

Because of the steric effect of the β-methyl group, crotonyl monomers (β-methylacrylic monomers) are well known to be very difficult to homopolymerize by a radical mechanism. However, in radical copolymerization, the crotonyl monomer reacts with a polymer radical to form a radical carrying the unpaired electron on its α-carbon. Therefore, the effect of the α-substituents on the reactivities of crotonyl monomers seems to be comparable with that of acrylic monomers.

In the present study, the reactivities of α-substituted crotonyl monomers in the copolymerizations were determined and are discussed on the basis of the nature of the substituents. The monomers used had the structure I:

$$CH_3 \diagdown \quad \diagup X$$
$$C=C$$
$$H \diagup \quad \diagdown Y$$

I
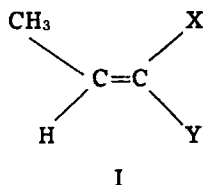
where X was OCH_3, CH_3, H, C_6H_5, Cl, Br, $COOC_2H_5$, $COCH_3$, and CN, and Y was $COOCH_3$, $COOC_2H_5$, and CN.

EXPERIMENTAL

Preparations of the crotonyl monomers and copolymerization procedure have been described elsewhere [7]. α-Phenylcrotonitrile was prepared by the condensation of benzyl cyanide with acetaldehyde. Commercially available crotonitrile, styrene (St), and acrylonitrile (AN) were used after the usual purification. NMR and gas chromatographic determinations indicated that the crotonyl monomers used were mainly in the form of the trans isomer (see Table 1).

The composition of the copolymers was determined from the results of elementary analyses. The monomer reactivity ratios were calculated by a nonlinear least-squares procedure with consideration of the weight of experimental data, by using a computer [7].

RESULTS AND DISCUSSION

The results of radical copolymerizations of crotonyl monomers (M_1) with St and AN (M_2) at 60°C are summarized in Table 1, in which the monomer reactivity ratios for methyl crotonate and crotonitrile were recalculated from the data of Minoura et al. [8].

Since some of crotonyl monomers used were mixtures of cis and trans isomers, the difference in reactivities of these isomers must be considered. It is known that trans monomers are generally more reactive than cis monomers, and that the higher reactivities of the former are ascribed to greater resonance stabilization in the transition

TABLE 1. Monomer Reactivity Ratios for Radical Copolymerizations of α-Substituted Crotonyl Monomers ($CH_3CH{=}CXY$, M_1) with St and AN (M_2) at 60°C

No.	X	Y	Trans isomer (%)	M_2 = St		M_2 = AN	
				r_1	r_2	r_1	r_2
1	OCH_3	$COOCH_3$	18	0.04[a]	18.4	0.00	1.00
2	CH_3	$COOCH_3$	100	0.02[b]	30.7	0.00	2.97
3	H	$COOC_2H_5$	100	0.00[c]	27.0[c]	0.00	25.2
4	Cl	$COOC_2H_5$	85	0.00	5.13	0.00	9.53
5	Br	$COOC_2H_5$	100	0.00	4.42	-	-
6	$COOC_2H_5$	$COOC_2H_5$	-	0.00	8.24	0.00	18.7
7	$COCH_3$	$COOCH_3$	70	0.00	2.70	0.00	8.68
8	CN	$COOC_2H_5$	100	0.02[d]	0.26	0.06[e]	11.4
9	H	CN	100	0.00	23.8	-	-
10	C_6H_5	CN	0	0.00	0.43	-	-

[a] ± 0.04.
[b] ± 0.02.
[c] Recalculated from the data of Minoura et al. for X = H and Y = $COOCH_3$ [8].
[d] ± 0.03.
[e] ± 0.06.

state of propagation [9-11]. Therefore, the reactivities of pure trans isomers of methyl α-methoxycrotonate, ethyl α-chlorocrotonate, and methyl α-acetylcrotonate are expected to be slightly greater than those obtained in this study (Table 1).

Moreover, the crotonyl monomers used were in the form of the methyl or ethyl esters; both esters seem to have almost identical reactivities. This would appear to be quite reasonable, since methyl methacrylate is more reactive than ethyl methacrylate toward the attack of polystyryl radical by a factor of only 1.01 [12].

