Radical Copolymerization of Crotonyl Compounds with Styrene

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Synopsis

The monomer reactivity ratios for the radical copolymerization of crotononitrile (CN), methyl crotonate (MC), and n-propenyl methyl ketone (PMK) with styrene (St) were measured at 60°C. in benzene and little penultimate unit effect was shown for these systems. The values obtained were: St–CN, $r_1 = 24.0$, $r_2 = 0$; St–MC, $r_1 = 26.0$, $r_2 = 0.01$; St–PMK, $r_1 = 13.7$, $r_2 = 0.01$. The rate of copolymerization and the viscosity of the copolymer decreased markedly as the molar fraction of the crotonyl compound in the monomer mixture increased. The Q–e values were also calculated to be as follows: CN, $e = 1.13$, $Q = 0.009$; MC, $e = 0.36$, $Q = 0.015$; PMK, $e = 0.61$, $Q = 0.024$. A linear relationship was obtained between the e values of the crotonyl compounds and their Hammett constants σ_m.

INTRODUCTION

The radical homopolymerization of crotonyl compounds is very difficult due to their being 1,2-disubstituted olefins, but the copolymerization with styrene by use of a radical initiator, is easy. Many workers have investigated the copolymerization of crotonyl compounds, such as crotonic acid,[1-4] crotonaldehyde,[5] butyl crotonate,[6] crotonamide,[7] and crotononitrile,[8] with vinyl monomers.

In the present work, crotononitrile (CN), methyl crotonate (MC), and n-propenyl methyl ketone (PMK) were copolymerized with styrene (St), and the copolymerizability of these crotonyl compounds and the effect of the substituted groups in the crotonyl compounds on the Alfrey-Price Q,e values is discussed. Moreover, the fact[8-11] that a penultimate unit effect exists in the copolymerization system of a monomer which has a strongly polar group, such as a nitrile or carbonyl group, led the authors to discuss this point in detail.

EXPERIMENTAL

Materials

Crotononitrile (CN) was a commercially available reagent. The *trans* isomer, which was the main component separated from it by means of gas chromatography, was dried over calcium sulfate and distilled under nitrogen before use; b.p. 45–46°C./64 mm. Hg.

Methyl crotonate (MC) was a commercially available reagent, and it was purified before use by the method used for the purification of methyl methacrylate; b.p. 127–128°C.

n-Propenyl methyl ketone (PMK) was prepared by the aldol condensation of acetoaldehyde with acetone. It was distilled under nitrogen after drying over calcium sulfate; b.p. 43–44°C./81 mm. Hg.

Styrene (St) was a commercially available reagent. The inhibitor was removed from the reagent by washing with alkali, and it was distilled under nitrogen before use; b.p. 54°C./30 mm. Hg.

Benzoyl peroxide was precipitated from chloroform with methanol.

Benzene was purified before use by the usual method.

Copolymerization Procedure

The copolymerization was carried out in a tube containing the required amounts of the two monomers, the initiator, and the solvent. The tube was degassed, sealed off under vacuum, and placed in a constant temperature bath (60 ± 0.01°C.) and the copolymerization was carried out up to 10% conversion. After the copolymerization, the contents of the tube were poured into a large amount of methanol to precipitate the product; the precipitate was washed thoroughly with methanol and then weighed.

Analysis of Copolymer

The composition of the resulting copolymer was determined by elementary analyses (N for crotononitrile and C, H for methyl crotonate and n-propenyl methyl ketone).

Viscosity Measurements

The viscosity of the copolymer was measured in benzene solution at 25°C. in an Ubbelohde viscometer.

RESULTS AND DISCUSSION

Monomer Reactivity Ratio

The results of the copolymerization for each system, crotononitrile, methyl crotonate, and n-propenyl methyl ketone, with styrene are shown in Tables I, II, and III, and the composition curves for these are shown in ·Figures 1, 2, and 3.

