

This article was downloaded by:

On: 24 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

Effect of Substituents on the Radical Copolymerization of Ring-Substituted Methyl 2-Cyano-3-Phenyl-2-Propenoates with Styrene

Gregory B. Kharas^a; Julie M. Eaker^a; Sandra A. Armatys^a; Kelly A. McManigal^a; Sanat K. Dhar^a;

Gregory R. Quinting^b

^a Chemistry Department, DePaul University, Chicago, Illinois, USA ^b Automotive Technical Center, Sherwin-Williams Co., Chicago, Illinois, USA

To cite this Article Kharas, Gregory B. , Eaker, Julie M. , Armatys, Sandra A. , McManigal, Kelly A. , Dhar, Sanat K. and Quinting, Gregory R.(1997) 'Effect of Substituents on the Radical Copolymerization of Ring-Substituted Methyl 2-Cyano-3-Phenyl-2-Propenoates with Styrene', *Journal of Macromolecular Science, Part A*, 34: 4, 627 – 640

To link to this Article: DOI: 10.1080/10601329708014989

URL: <http://dx.doi.org/10.1080/10601329708014989>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

EFFECT OF SUBSTITUENTS ON THE RADICAL COPOLYMERIZATION OF RING-SUBSTITUTED METHYL 2-CYANO-3-PHENYL-2-PROPENOATES WITH STYRENE

GREGORY B. KHARAS,* JULIE M. EAKER,
SANDRA A. ARMATYS, KELLY A. McMANIGAL,
and SANAT K. DHAR

Chemistry Department
DePaul University
1036 West Belden Avenue, Chicago, Illinois 60614-3214, USA

GREGORY R. QUINTING

Automotive Technical Center
Sherwin-Williams Co.
10909 S. Cottage Grove Avenue, Chicago, Illinois 60628, USA

ABSTRACT

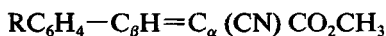
Copolymerizations of ring-substituted methyl 2-cyano-3-phenyl-2-propenoates, $RC_6H_4CH=C(CN)CO_2CH_3$ ($R = C_2H_5, CH_3O, Cl, Br, F$) with styrene (M_1) were studied in solution in the presence of a radical initiator. Terminal and penultimate kinetic models were applied for best prediction of the copolymer composition. The Alfrey-Price Q and e parameters calculated for the monomers correlate well with the relative reactivity ($1/r_1$). The relative reactivity showed a tendency to increase with increasing Hammett constant σ , cyclic voltammetric reduction potential, E_p , calculated atomic charge, and ^{13}C -NMR chemical shift on the olefinic α -carbon of the ring-substituted monomers.

INTRODUCTION

Trisubstituted ethylene (TSE) monomers containing substituents larger than fluorine exhibit no tendency to undergo vinyl polymerization, apparently due to kinetic considerations superimposed on the thermodynamic factor responsible for the difficulty with which 1,1- and 1,2-disubstituted ethylenes polymerize [1]. It was early recognized that radical copolymerization provides the most general method of overcoming problems encountered in the homopolymerization of TSE monomers. This approach has been particularly successful in preparing copolymers from electrophilic TSE monomers having a double bond substituted with halo, cyano, and carbonyl groups [2–8]. These electron-poor TSE monomers copolymerize readily with monosubstituted electron-rich monomers like styrene [2–5], vinyl acetate [4, 6], vinyl ethers [4, 7], *N*-vinyl carbazole [4], and *N*-vinyl pyrrolidone [8].

α -Cyanocinnamates (esters of 2-cyano-3-phenyl-2-propenoic acid) were used as model compounds in various studies of monomer reactivity in the copolymerization of electron-poor TSE monomers and electron-rich monosubstituted alkenes [3, 6–11]. The effect of the ester groups structure on the relative reactivity of these TSE monomers toward the attack of a polystyryl radical was studied and correlated with semiempirical parameters such as Hammett's substituent constant [9]. The kinetic scheme of the TSE monomers fits to the penultimate model of copolymerization. The copolymerization of styrene with methyl 2-cyano-3-phenyl-2-propenoate, studied first in bulk by Gilath et al. [9], was reexamined in toluene with the increased number of experimental points and application of the Kelen-Tüdös linearization method ($r_{ST} = 0.256 \pm 0.062$ and $r'_{ST} = 1.251 \pm 0.255$) [10]. These parameters were later refined for an expanded conversion range (3–21 wt%) [11].