As can be seen from Table 1, all the values of r_1 are equal to zero within experimental error. This is consistent with the result that crotonyl monomers are scarcely polymerized by a radical mechanism.
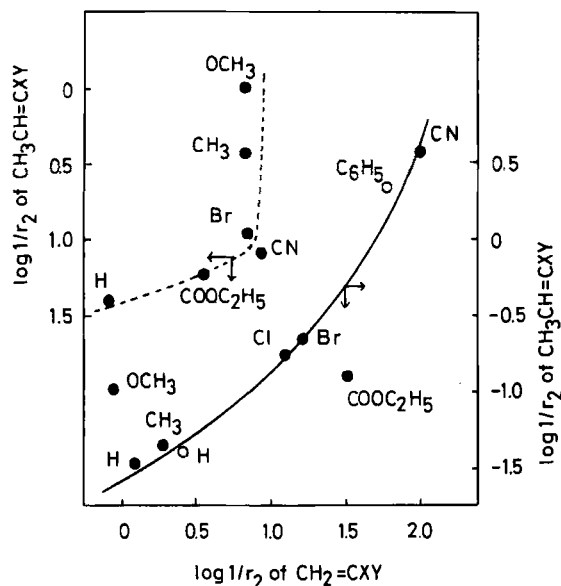
FIG. 1. Relation between the effect of α-substituents on the reactivities of α-substituted crotonyl and acrylic monomers: (●) Y = COOR; (○) Y = CN; (—) reactivities toward poly-St radical; (--) reactivities toward poly-AN radical.

The r_2 values obtained change widely, depending on the nature of the α-substituent. Since St and AN were chosen as M_2, the $1/r_2$ values denote the reactivities of the crotonyl monomers toward poly-St and poly-AN radical relative to the additions of St and AN monomers, respectively.

In order to compare the contributions of the α-substituents in crotonyl monomers with those in acrylic monomers to their reactivities, the relative reactivities of crotonyl monomers toward these polymer radicals were plotted against those of the acrylic monomers, and the results are shown in Fig. 1. Apparently the relative reactivities of crotonyl monomers are much less than those of acrylic monomers.

A significant decrease in the reactivities of vinyl monomers by β-methyl substitution is well known for radical polymerization. The effect of the β-methyl group can be estimated as 1/38 and 1/60 of the reactivities between ethyl crotonate and methyl acrylate and between crotonitrile and AN toward the poly-St radical, respectively. A
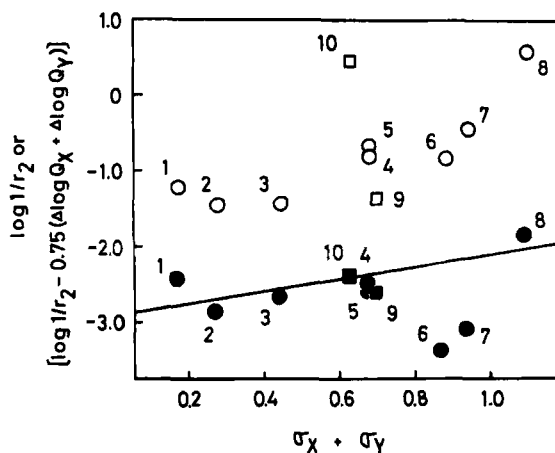
FIG. 2. Effects of α-substituent on the reactivities of the crotonyl monomers toward poly-St radical: ($\circ$) and ($\square$) plot of log $(1/r_2)$ vs. $(\sigma_X + \sigma_Y)$; ($\bullet$) and ($\blacksquare$) plot of $[\log (1/r_2) - 0.75 (\Delta\log Q_X + \Delta\log Q_Y)]$ vs. $(\sigma_X + \sigma_Y)$. Numbers are same as in Table 1.

similar decrease in the reactivities caused by β-methyl group is also estimated; the decrease is by a factor of 20, on comparing the relative reactivites of ethyl crotonate with methyl acrylate toward poly-AN radical.

Figure 1 shows the plots of relative reactivities $(1/r_1)$ of α-substituted crotonates against those of the α-substituted acrylate toward poly-St and poly-AN radicals. The observed plots are not straight line relationships for the attacks of both the polymer radicals, indicating that the reactivities of these monomers are not expressed by Eq. (1).

