

Copolymerization of Styrene. IV. Copolymerization with Esters of Benzylidenecyanoacetic Acid

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Synopsis

Styrene was copolymerized in bulk with a number of esters of benzylidenecyanoacetic acid. The kinetic scheme of all pairs fitted the improved scheme of copolymerization, taking into account the effect of the penultimate unit. The Alfrey-Price Q and e values were calculated. Using the modified Taft equation, $\log(1/r_1) = \rho^*\sigma^* + \delta E_s$, it was found that the relative reactivities of the ester monomers toward the polystyryl radical were correlated by the polar substituent constants σ^* of the ester alkyl groups ($\rho^* = 0.14$) and not by their steric substituent constants E_s ($\delta = 0.008$).

Résumé

Le styrène a été copolymérisé en masse avec certains esters de l'acide benzylidène-cyanoacétique. Le schéma cinétique de toutes les paires est conforme au schéma de copolymérisation amélioré qui tient compte de l'effet de l'unité pénultième. Les valeurs Q et e selon Alfrey-Price ont été calculées. Utilisant l'équation de Taft modifiée, $\log(1/r_1) = \rho^*\sigma^* + \delta E_s$, il a été trouvé que les réactivités relatives des comonomères à l'égard de l'attaque du radical polystyryle sont influencées par les constantes des substituants polaires σ^* ($\rho^* = 0.14$) mais non pas par les constantes des substituants stériques E_s ($\delta = 0.008$) des substituants alcoylés des esters.

Zusammenfassung

Styrol wurde in Substanz mit mehreren Ester der Benzylidencyanessigsäure copolymerisiert. Alle Paare entsprachen dem verbesserten Reaktionsschema der Copolymerisation, das den Einfluss der Vorletzten Gruppe berücksichtigt. Die Alfrey-Price Q und e Werte wurden berechnet. Bei Benützung der modifizierten Taft Gleichung, $\log(1/r_1) = \rho^*\sigma^* + \delta E_s$, wurde gefunden, dass die relativen Reaktivitäten der Ester Monomere gegen Polystyrolradikale von den polaren Substituentenkonstanten σ^* ($\rho^* = 0.14$), nicht aber von den sterischen Substituentenkonstanten E_s ($\delta = 0.008$) der Alkylgruppen der Ester abhängen.

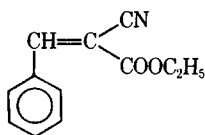
INTRODUCTION

The correlation between the structure and the reactivity of various alkyl acrylates and alkyl methacrylates,¹⁻⁵ alkyl cinnamates,⁶ alkyl thiolacrylates,⁷ and of α -alkyl- or aryl-substituted methyl acrylates^{8,9} in

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free radical-initiated polymerizations and copolymerizations has been studied recently.

Previously¹⁰ we studied the copolymerization of ethyl benzylidenecyanoacetate



with styrene. In the present work the copolymerization of the methyl, *n*-butyl, *n*-hexyl, cyclohexyl, 2-ethylhexyl, and benzyl ester of benzylidenecyanoacetic acid together with styrene is reported. The copolymerization parameters were determined and the Alfrey-Price *Q* and *e* values were calculated. Further it was attempted to correlate the effect of the alkyl groups in the esters on the relative reactivities $1/r_1$ of the various ester comonomers toward the attack of a polystyryl radical.

EXPERIMENTAL

Materials and Preparation of Monomers

Styrene. Practical Eastman or ICI product was purified by washing with aqueous sodium hydroxide, drying, and distilling at reduced pressure. The distillate was kept at Dry Ice temperature until used.

Comonomers. The various benzylidenecyanoacetates were synthesized from benzaldehyde and the appropriate ester of cyanoacetic acid.

Esters of Cyanoacetic Acid. Methyl and ethyl cyanoacetate were purchased (Eastman) and fractionated.

The other esters were prepared by the following procedure: A mixture of cyanoacetic acid, the appropriate alcohol, sulfuric acid as catalyst, and toluene as entrainer were boiled in a flask equipped with a magnetic stirrer

TABLE I
Reaction Conditions and Properties of Esters of Cyanoacetic Acid

	<i>n</i> -Butyl	<i>n</i> -Hexyl	Cyclohexyl	Benzyl	2-Ethylhexyl
Cyanoacetic acid, g (moles)	340 (4)	340 (4)	340 (4)	340 (4)	340 (4)
Alcohol, g (moles)	333 (4.5)	469 (4.6)	500 (5)	486 (4.5)	655 (5)
Toluene, ml	1000	1000	1000	1000	1000
Sulfuric acid (98%), ml	14	10	10	12	10
Time of reflux, hr	3.5	3	3	3	2.8
Product, g (yield %) ^a	480 (85)	480 (71)	390 (58)	450 (65)	658 (82)
Boiling range, °C/mm Hg	141/45	110/5; 94/0.5	166/35	135/0.8	130/0.6

^a Yield calculated in respect to cyanoacetic acid.