It is reasonable, from the failure of crotonyl compounds to homopolymerize, that the reactivity of the copolymerization was low, and that the content of the crotonyl compound in the copolymer was small compared with the initial amount of monomer for all the crotonyl compounds. The monomer reactivity ratios r_1, r_2 were obtained from the equation of Fineman and Ross:[12]

$$F(f - 1)/f = r_1 F^2/f - r_2 \qquad (1)$$

TABLE I

Results of Copolymerization of St–CN System in Benzene
at 60°C., [BPO] = 2.41 × 10⁻² mole/l.

| Expt. no. | Feed monomer | | | Time, hr. | Conversion, % | Copolymer CN, mole-%[a] |
	[St] × 10⁻¹, mole/l.	[CN] × 10⁻¹, mole/l.	[CN], mole-%			
0	40.59	0	0	2	3.72	0
4	27.29	18.82	40.90	3	3.76	2.94
5	23.42	22.89	49.43	3.5	3.68	3.64
6	18.56	28.11	60.23	4.5	3.75	6.49
7	14.01	31.98	69.54	6	3.79	7.24
8	9.28	37.65	80.23	7	2.84	15.14
9	4.67	41.82	89.96	8	1.48	19.69

[a] Calculated from N elementary analysis.

TABLE II

Results of Copolymerization of St–MC System
in Benzene at 60°C., [BPO] = 2.41 × 10⁻² mole/l.

| Expt. no. | Feed monomer | | | Time, hr. | Conversion, % | Copolymer MC, mole-%[a] |
	[St] × 10⁻¹, mole/l.	[MC] × 10⁻¹, mole/l.	[MC], mole-%			
11	40.54	0	0	2	3.72	0
12	36.54	4.56	11.09	2	3.33	2.0
13	32.48	9.13	21.94	3	4.24	2.7
14	28.42	13.69	32.51	4	4.57	3.3
15	24.36	18.26	42.84	5	4.47	3.0
16	20.30	22.82	52.92	7	4.91	4.3
17	16.24	27.38	62.76	10	4.54	4.3
18	12.18	31.35	72.01	15	5.01	7.6
19	8.12	36.51	81.80	18	3.36	11.1
20	4.06	41.08	89.92	20	0.90	21.1

[a] Calculated from C,H elementary analysis.

where F is the molar ratio ($[M_1]/[M_2]$) of the feed monomers, and f is the molar ratio ($d[M_1]/d[M_2]$) in the copolymer. For the data of Tables I–III, $F(f-1)/f$ was plotted against F^2/f as shown in Figures 4–6.

From the slopes and the intersects of the above straight lines, the monomer reactivity ratios were determined, as shown in Table IV.

If $r_2 = 0$, eq. (1) reduces to:

$$(f - 1) = r_1 F \qquad (2)$$

Therefore the relationship between $(f - 1)$ and F is a straight line passing through the origin. In fact, proportional relationships were obtained, as shown in Figure 7.
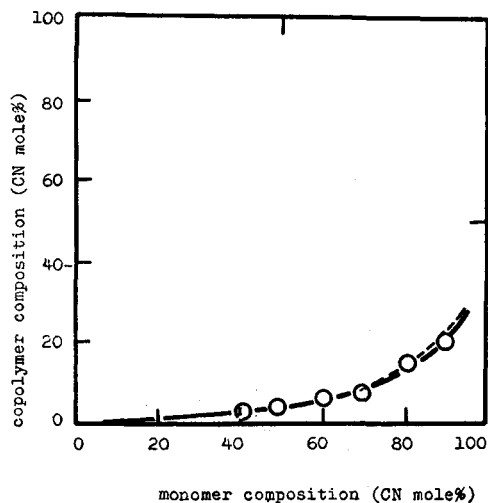
Fig. 1. Composition curve for St–CN copolymer: (——) terminal model, $r_1 = 24.0, r_2 = 0$; (- - -) penultimate model, $r_1 = 23.0, r_1' = 20.0, r_2 = r_2' = 0$.

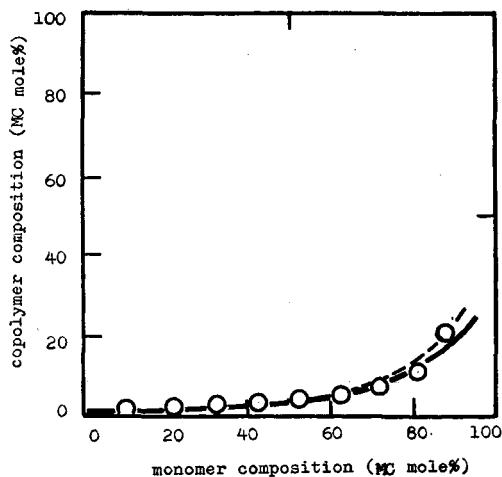Fig. 2. Composition curve for St–MC copolymer: (——) terminal model, $r_1 = 26.0, r_2 = 0.01$; (- - -) penultimate model; $r_1 = 27.0, r_1' = 33.0, r_2 = r_2' = 0$.