Recently a number of ring substituted methyl 2-cyano-3-phenyl-2-propenoates were prepared and characterized [12, 13]. The present paper describes the substituents effect on the radical copolymerization of these methyl 2-cyano-3-phenyl-2-propenoates with styrene (ST). The TSE monomers used in this study are shown in Scheme 1:



where R = *p*-C₂H₅ (4ECP), *p*-CH₃O (4MOCP), *m*-CH₃O (3MOCP), *o*-CH₃O (2MOCP), *o*-Cl (2CCP), *m*-Cl (3CCP), *p*-Cl (4CCP), *p*-Br (4BCP), *p*-F (4FCP).

EXPERIMENTAL

The TSE monomers were prepared according to the general procedure of the Knoevenagel condensation by reacting an appropriate ring-substituted benzaldehyde with methyl cyanoacetate, as described in previous work [12, 13]. ¹³C-NMR spectra of 4–10% CDCl₃ solutions of the monomers were obtained on a Bruker Omega 400WB spectrometer with a 9.4T 89 mm bore magnet at room temperature. Parameters for the carbon spectra were: 6.5 μ s pulse width ($\sim 30^\circ$), 3 second pulse delay, 16,384 acquisition points, 128 scans, with broadband proton decoupling. The ¹³C-NMR analysis of the monomers showed the presence of a single (*E*)-isomer with the ester group trans to the phenyl group, which is consistent with the NMR data on a variety of substituted 2-cyano-3-phenyl-2-propenoates [14, 15].

The molecular weights of the copolymers were determined relative to polystyrene standards in chloroform solutions with sample concentrations 0.8% (w/v) by gel permeation chromatography (GPC) using a Waters Model 510 pump at an elution rate of 1.0 mL/min through 500, 1000, and 10,000 Å Phenogel (Phenomenex) columns at 35°C, and a Model 410 refractive index detector.

The cyclic voltammetric reduction potentials (E_p) were measured in CH₃CN (Reagent grade, Baker) and a nitrogen atmosphere with a CV-50W voltammetric analyzer (Bioanalytical Systems, Inc.). Lithium perchlorate (Aldrich) was used as a supporting electrolyte. A saturated calomel electrode served as the reference electrode in combination with a glassy carbon working electrode and a platinum auxiliary electrode.

Atomic charge distributions were calculated (AM1) by using HYPERCHEM software (AUTODESK Inc.).

Styrene (ST) (Aldrich) was purified by washing with aqueous sodium hydroxide, drying and subsequently distilling at reduced pressure. Ethyl acetate (Aldrich) was used as received. 2,2'-Azobisisobutyronitrile (AIBN) (Aldrich) was twice recrystallized from ethyl alcohol and then dried under reduced pressure at room temperature. Copolymers of the TSE monomers and ST were prepared in 50-mL Pyrex screw cap ampules at various ratios of the monomer feed using 0.0045 mol/L of AIBN at an overall monomer concentration 2 mol/L in 20 mL of ethyl acetate. The copolymerization was conducted at 80°C. After a predetermined time the mixture was cooled to room temperature and precipitated by the dropwise addition to methanol. The crude copolymers were purified by reprecipitation by addition of a chloroform solution to an excess of methanol. The composition of the copolymers were determined based on the nitrogen content with a precision of 0.1 wt%. Elemental analyses were performed by Quantitative Technologies Incorporated (New Jersey).