TABLE II
Reaction Conditions and Properties of Esters of Benzylidenecyanoacetic Acid

	Methyl	Ethyl	<i>n</i> -Butyl	<i>n</i> -Hexyl	Cyclohexyl	Benzyl	2-Ethylhexyl
Cyanoacetate, g (moles)	468 (4.73)	905 (8)	480 (3.4)	480 (2.84)	390 (2.34)	450 (2.56)	658 (3.33)
Benzaldehyde, g (moles)	496 (4.7)	848 (8)	360 (3.4)	300 (2.83)	248 (2.34)	273 (2.56)	353 (3.33)
Ethanol, ml	600	800	420	300	250	300	350
Piperidine, drops	25	40	20	15	12	13	20
Time of reflux, hr	1.25	1.5	1	1	1	1	4
Product, g (yield %)	790 (90)	1260 (79)	500 (64)	700 (95)	560 (94)	680 (~100)	410 (43)
Melting point, °C	89	52	48	45	73	84	27.5
Chem. anal., % found (% calc.)							
C	70.8 (70.6)	71.16 (71.7)	73.34 (73.4)	74.87 (74.68)	75.07 (75.20)	77.61 (77.56)	—
H	4.86 (4.81)	5.52 (5.46)	6.53 (6.55)	7.57 (7.44)	6.62 (6.70)	5.00 (4.98)	—
N	7.47 (7.48)	6.94 (6.96)	6.12 (6.12)	5.47 (5.44)	5.48 (5.49)	5.38 (5.32)	4.93 (4.92)

and with a Dean-Stark trap fitted with a reflux condenser. The extent of the reaction was followed up by the amount of water which separated in the trap. At the end of the reaction, the cooled reaction mixture was washed with a saturated aqueous solution of sodium chloride, then with an aqueous solution of sodium carbonate (10%), and again with the sodium chloride solution. The dried ester was fractionated.

Details on the reaction conditions and properties of five esters of cyanoacetic acid are summarized in Table I.

Esters of Benzylidenecyanoacetic Acid. All the benzylidenecyanoacetates were prepared according to the following procedure:¹⁰ To a solution of freshly distilled benzaldehyde and of the distilled ester of cyanoacetic acid in absolute ethanol, piperidine was added. After refluxing, the solution was left overnight at room temperature. In most preparations, the esters crystallized out directly, but sometimes solidification occurred only after cooling. The esters were recrystallized from ethanol.

Details on the preparation of the esters are summarized in Table II.

Copolymerization. The parameters of copolymerization were determined by polymerization in bulk using benzoyl peroxide as initiator. Copolymerizations were carried out in the usual manner¹⁰ at a fixed temperature (70° or 80°C) to conversions up to 10%. The copolymers were separated and purified by two precipitations and their composition was determined by analysis of their nitrogen content.

TABLE III
Copolymerization of Styrene (M_1) and Benzylidenecyanoacetates (M_2)
at 70°C Using 0.1% Benzoyl Peroxide as Initiator

M_2	M_2 , mole fraction of monomer 2	Conversion, %/hr	Nitrogen content of copolymer, %	m_2 , mole fraction in polymer
Methyl	0.100	3.40	2.08	0.179
	0.200	3.37	2.91	0.271
	0.300	5.15	3.01	0.285
	0.400	5.60	3.42	0.348
	0.500	5.10	3.72	0.403
Hexyl	0.100	3.95	1.96	0.185
	0.200	4.9	2.58	0.255
	0.300	5.7	2.93	0.323
	0.400	5.5	3.30	0.383
	0.500	5.5	3.19	0.363
Cyclohexyl	0.100	3.1	2.02	0.192
	0.200	4.4	2.53	0.258
	0.300	5.15	2.91	0.315
	0.400	5.3	3.16	0.356
	0.500	4.5	3.24	0.369
Benzyl	0.100	4.1	1.90	0.180
	0.200	5.3	2.58	0.271
	0.300	5.9	2.83	0.308
	0.400	7.4	3.16	0.366
	0.500	7.5	3.29	0.390

TABLE IV
Copolymerization of Styrene (M_1) and Benzylidenecyanoacetates (M_2) at 80°C
Using 0.2% Benzoyl Peroxide as Initiator

M_2	M_2 , mole fraction of monomer 2	Con- version, %/hr	Nitrogen content of copolymer, %	m_2 , mole fraction in polymer
Butyl	0.098	15.6	1.92	0.172
	0.199	17.75	2.51	0.24
	0.304	20.4	3.05	0.311
	0.403	19.8	3.23	0.337
	0.507	18.9	3.45	0.37
	0.611	17.4	3.71	0.412
	0.671	15.6	3.71	0.412
2-Ethylhexyl	0.708	15.8	3.81	0.429
	0.101	14.0	1.72	0.164
	0.212	18.0	2.28	0.24
	0.291	18.4	2.57	0.286
	0.304	17.2	2.60	0.291
	0.345	18.0	2.74	0.315
	0.422	19.8	2.92	0.349
	0.447	20.8	2.96	0.356
	0.507	18.0	3.05	0.374
	0.601	15.8	3.16	0.397

Details on the conditions of the copolymerizations and the results are summarized in Tables III and IV.