Figure 7 indicates that the penultimate unit effect, which is generally accepted in the case of the styrene–acrylonitrile[11] and styrene–crotono-nitrile[9] systems, did not need to be considered. Nevertheless, it was at-tempted to treat the results in this work on the basis of the penultimate unit effect.[10] The reactivity of polymer radical is determined not only by its terminal unit, but also by the nonterminal units of the radical. If the terminal and penultimate units alone are considered to be influential, and
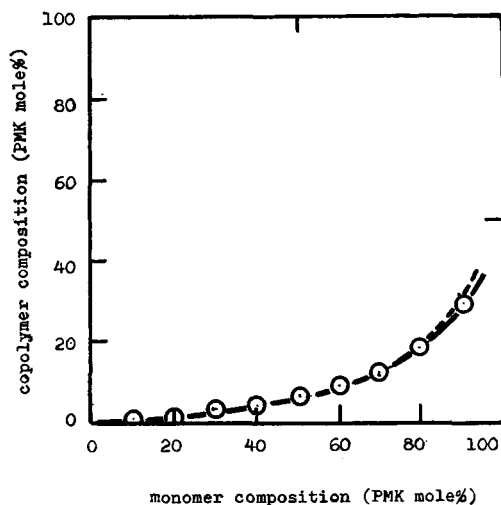
Fig. 3. Composition curve for St–PMK copolymer: (——) terminal model, $r_1 = 13.7$; $r_2 = 0.01$; (- - -) penultimate model, $r_1 = 14.0$, $r_1' = 11.1$, $r_2 = r_2' = 0$.

TABLE III

Results of Copolymerization of St–PMK System in Benzene
at 60°C., [BPO] $= 2.4 \times 10^{-2}$ mole/l.

| Expt. no. | Feed monomer | | | Time, hr. | Conversion, % | Copolymer PMK, mole-%[a] |
	[St] $\times 10^{-1}$, mole/l.	[PMK] $\times 10^{-1}$, mole/l.	[PMK], mole-%			
21	40.59	0	0	1	1.86	0
22	35.96	4.04	10.09	1.5	2.55	0.4
23	31.90	8.08	20.21	2	2.96	1.7
24	27.84	12.12	30.33	3	3.80	3.3
25	23.78	16.16	40.46	4	4.15	4.1
26	19.82	20.20	50.60	6	4.92	6.5
27	16.24	24.24	59.88	6	3.75	9.1
28	12.18	27.61	69.38	10	4.57	12.8
29	8.12	31.65	79.58	16	4.06	12.8
30	4.06	38.45	90.45	33	2.48	29.6

[a] Calculated from C,H elementary analysis.

TABLE IV

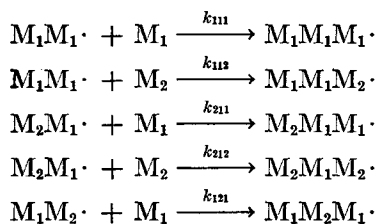Copolymerization Parameters of Crotonyl Compounds with St (M_1)

| M_2, R in $CH_3CH=CHR$ | Terminal model | | | | Penultimate model[a] | | |
	$r_1(=k_{11}/k_{12})$	$r_2(=k_{22}/k_{21})$	e_2	Q_2	$r_1(=k_{111}/k_{112})$	$r_1(=k_{211}/k_{212})$	r'_1/r_1
CN	24.0	0	1.13	0.009	23.0	20.0	0.8
COOCH$_3$	26.0	0.01	0.36	0.015	27.0	33	1.2
COCH$_3$	13.7	0.01	0.61	0.024	14.0	11.1	0.7