RESULTS AND DISCUSSION

An attempted homopolymerization of the TSE monomers in the presence of AIBN did not produce any polymer as indicated by the lack of a precipitate in methanol. Inability of the monomers to polymerize is associated with steric difficulties encountered in homopolymerization of 1,1- and 1,2-disubstituted ethylenes [1]. This type of steric hindrance would increase the activation energy required for addition and slow down the rate of propagation to such an extent as to favor the occurrence of a chain transfer or termination instead. Homopolymerization of ST under conditions identical to those in the copolymerization experiments yielded 18.3% of polystyrene, when polymerized for 30 minutes. Copolymerization of the ring-substituted methyl 2-cyano-3-phenyl-2-propenoates with ST resulted in formation of copolymers with a number-average molecular weight of 3×10^4 to 1×10^5 . Copolymer composition curves of the copolymerizations of some methoxy-substituted methyl 2-cyano-3-phenyl-2-propenoates are presented in Fig. 1. As can be seen in this figure, the curves vary with the position of the methoxy substituents on the benzene ring of the propenoates. Reaction conditions and compositions of the resulting copolymers are summarized in Table 1. According to elemental analysis of the copolymers, a substantial amount of trisubstituted ethylene monomer is

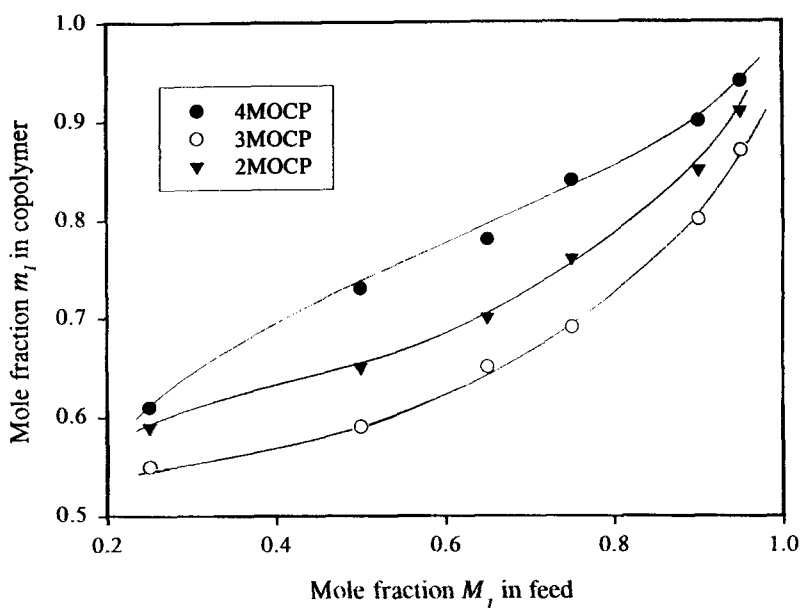


FIG. 1. Copolymer composition curves for the copolymerization of styrene (M_1) with ring-substituted TSE monomers (M_2).

present in the copolymers, which is indicative of relatively high reactivity of the TSE monomers toward styrene radical.

With respect to the propagation reactions, two mechanisms have been proposed to explain the strong alternating tendency between electron-donor and electron-acceptor monomers. One mechanism states that the transition state of the cross-propagation is stabilized by partial electron transfer between the electron-acceptor and electron-donor monomers or radicals [16]. The second mechanism suggests that formation of donor-acceptor monomer dyads in the copolymer results from homopolymerization of monomer electron donor acceptor complexes [17]. The complexation can lead to radical formation by electron transfer between monomers [18]. Both the cross-propagation and complex mechanisms are probably operative in copolymerizations which lead to copolymers with a high content of alternating structures. It has been shown that the chemical composition of a copolymer, both in the crude sense of overall composition and in the more detailed sense of the distribution of the units along the chain, is controlled almost completely by the nature of the propagation steps. Assuming the reactivity of the propagating chain in a copolymerization is dependent on 1) the terminal monomer unit, 2) the penultimate monomer unit, or 3) a participation of both free monomers and monomer complexes, different kinetic models [19-21] can be applied to compositional data for best prediction of the copolymer composition.