Glass Transition Temperature

The glass transition temperature of the copolymers was determined according to the method of Edgar and Ellery¹¹ on heat-molded specimens in the manner as described before.¹² The values are given in Figure 11.

DISCUSSION

The reactivity ratios r_1 and r_2 were determined by the graphical method¹³ using the following equation:

$$r_2 = \frac{M_1}{M_2} \left[\frac{m_2}{m_1} \left(1 + \frac{M_1}{M_2} r_1 \right) - 1 \right]. \quad (1)$$

As already stated regarding the copolymerization of ethyl benzylidenecyanoacetate with styrene,¹⁰ also for the copolymerization of the now reported esters of benzylidenecyanoacetic acid with styrene, negative r_2 values were obtained by plotting r_1 against r_2 (Figs. 1, 2). Consequently, the improved kinetic scheme taking into consideration the penultimate unit as proposed by Merz¹⁴ was applied.

As the ester comonomers do not polymerize by themselves, $r_2 = r_2' = 0$, the equation developed by Merz is reduced to

$$r_1 = (n - 1)/x^2(1/r_1') + (n - 2)/x \quad (2)$$

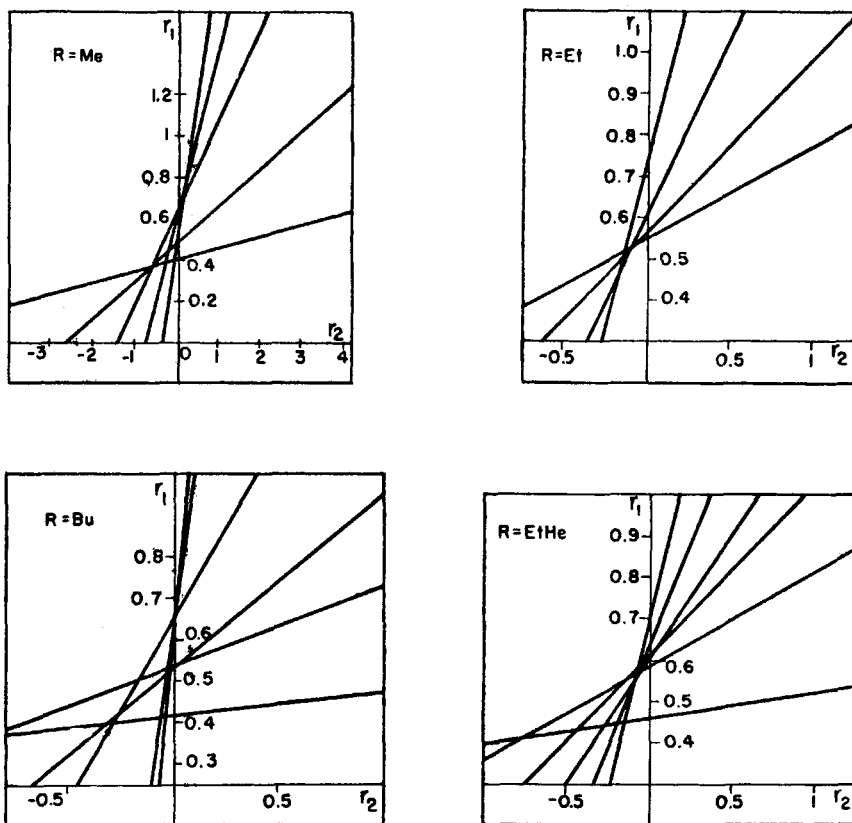


Fig. 1. Copolymerization of styrene (M_1) with the methyl (Me), ethyl (Et), *n*-butyl (Bu), and 2-ethylhexyl (EtHe) ester of benzylidenecyanoacetic acid (M_2) at 70°C. Determination of r_1 and r_2 using eq. (1).

when $x = M_1/M_2$ and $n = m_1/m_2$.¹⁵ Accordingly, r_1 and r_1' were calculated (Figs. 3, 4). The values for r_1 and r_2 , determined by the simple kinetic model, and the values for r_1 and r_1' , determined by the penultimate model, are summarized in Table V. Further, the values for r_1'/r_1 which express the degree of the effect of the penultimate unit are given, thus showing the presence of this effect for all esters studied. The Alfrey-Price Q_2 and e_2 values¹⁶ (Table V) were calculated according to the equation

$$r_1 = \frac{Q_1}{Q_2} \exp\{-e_1(e_1 - e_2)\}. \quad (3)$$

The r_1 values were obtained from the copolymerization of the various ester comonomers with styrene (see Table V) and from their copolymerization with acrylonitrile (see footnote), using the values $Q_1 = 1.0$ and $e_1 = -0.8$ for styrene and $Q_1 = 0.60$ and $e_1 = 1.20$ for acrylonitrile. (The value of $r_1 = 18$ was used for the copolymerization of all the esters with acrylonitrile. This assumption is based on the determination of $r_1 =$

TABLE V
Copolymerization Parameters for Esters of Benzylidenecyanoacetic Acid
(M_2) With Styrene (M_1)