[a] Assuming $r_2(=k_{222}/k_{221}) = 0$, $r'_2(=k_{122}/k_{121}) = 0$.
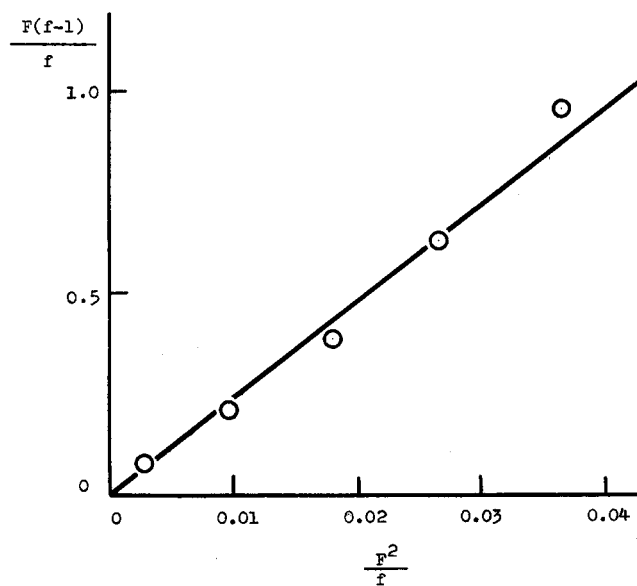
Fig. 4. Fineman-Ross plot for St(M_1)–CN (M_2) system.
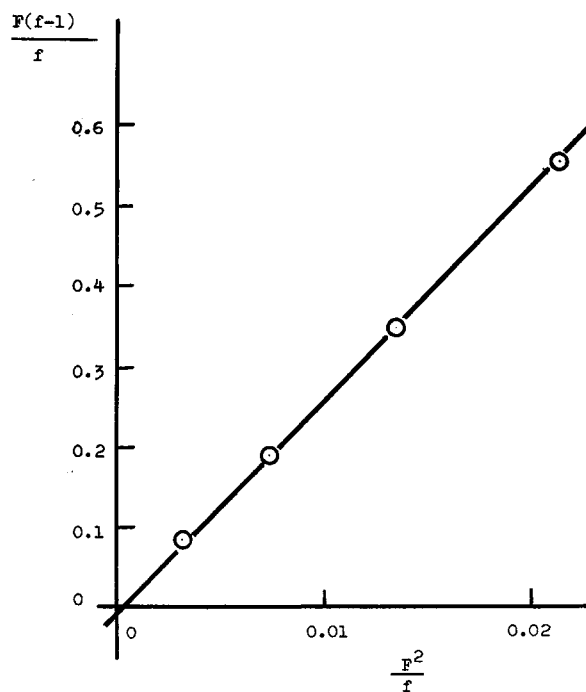
Fig. 5. Fineman-Ross plot for St(M_1)–MC (M_2) system.
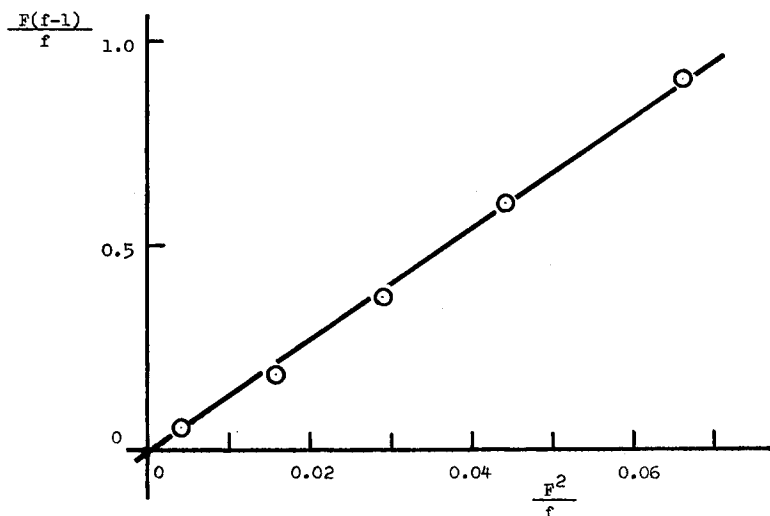
Fig. 6. Fineman-Ross plot for St (M_1)–PMK (M_2) system.
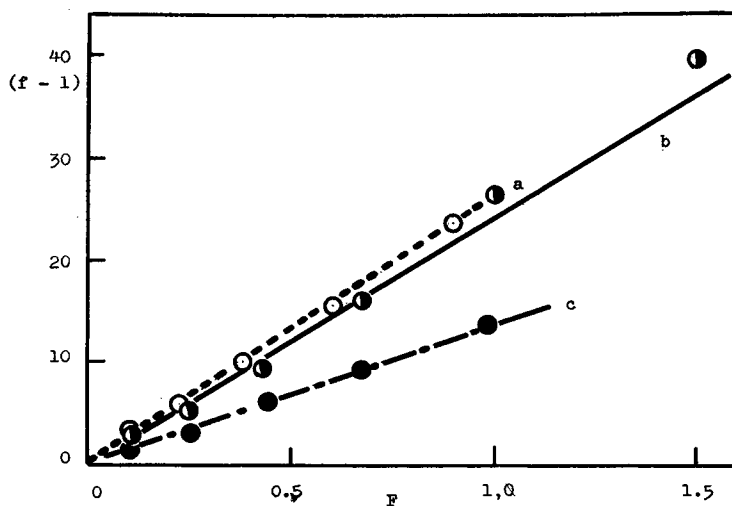
Fig. 7. Plots of $(f-1)$ vs. F: (a) St–MC system; (b) St–CN system; (c) St–PMK system.