In an attempt to correlate the observed monomer reactivities, two copolymerization models, the terminal [19] and the penultimate [20], were examined for consistency with composition data obtained at various monomer feeds. The complex model will be considered elsewhere. In the absence of the TSE monomer self-propagation ($k_{22} = 0$, $r_2 = 0$), Eq. (1) [19]

TABLE 1. Copolymerization of ST (M_1) with TSE (M_2)

Experiment	Mole fraction M_1 in the feed	Time, minutes	Conversion, wt%	Nitrogen content, wt%	Mole fraction m_1 in the copolymer
4ECP:					
1	0.95	60	8.28	1.13	0.87
2	0.90	60	8.46	1.73	0.86
3	0.75	60	12.8	2.65	0.75
4	0.65	60	10.7	3.21	0.68
5	0.50	60	11.51	3.50	0.64
6	0.25	168 ^a	25.0	3.85	0.59
4MOCP:					
7	0.95	240	18.9	0.82	0.94
8	0.90	240	15.4	1.17	0.90
9	0.75	240	11.3	1.84	0.84
10	0.65	240	15.1	2.39	0.78
11	0.50	240	12.9	2.81	0.73
12	0.25	168 ^a	21.5	3.69	0.61
3MOCP:					
13	0.95	30	4.84	1.49	0.87
14	0.90	30	4.99	2.25	0.80
15	0.75	30	6.34	3.13	0.69
16	0.65	30	7.88	3.43	0.65
17	0.50	30	7.53	3.84	0.59
18	0.25	168 ^a	25.6	4.08	0.55
2MOCP:					
19	95	30	4.32	1.09	0.91
20	90	30	4.99	1.73	0.85
21	75	30	5.42	2.58	0.70
22	65	30	5.55	3.05	0.70
23	50	30	5.83	3.43	0.65
24	25	168 ^a	22.4	3.78	0.59
2CCP:					
25	95	90	13.9	1.65	0.86
26	90	90	16.3	2.24	0.79
27	75	90	12.0	2.93	0.71
28	65	90	14.4	3.22	0.67
29	50	90	17.0	3.72	0.60
30	25	168 ^a	19.0	3.69	0.60
3CCP:					
31	0.95	75	13.1	1.82	0.84
32	0.90	75	10.6	2.53	0.75
33	0.75	75	16.8	3.33	0.66
34	0.65	75	16.7	3.6	0.62
35	0.50	75	11.7	3.86	0.61
36	0.25	168 ^a	18.9	4.18	0.52

(continued)

TABLE 1. Continued

Experiment	Mole fraction M_1 in the feed	Time, minutes	Conversion, wt%	Nitrogen content, wt%	Mole fraction m_1 in the copolymer
4CCP:					
37	0.95	90	10.1	1.63	0.86
38	0.90	90	8.6	2.16	0.80
39	0.75	90	13.9	3.17	0.68
40	0.65	90	11.1	3.44	0.64
41	0.50	90	14.3	3.88	0.57
42	0.25	168 ^a	20.7	4.05	0.54
4BCP:					
43	0.95	120	12.1	1.53	0.86
44	0.90	120	12.7	2.02	0.80
45	0.75	120	15.6	2.69	0.71
46	0.65	120	13.9	3.17	0.63
47	0.50	120	16.0	3.37	0.59
48	0.25	168 ^a	21.1	3.71	0.52
4FCP:					
49	0.95	480	10.8	1.28	0.90
50	0.90	480	9.1	1.89	0.84
51	0.75	480	12.7	2.86	0.73
52	0.65	480	14.0	3.29	0.68
53	0.50	480	12.3	3.61	0.63
54	0.25	168 ^a	24.6	3.96	0.59

^aHours.

$$m_1/m_2 = M_1(r_1M_1 + M_2)/M_2(M_1 + r_2M_2) \quad (1)$$

(m_1 and m_2 are mole fractions of ST and a TSE monomer units in the copolymer, respectively; M_1 and M_2 are the concentrations of ST and TSE in the monomer feed, respectively) yields

$$Y - 1 = r_1X \quad (2)$$

where Y denotes the ratio of the mole fractions of the two monomers in the copolymer (m_1/m_2), X is the ratio of the two monomers in the feed (M_1/M_2), and the copolymerization parameter $r_1 = k_{11}/k_{12}$.