Therefore, generalization of Eq. (1) gives the following equations [Eqs. (4) and (5)]:

$$\log \left[(1/r_2)_{CH_3 CH=CXY} \big/ (1/r_2)_{CH_3 CH=CHY} \right] = \rho\sigma_X + A(\Delta\log Q_X) \tag{4}$$

or

$$\log \left[(1/r_2)_{CH_3 CH=CXY} \big/ (1/r_2)_{CH_3 CH=CH_2} \right] = \rho (\sigma_X + \sigma_Y)$$
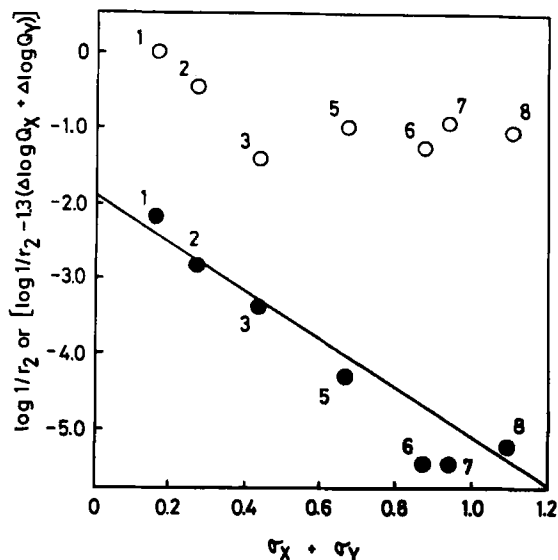$$+ A(\Delta\log Q_X + \Delta\log Q_Y) \tag{5}$$

FIG. 3. Effects of α-substituents on the reactivities of the crotonyl monomers toward poly-AN radical: ($\circ$) plot of log $(1/r_2)$ vs. $(\sigma_X + \sigma_Y)$; ($\bullet$) plot of $[\log (1/r_2) - 1.3 (\Delta\log Q_X + \Delta\log Q_Y)]$ vs. $(\sigma_X + \sigma_Y)$. Numbers are same as in Table 1.

where σ and $\Delta\log Q$ are polar and resonance substituent constants, respectively, described above, and ρ and A are reaction constants giving the susceptibilities of the polar and resonance contributions by the substituents, respectively. Various $\Delta\log Q$ values were reported in a previous paper [2], and that for $COCH_3$ substituent was newly evaluated as 1.85 by introducing Q = 0.69 reported for methyl vinyl ketone [1] into Eq. (2).

To ascertain whether Eq. (5) is applicable for the reactivities of crotonyl monomers, the values of $[\log (1/r_2)_{CH_3 CH=CXY} - A(\Delta\log Q_X + \Delta\log Q_Y)]$ were plotted against $(\sigma_X + \sigma_Y)$ for an A value selected to give a straight line relationship. These plots are shown in Figs. 2 and 3, from which fairly good straight lines relationships with A = 0.75 and A = 1.3 are obtained toward attacks of poly-St and poly-AN radicals, respectively. From their slopes, the ρ values are obtained as 0.66 and -3.20 respectively. However, the plots for diethyl ethylidemalonate and methyl α-acetylcrotonate deviated from

these lines, probably due to inhibition of resonance caused by the bulky α-substituents.

Therefore, the relative reactivities of the crotonyl monomers are expressed by Eqs. (6) and (7).

Toward poly-St radical:

$$\log \left(1/r_2\right)_{CH_3\,CH=CXY} = 0.66\ (\sigma_X + \sigma_Y) + 0.75\ (\Delta\log Q_X + \Delta\log Q_Y)$$
$$- 2.851$$

Toward poly-AN radical:

$$\log \left(1/r_2\right)_{CH_3\,CH=CXY} = -3.20(\sigma_X + \sigma_Y) + 1.3(\Delta\log Q_X + \Delta\log Q_Y)$$
$$- 1.914$$

From comparison of the values of A for the reactivities of α-substituted crotonyl monomers with those of acrylic monomers (1.0 and 1.8) toward poly-St and poly-AN radicals, respectively, it is found that the effect of α-substitution on resonance in acrylic monomers seems to be almost identical or slightly lowered in the transition state of both propagation reactions. The observed ρ values are different from those observed for acrylic monomers ($\rho = 0.83$ and -2.63 toward attacks of poly-St and poly-AN radicals, respectively). The reactions of poly-St and poly-AN radicals with crotonyl monomers therefore seem to occur more nucleophilically and more electrophilically, respectively, than those with acrylic monomers.

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