Ester group in M_2	Simple model				Penultimate model			Reference
	r_1	r_2	e_2	Q_2	r_1	r_1'	r_1'/r_1	
Methyl	0.45	—	2.49	0.14	0.325	1.33	4.1	this paper
Ethyl	0.51	—	2.44	0.14	0.3	1.3	4.23	12, 10
<i>n</i> -Butyl	0.53	—	2.42	0.14	0.42	1.02	2.44	this paper
<i>n</i> -Hexyl	0.42	—	2.58	0.16	0.315	1.0	3.5	this paper
Cyclohexyl	0.44	—	2.56	0.15	0.30	0.925	3.12	this paper
2-Ethylhexyl	0.59	—	2.36	0.13	0.47	0.91	1.93	this paper
Benzyl	0.43	—	2.57	0.15	0.34	0.715	2.09	this paper
Benzylidene- malononitrile (BMN)			2.35	0.38				12
Diethylechloro- diethyl maleate (DCM)			1.65	0.056				16

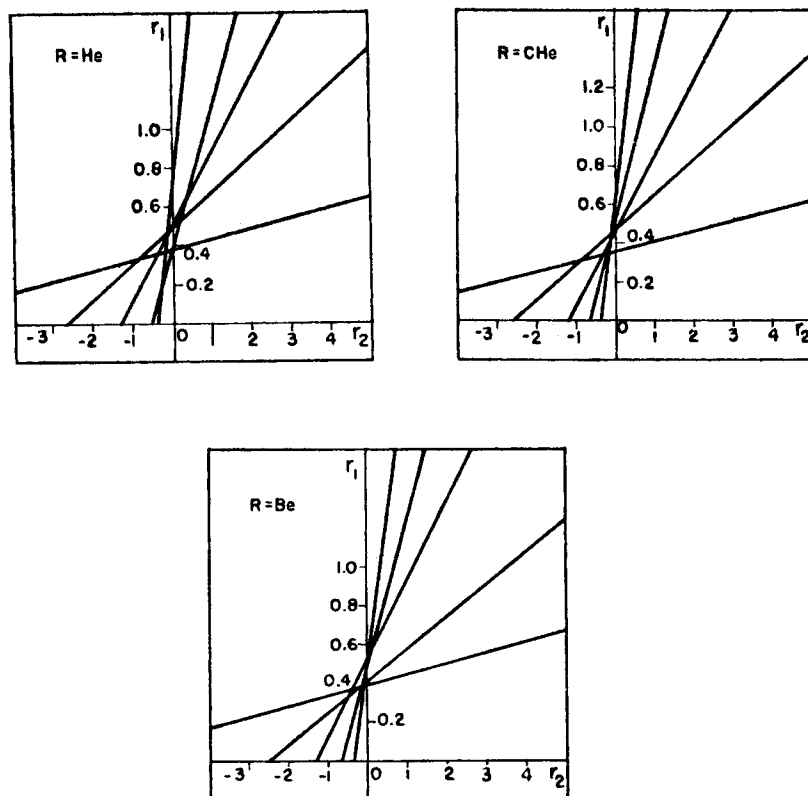


Fig. 2. Copolymerization of styrene (M_1) with the *n*-hexyl (He), cyclohexyl (CHe), and benzyl (Be) ester of benzylidenecyanoacetic acid (M_2) at 70°C. Determination of r_1 and r_2 using eq. (1).