if $r_2 = r'_2 = 0$, then the modified kinetic scheme requires five propagation steps and two new reactivity ratios:

$$M_1M_1\cdot \; + \; M_1 \xrightarrow{\;k_{111}\;} M_1M_1M_1\cdot$$

$$M_1M_1\cdot \; + \; M_2 \xrightarrow{\;k_{112}\;} M_1M_1M_2\cdot$$

$$M_2M_1\cdot \; + \; M_1 \xrightarrow{\;k_{211}\;} M_2M_1M_1\cdot$$

$$M_2M_1\cdot \; + \; M_2 \xrightarrow{\;k_{212}\;} M_2M_1M_2\cdot$$

$$M_1M_2\cdot \; + \; M_1 \xrightarrow{\;k_{121}\;} M_1M_2M_1\cdot$$

where

$$r_1 = k_{111}/k_{112}$$

$$r'_1 = k_{211}/k_{212}$$

The corresponding copolymer composition equation is:

$$(f - 1) = r'_1 F(1 + r_1 F)/(1 + r'_1 F) \tag{3}$$

if $1/r'_1 = 0$, eq. (3) reduces to:

$$(f - 2) = r_1 F$$

and a linear relationship results. The results of the determinations using equation (3) are shown in Table IV.

In Table IV, r_1'/r_1, which is the degree of the penultimate unit effect, is nearly unity. Therefore, from the above two facts, even if a penultimate unit effect does exist, its influence on the monomer reactivity ratio is comparatively small.

Rate of Copolymerization and Viscosity of Copolymer

The rates of copolymerization and the viscosity of the copolymers are shown in Figures 8 and 9, respectively.

Figure 8 shows that the rate of copolymerization decreased linearly with increase in the molar ratio of the crotonyl compound to the comonomer for each system. In the case of the viscosity of the copolymer, a similar tendency was also observed, as can be seen in Figure 9. This suggests that
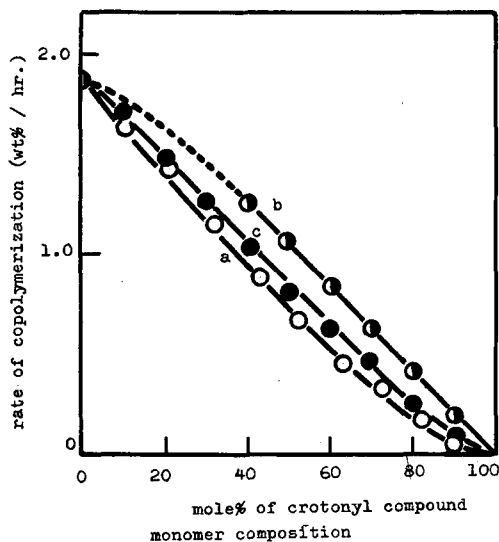
Fig. 8. Relationship between R_p and monomer composition: (a) St–MC system; (b) St–CN system; (c) St–PMK system.
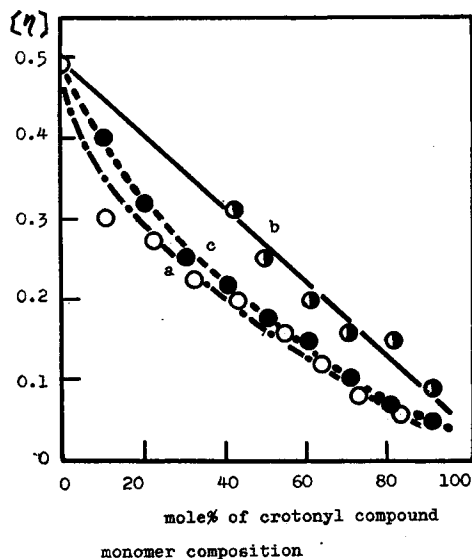
Fig. 9. Relationship between [η] in benzene at 25°C. and monomer composition: (a) St–MC system; (b) St–CN system; (c) St–PMK system.

the rate of propagation decreases with the increase in the molar ratio of the monomer which does not homopolymerize.