An application of the terminal model to the compositional data for ST-3MOCP copolymerization (Table 1) is presented in Fig. 2. The model does not predict well the copolymer composition, particularly at high ST content in the monomer feed. Similar deviations were observed for all ST-TSE copolymerizations. Deviations from the terminal model of the copolymerization of alkyl 2-cyano-3-phenyl-2-propenoates with styrene were attributed to the influence of penultimate units [9]. The copolymer composition equation of the penultimate model proposed by Merz et al. [20] was applied to the copolymerization of ST and the TSE monomers with $r_2 = r'_2 = 0$ ($r_2 = k_{222}/k_{221}$, $r'_2 = k_{122}/k_{121}$) in the form of

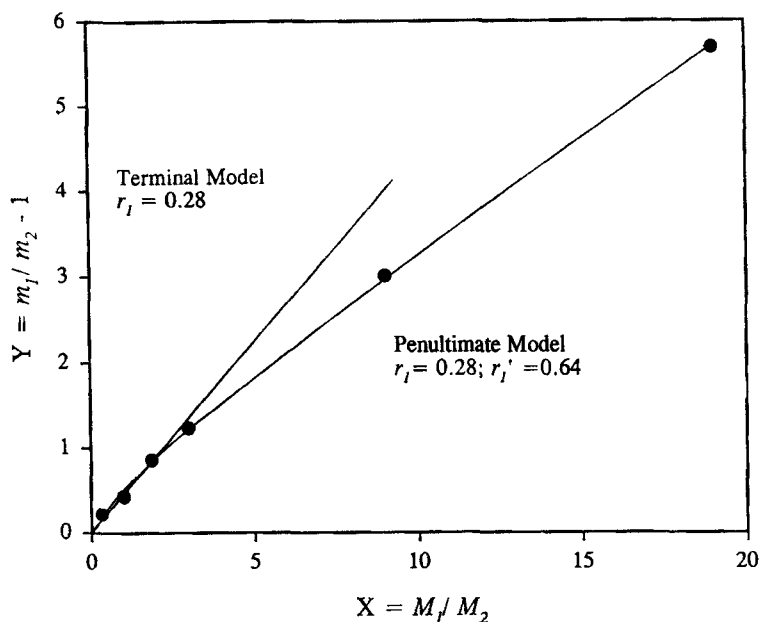


FIG. 2. Analysis of the copolymer compositional data ($M_1 = \text{ST}$, $M_2 = \text{3MOCP}$) in terms of the terminal and penultimate models.

$$Y - 1 = r_1'X(1 + r_1X)/(1 + r_1'X) \quad (3)$$

The values for r_1 (k_{111}/k_{112}) and r_1' ($r_1' = k_{211}/k_{212}$), determined by the penultimate model, are summarized in Table 2. The monomer reactivity ratios were calculated by using nonlinear curve fitting based on the Marquardt-Levenberg algorithm. A

TABLE 2. Copolymerization Parameters in the Radical Copolymerization of Ring-Substituted Methyl 2-Cyano-3-phenyl-2-propenoates (M_2) with Styrene (M_1)

TSE	r_1	r_1'	r_1'/r_1	Q_2	e_2	$1/r_1$
2MOCP	0.44 ± 0.02	1.82 ± 0.46	4.14	0.22	2.90	2.27
3MOCP	0.28 ± 0.01	0.64 ± 0.06	2.29	0.28	3.10	3.57
4MOCP	1.27 ± 0.11	2.19 ± 0.74	1.72	0.13	2.47	0.79
4ECP	0.52 ± 0.02	1.02 ± 0.21	1.96	0.20	2.82	1.92
2CCP	0.21 ± 0.01	1.83 ± 0.36	8.71	0.32	3.22	4.76
3CCP	0.15 ± 0.02	0.62 ± 0.13	4.13	0.38	3.36	6.67
4CCP	0.35 ± 0.11	0.41 ± 0.11	1.17	0.25	3.00	2.86
4BCP	0.26 ± 0.04	1.07 ± 0.11	4.12	0.29	3.13	3.85
4FCP	0.41 ± 0.01	1.10 ± 0.17	2.68	0.23	2.94	2.43
UCP ^a	0.26 ± 0.26	1.25 ± 0.26	4.80	0.29	3.13	4.36

^aCited from Ref. 10.

nonlinear regression curve calculated for the 3MOCP-ST copolymerization data is presented in Fig. 2. 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 TSE monomers studied. The ratios r'_1/r_1 for various esters of 2-cyano-3-phenyl-2-propenoic acid were found in the range 1.93–4.23 [9].