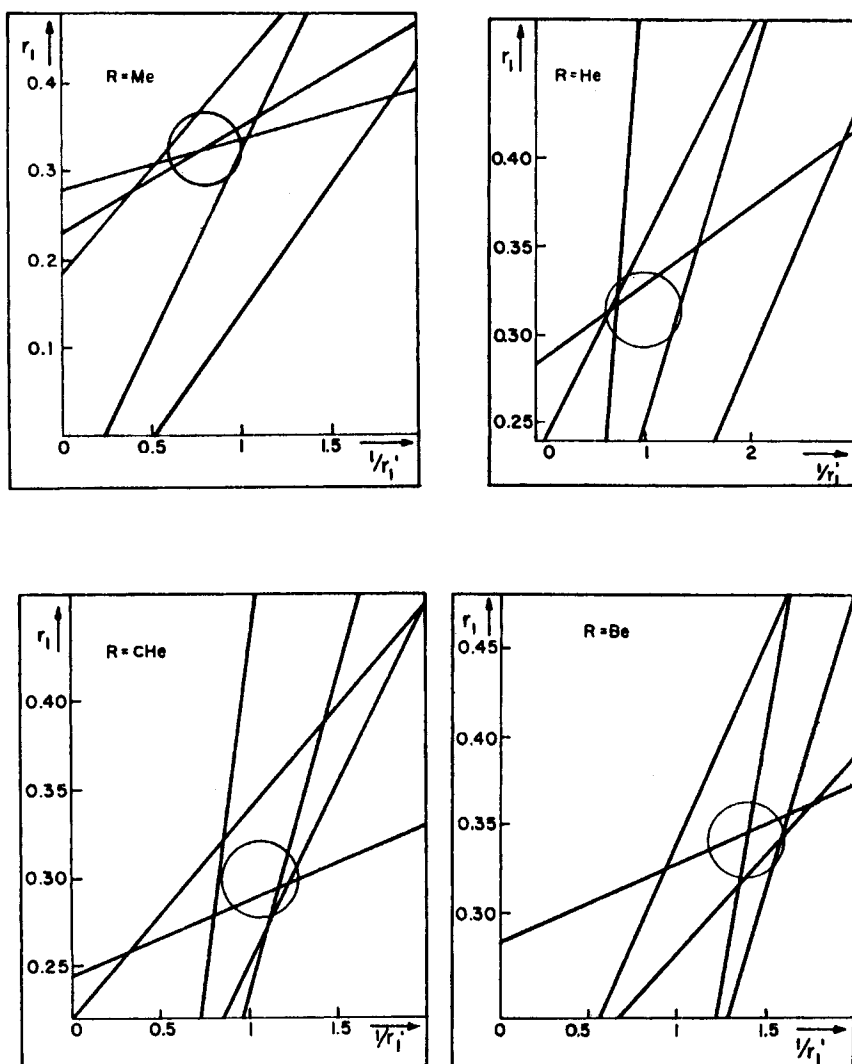


Fig. 3. Copolymerization of styrene (M_1) with the methyl (Me), *n*-hexyl (He), cyclohexyl(CHe), and benzyl (Be) ester of benzylidenecyanoacetic acid (M_2) at 70°C . Determination of r_1 and r_1' using eq. (2).

18 ± 2 for the pair acrylonitrile–ethyl benzylidenecyanoacetate¹² and $r_1 = 21 \pm 1$ for the pair acrylonitrile–methyl benzylidenecyanoacetate.) The calculated Q_2 and e_2 values for all pairs are of the same magnitude. The Q_2 and e_2 values of other 1,1,2-trisubstituted monomers containing polar substituents, such as BMN and DCM, are given for comparison (Table V).

The relationship between the composition of the copolymers (m_2) and the composition of the monomer mixtures (M_2) is given in Figures 5 and 6.

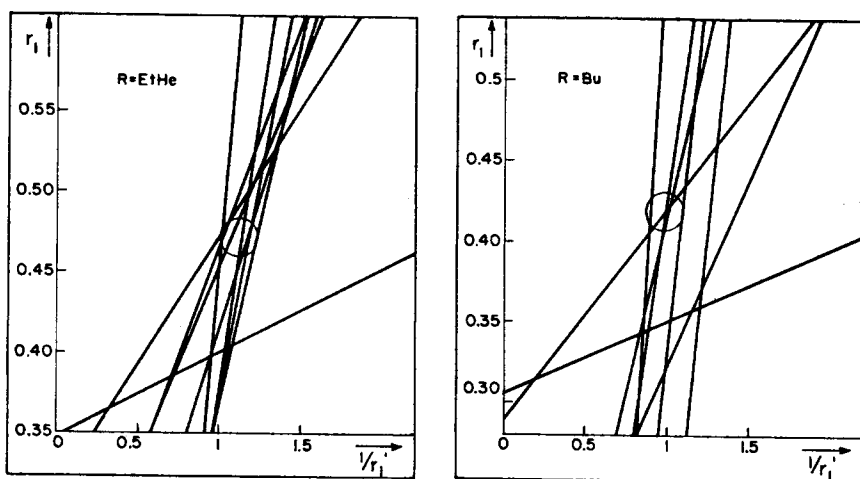


Fig. 4. Copolymerization of styrene (M_1) with the *n*-butyl (Bu) and 2-ethylhexyl (EtHe) ester of benzylidenecyanoacetic acid (M_2) at 80°C. Determination of r_1 and r_1' using eq. (2).

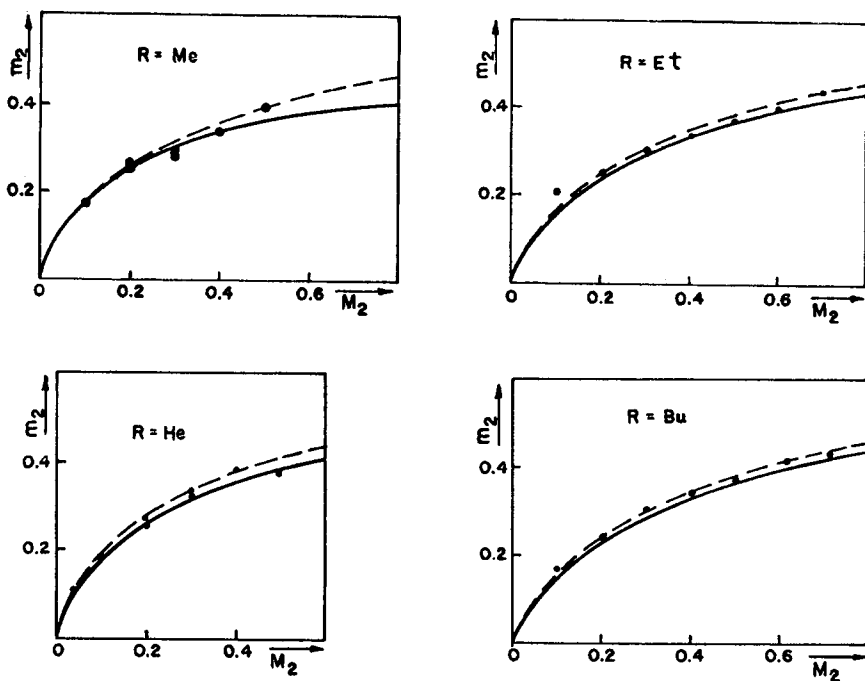


Fig. 5. Relationship between the composition of the copolymers and the monomer mixtures for methyl (Me), ethyl (Et), *n*-butyl (Bu), and *n*-hexyl (He) ester of benzylidenecyanoacetic acid (M_2): (---) calculated according to eq. (1); (—) calculated according to eq. (2).