Infrared Spectra of Copolymers

The infrared spectra of the copolymers are shown in Figures 10–12.

The infrared spectra of all the copolymers showed the absorption bands characteristic of polystyrene. Bands were observed at 2230 cm.$^{-1}$ for the CN copolymer, at 1735 cm.$^{-1}$ for the MC copolymer and at 1710 cm.$^{-1}$ for the PMK copolymer, due to the C—N, COOCH$_3$ and C=O groups, respectively.

Melting Point of Copolymer

The relationship between the melting point of the copolymer and the copolymer composition is shown in Figure 13.

From the results, in the cases of the St–MC system and the St–PMK system, it was found that the melting point of the copolymer decreased with increasing molar ratio of the MC or PMK to the styrene in the copolymer. It is not clear, however, whether this is due to the essential nature of the copolymer or to the decrease in the molecular weight of the copolymer. On the other hand, in the case of the St–CN system, the melting point of the copolymer increased with increase in the molar ratio of the CN to the styrene in the copolymer, in spite of the decrease in the molecular weight of the copolymer. This suggests that this copolymer has a better heat resistance than polystyrene.
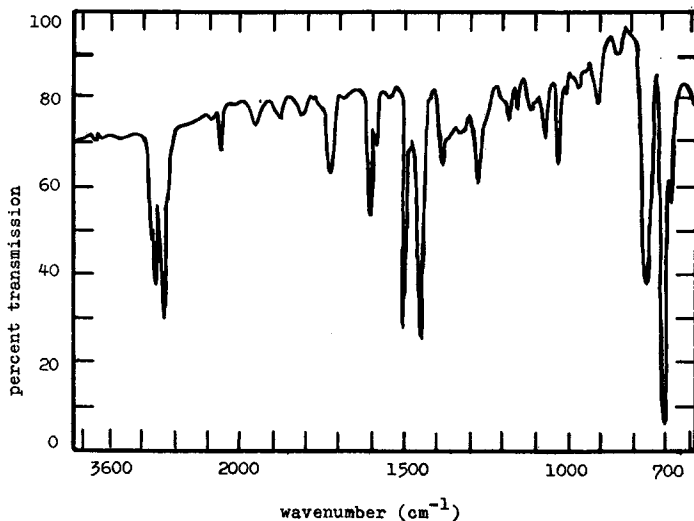
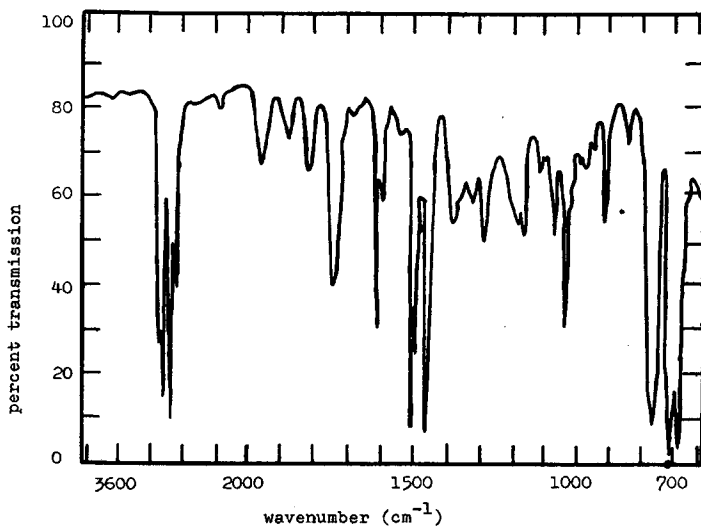Fig. 10. Infrared spectrum of St–CN copolymer (sample 9).

Fig. 11. Infrared spectrum of St–MC copolymer (sample 15).