The Alfrey-Price Q_2 and e_2 values [22] (Table 2) were calculated according to

$$r_1 = Q_1/Q_2 \exp\{-e_1(-e_1 - e_2)\} \quad (4)$$

with Q , a measure of the resonance stability of a monomer in copolymerization, and e , a polar factor. The r_1 values were obtained from the copolymerization of the various TSE monomers with ST (Table 2) and from the copolymerization of ring-unsubstituted methyl 2-cyano-3-phenyl-2-propenoate (UCP) with acrylonitrile, using the values $Q_1 = 1.0$ and $e_1 = -0.8$ for styrene and $Q_1 = 0.6$ and $e_1 = 1.2$ for acrylonitrile (the value of $r_1 = 21$ was used for the TSE monomers. This assumption is based on the determination of $r_1 = 21 \pm 1$ for the pair acrylonitrile-UCP [9]). The resonance and polar parameters, Q_2 and e_2 , are of the same magnitude for the ring-substituted TSE monomers. Similar Q_2 and e_2 values were found in the case of 1,2-disubstituted ethylenes, diethyl fumarate ($Q = 0.25$, $e = 2.26$), and fumaronitrile ($Q = 0.29$, $e = 2.73$) [23]. The TSE monomers have comparable Q values and higher e values than alkyl cinnamates ($C_6H_5CH=CHCOOR$, $Q = 0.18$ – 0.28 , $e = 0.56$) [24] and ring-substituted *trans*-cinnamonitriles ($RC_6H_4CH=CHCN$, $Q = 0.06$ – 0.7 , $e = -0.52$ – 1.35) [25].

In general, the reactivity of a monomer in a copolymerization reaction depends on: 1) the polarity of the double bond, 2) the stability of the free radical formed by addition of a growing chain to the monomer, and 3) steric hindrance in the transition state [1]. ST has a high electron-availability at the double bond as measured by its e -value of -0.80 and relatively high resonance factor $Q = 1$. The benzyl radical is highly stabilized by resonance with the phenyl ring. The addition of a growing chain end to styrene should not be affected by the presence of the bulky phenyl group, because the normal direction of attack on the styrene monomer is toward the β -carbon, to which only two hydrogen atoms are attached. The significant conclusion from the early copolymerization studies is that $1/r_1$ and the tendency toward alternation of monomer units in the copolymer both increase as the difference in polarity between two monomers increases [1]. For the ring-substituted TSE monomers a good correlation of relative reactivity with both Q_2 and e_2 was observed (Fig. 3). One can see that the TSE relative reactivity increases faster with the polar parameter e than with the resonance parameter Q .

Linear-free-energy relationships such as the Hammett equation, $\log_{10}(1/r_1) = \rho\sigma$ [25], have been used to correlate copolymerization behavior with structure, particularly for a series of monomers which are similar in structure. The Hammett substituent constant σ is a quantitative measure of that substituent's total electron-donating or electron-withdrawing effect by both resonance and induction. Electron-withdrawing and electron-donating substituents have positive and negative sigma constants, respectively (Table 3). The reaction constant ρ is a measure of the sensitivity of the reaction to the electronic effects of the various substituent groups. Substituents in the ortho position are not considered due to complication by steric effects [26]. The reactivity of the TSE monomers is correlated to the Hammett constants σ of the substituents, and the value of $\log_{10}(1/r_1)$ has a tendency to increase