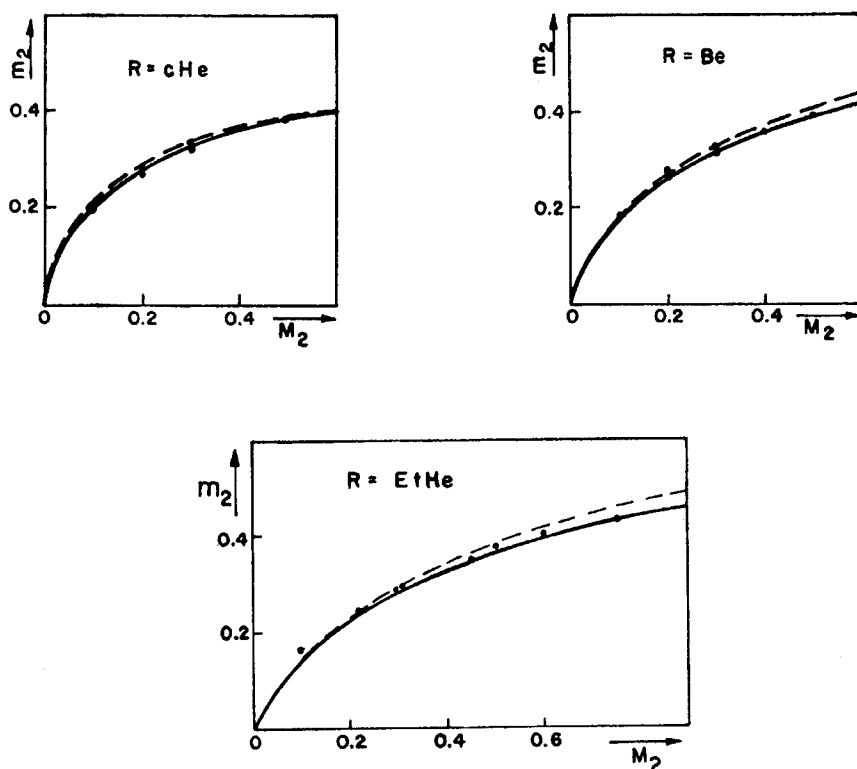


Fig. 6. Relationship between the composition of the copolymers and the monomer mixtures for cyclohexyl (CHe), benzyl (Be), and 2-ethylhexyl (EtHe) ester of benzylidene cyanoacetic acid (M_2): (---) calculated according to eq. (1); (—) calculated according to eq. (2).

The curves are calculated both according to eq. (1) and according to eq. (2) and all show azeotropic conditions at about $M_2 = 0.3$.

It has been reported¹⁻⁹ that the relative reactivities $1/r_1$ of various acrylate comonomers toward the attack of a polystyryl radical are correlated by a modified Taft eq.¹⁷

$$\log (1/r_1) = \rho^* \sigma^* + \delta E_s \quad (4)$$

where σ^* is the polar substituent constant, E_s is the steric substituent constant, and ρ^* and δ are reaction constants which express the susceptibility for a given reaction series due to polar and steric effects of the substituents, respectively. The values for ρ^* and δ as reported¹⁻⁹ were obtained as the respective slopes by plotting $\log (1/r_1)$ separately against σ^* and E_s . However, for treatment by least squares, explicit recognition had to be given to the vertical shift of the plot by introducing the optimized value of $\log (1/r_1)_{Me}$ for the copolymerization with the methyl ester as a third parameter. Applying

$$\log (1/r_1) = \log (1/r_1)_{Me} + \rho^* \sigma^* + \delta E_s \quad (5)$$

and using the values for σ^* and E_s as given in Table VI, the following values

TABLE VI
 σ^* and E_s Values for Alkyl Groups^a

	Alkyl group in comonomer						
	Methyl	Ethyl	<i>n</i> -Butyl	<i>n</i> -Hexyl	Cyclohexyl	2-Ethylhexyl	Benzyl
σ^*	0	-0.1	-0.13	-0.13 ^b	-0.15	-0.125 ^c	+0.215
E_s	0	-0.07	-0.39	-0.40 ^d	-0.79	-0.95 ^e	-0.38

^a From Taft.¹⁷

^b Estimated to be as for *n*-butyl.

^c Estimated to be as for iso-butyl ($\sigma^* = -0.125$).

^d Estimated to be as for *n*-pentyl ($E_s = -0.40$).