Q and e Values of Crotonyl Compounds

The Q and e values for the crotonyl compounds were calculated from the r_1 and r_2 values shown in Table IV, by assuming the values for St: $Q = 1.0, e = -0.80$.

In general, both the e value and the Hammett constant σ are terms related to the polarity. Furukawa[13] has found a linear relationship between them using σ_p instead of σ. In order to check this point in this study, the e values
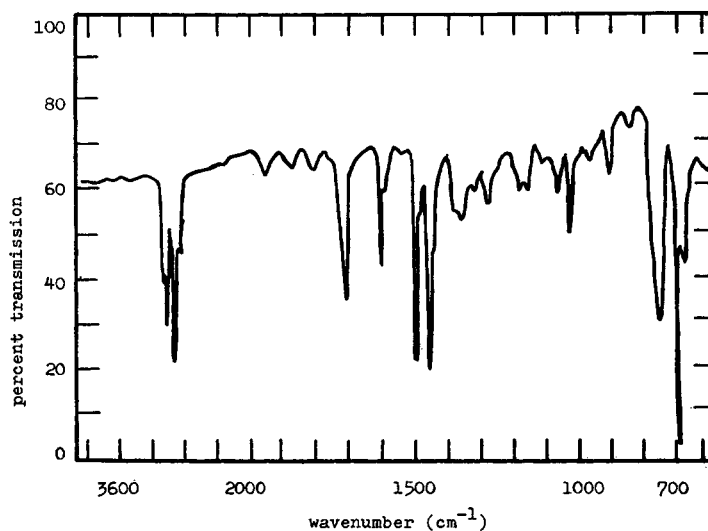
Fig. 12. Infrared spectrum of St–PMK copolymer (sample 25).

mole% of crotonyl compound
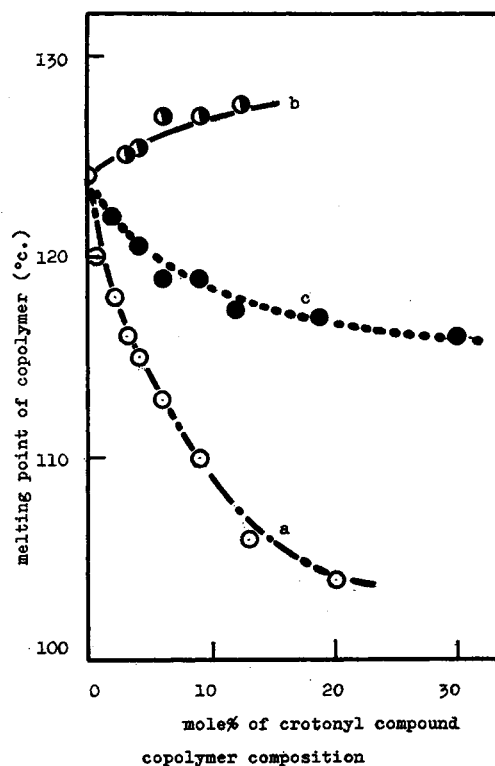
copolymer composition

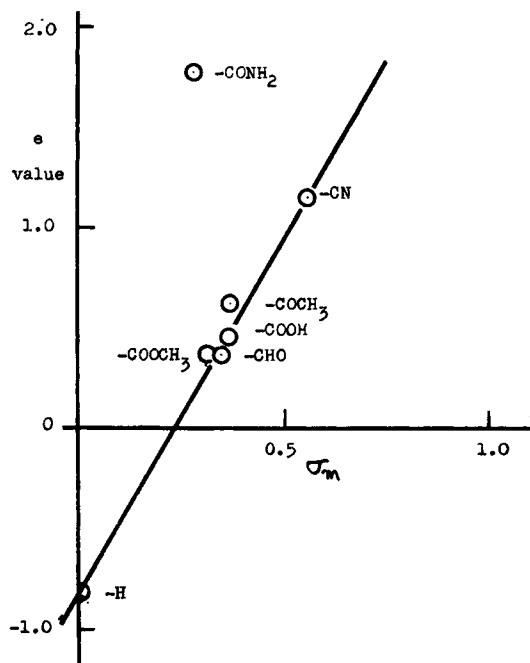Fig. 13. Relationship between melting point and composition of copolymers: (a) St–MC system; (b) St–CN system; (c) St–PMK system.