^e Estimated to be similar to isobutyl ($E_s = -0.93$) and to cyclohexylmethyl ($E_s = -0.98$).

for the least squares parameters were obtained: $\log (1/r_1)_{Me} = 0.324$; $\rho^* = 0.14$; and $\delta = 0.008$.

The results indicate that the dependence of the relative reactivities on the steric factor E_s is clearly negligible (Fig. 7); yet, the large scatter notwithstanding, there does exist a dependence on the polar character of the alkyl groups in the ester (Fig. 8). Thus the relative reactivities of the benzylidenecyanoacetates toward the polystyryl radical decrease with the increase of the electron-releasing nature of the alkyl substituents in the ester. This behavior was also observed by Otsu et al.^{2,3} for alkyl acrylates and alkyl methacrylates. They explain that this reduction of relative reactivities is due to the presence of electron-releasing alkyl groups in the ester, which render their carbonyl groups more polar and thus enhance their nature of single bonding

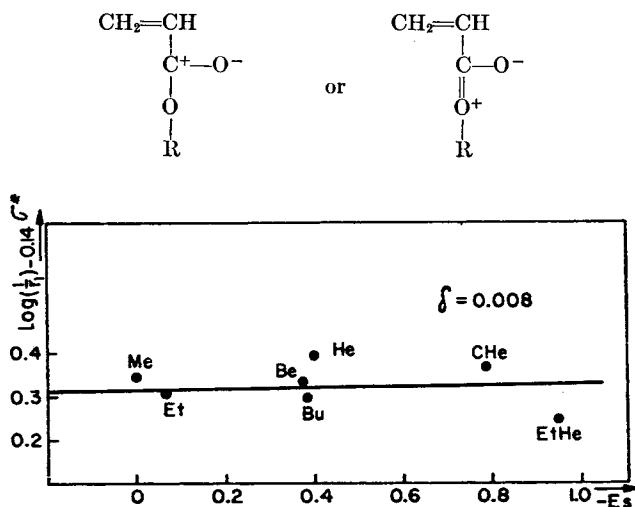


Fig. 7. Relationship between $\log (1/r_1) - \rho^* \sigma^*$ and the E_s constants of the alkyl groups.

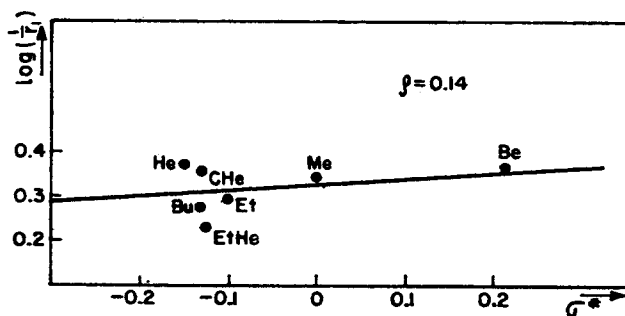


Fig. 8. Relationship between $\log(1/r_1)$ and the σ^* constants of the alkyl groups.

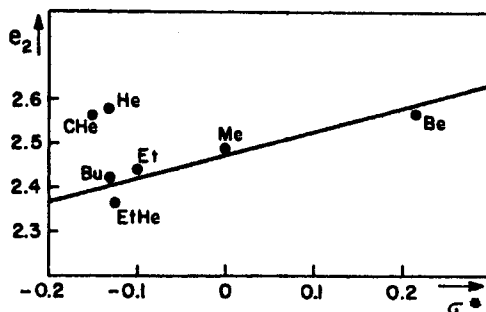


Fig. 9. Relationship between e_2 values and the σ^* constants of the alkyl groups.

This results in a decrease of the conjugation of the vinyl group with the carbonyl group and consequently in a decrease of Q and e values as a function of the electron-releasing character of the alkyl groups. Yet, as expected for our comonomers, any change in the nature of the alkyl group should not affect too markedly the general behavior of the α,β,β' -trisubstituted comonomers, because all the comonomers contain, in addition to an ester group, the highly polar nitrile group and a phenyl ring on the α -carbon atom. Thus for comparison, the values of ρ^* for the alkyl acrylates ($\rho^* = 0.56$)² and for the alkyl methacrylates ($\rho^* = 0.33$)¹ are definitely higher than the values for alkyl cinnamates ($\rho^* = 0.13$)⁶ and for our comonomer series ($\rho^* = 0.14$). Regarding the steric effect due to the alkyl groups, it is rather surprising that even such large and bulky groups like 2-ethylhexyl, cyclohexyl, etc., have nearly no influence on the relative reactivities of the comonomers toward the polystyryl radical ($\delta = 0.008$). Similarly, also for the alkyl acrylates^{3,5} and for the alkyl methacrylates⁴ the values for δ are reported as $\delta = 0$. According to Cameron and Kerr,⁹ there is no steric interference due to the ester alkyl group because it is removed far enough from the reaction site. On the other hand, in the copolymerization of styrene with the bulkier methyl α -alkylacrylates,^{8,9} the relative reactivities are controlled by steric factors.