Fig. 14. Relationship between e values and Hammett constants σ_m for crotonyl compounds (CH_3—CH=CHR).

were plotted against the Hammett constants (σ_m) for the crotonyl compounds, which are shown in Table V, and a linear relationship was confirmed between them, as shown in Figure 14.

This fact suggests that the influence of the substituted group on the double bond is an electroinductive effect rather than a resonance effect, in the case of 1,2-disubstituted olefins. It was found, however, that the e values ran parallel to the σ_m of the substituted groups.

TABLE V
Q,e Values and Hammett Constants for Crotonyl Compounds

R in CH₃—CH=CHR	e	Q	σ_m
H[a]	−0.78	0.002	0
CN	1.13	0.009	0.560
COOCH₃	0.36	0.015	0.315
COCH₃	0.61	0.024	0.376
CONH₂[b]	1.76	0.0085	0.280
CHO[a]	0.36	0.013	0.355
COOH[c]	0.45	0.013	0.370

[a] Data of Ham.[5]
[b] Data of Ywakob and Truchmanov.[7]
[c] Data of Mayo and Walling.[1]

It is not yet clear, however, whether the styryl radical of the growing chain end adds to the crotonyl monomer at the position of the methyl group side or at the position of the other group side of the crotonyl monomer. The penultimate unit effects are discussed as follows:

In the systems of St–CN and St–PMK, the following relationship was obtained; r_1 (= k_{111}/k_{112}) > r'_1 (= k_{211}/k_{212}). If $k_{111} \doteqdot k_{211}$, then $k_{112} < k_{212}$. This may be so because in the case where the penultimate unit is styrene, the resonance energy between the chain terminal radical and the penultimate unit is high, so the reactivity is small compared with that for the case where the penultimate unit is crotononitrile or n-propenyl methyl ketone. On the other hand, in the St–MC system, the relationship $r_1 < r'_1$ was obtained. Therefore if $k_{111} \doteqdot k_{211}$, then $k_{112} > k_{212}$. This may follow from the fact that where the penultimate unit is styrene, there is no penultimate unit effect. In the case of methyl crotonate, however, steric hindrance is involved, and the reactivity becomes small.

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Résumé

Les rapports de réactivité monomérique pour la copolymérisation radicalaire du nitrile crotinique (CN), du crotonate de méthyle (MC) et de la n-propénylméthylcétone (PMK) avec le styrène (ST) ont été mesurés à 60°C, dans le benzène et l'effet de l'unité pénultième a été trouvé dans ces systèmes: St–CN, $r_1 = 24.0$, $r_2 = 0$; St–MC, $r_1 = 26.0$, $r_2 = 0.01$; St–PMK, $r_1 = 13.7$, $r_2 = 0.01$. La vitesse de copolymérisation et la viscosité du copolymère décroissaient notablement lorsque la fraction molaire du composé crotonique dans le mélange monomérique croissait. Les valeurs Q–e ont également été calculées et trouvées comme suit: CN, $e = 1.13$, $Q = 0.009$; MC, $e = 0.36$, $Q = 0.015$; PMK, $e = 0.61$, $Q = 0.024$. Une relation linéaire a été obtenue entre les valeurs de e des composés crotonques et leur σ_m.

Zusammenfassung

Die Copolymerisationsparameter für die radikalische Polymerisation von Crotonnitril (CN), Methylcrotonat (MC) und n-Propenylmethylketon (PMK) mit Styrol (St) wurden bei 60°C in Benzol bestimmt und dabei nachgewiesen, dass der vorletzten Einheit in den wachsenden Ketten in diesen Systemen eine geringe Bedeutung zukommt: St–CN, $r_1 = 24,0$, $r_2 = 0$; St–MC, $r_1 = 26,0$, $r_2 = 0,01$; St–PMK, $r_1 = 13,7$, $r_2 = 0,01$.

Die Copolymerisationsgeschwindigkeit und die Viskositätszahl der Copolymeren nahm deutlich mit steigendem Molenbruch der Crotonylverbindung in der Monomerenmischung ab. Die Q–e-Werte wurden ebenfalls berechnet. Sie betragen: CN, $e = 1{,}13$, $Q = 0{,}009$; MC, $e = 0{,}36$, $Q = 0{,}015$; PMK, $e = 0{,}61$, $Q = 0{,}024$. Zwischen den e-Werten der Crotonylverbindungen und ihren σ_m-Werten besteht, wie gefunden wurde, ein linearer Zusammenhang.