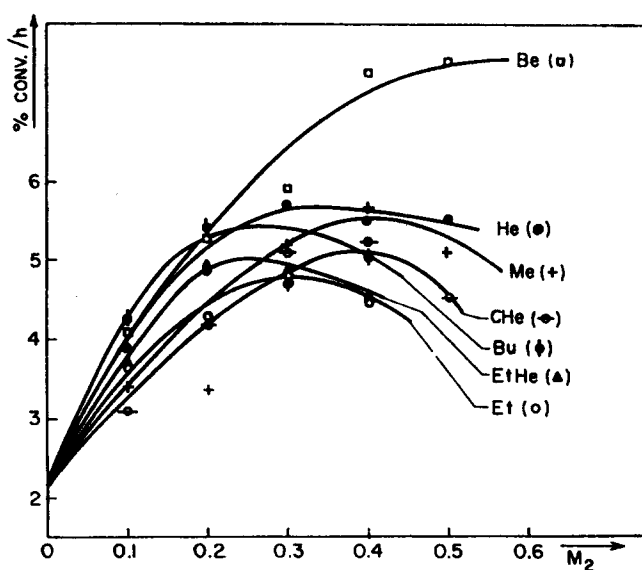


Fig. 10. Dependence of rate of conversion of the copolymers on composition of the monomer mixtures.

There is a correlation of the e_2 values of our comonomers and the σ^* constants of the alkyl groups, although the points for hexyl and cyclohexyl are quite above the line drawn through the other points (Fig. 9). Our Q_2 values are rather close to each other and there is no clear correlation with the σ^* constants. The rates of copolymerization of all pairs rise with increasing comonomer concentration, showing a maximum between $m_2 = 0.25$ and $m_2 = 0.4$ (Fig. 10), except for the benzyl ester copolymer, where the maximum is at about $m_2 = 0.5$. With further increase of the comonomer content, the rates decrease. These findings are in accordance with the behavior of the ethyl ester, as reported previously.¹⁰

The effect of the alkyl group on the rates of polymerization has been studied by Otsu et al.⁴ by copolymerizing various alkyl methacrylates with styrene. According to these authors, the substitution of an electron-withdrawing alkyl group in the methacrylate increases the rate of copolymerization with styrene. Similar results were also obtained in the copolymerization of various alkyl acrylates with styrene.³ Comparing the rates of conversion of the pairs of this investigation, actually all values are of the same magnitude, except for the benzyl ester copolymer, where the rate increase is quite obvious.

As already reported before, the melting range¹⁰ and the Vicat softening point¹⁸ for the copolymer of the ethyl ester with styrene are considerably higher than those for homopolystyrene. This is also true for the other copolymers now under investigation, and the glass transition temperature rises for all pairs with increasing comonomer content (Fig. 11). The rise of

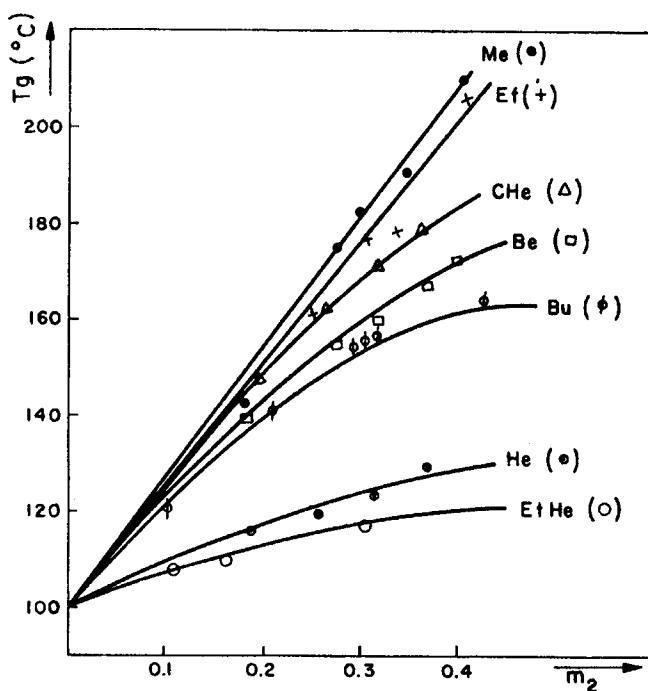


Fig. 11. Dependence of T_g on composition of the copolymers.

T_g is rather steep for the methyl and for the ethyl ester copolymers. Yet, the T_g values even for the cyclohexyl, benzyl, and butyl ester copolymers are still high, although a certain plasticization effect exists already. This effect is more pronounced for the hexyl and ethylhexyl ester copolymers, where the rise of T_g with increasing m_2 is much lower. Except for the methyl and ethyl ester copolymers, one can see that the T_g reaches a maximum at $m_2 = 0.4$ till $m_2 = 0.6$. This behavior can be explained by the introduction of the highly polar comonomers into the polystyrene chain. At first, with increasing comonomer content, there is a steady rise of the T_g until a maximum is reached. Beyond it, with increasing concentration of the comonomers, the larger alkyl groups in the ester reduce the intermolecular bonding due to the polar nitrile and ester groups, resulting in a lowering of T_g . This effect is not apparent for the smaller methyl and ethyl groups up to $m_2 = 0.5$.

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