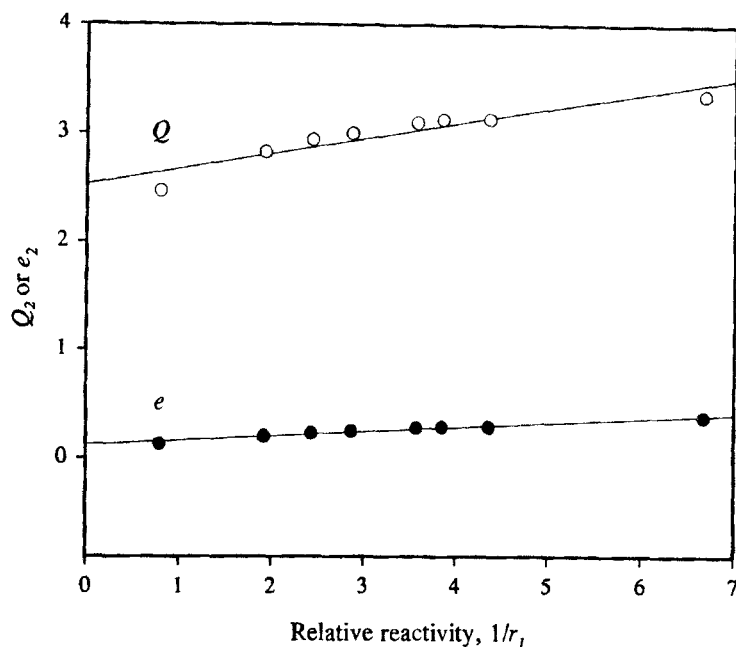


FIG. 3. The correlation between Q and e values of the TSE monomers and relative reactivity, $1/r_1$.

with increasing σ of the ring substituents (Fig. 4). Such a relationship between $\log_{10}(1/r_1)$ and the σ values observed demonstrates that the steric contribution to the copolymerization reactivity is nearly the same for each TSE monomer studied, and hence the difference of the copolymerizability of the propenoates seems to depend on the polarity of the substituents. A linear regression analysis gives

TABLE 3. Relative Reactivity, Hammett Constants, Charge Distribution, and ^{13}C -NMR Shifts of the Double Bond Carbons, and Reduction Potentials of the TSE Monomers

TSE	$\text{Log}_{10} 1/r_1$	σ	Charge on C_α	Charge on C_β	$^{13}\text{C}_\alpha$, ppm	$^{13}\text{C}_\beta$, ppm	E_p , V
3MOCP	0.55	0.12	-0.073	0.027	104.1	153.4	-1.32
4MOCP	-0.10	-0.27	-0.096	0.039	99.7	154.9	-1.44
4ECP	0.28	-0.15	-0.087	0.032	100.9	155.0	-1.39
3CCP	0.82	0.37	-0.073	0.021	104.1	153.4	-1.16
4CCP	0.46	0.23	-0.075	0.023	102.8	153.5	-1.26
4BCP	0.59	0.23	-0.067	0.021	103.0	153.6	-1.27
4FCP	0.39	0.15	-0.074	0.030	102.0	153.0	-1.28
UCP	0.64	0.00	-0.080	0.027	102.8	155.0	-1.30

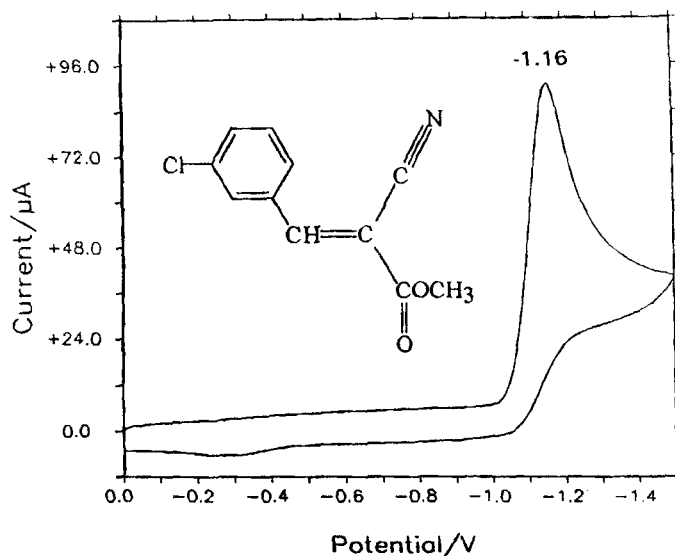


FIG. 4. Cyclic voltammogram of methyl 2-cyano-3-(3-chlorophenyl)-2-propenoate.

$$\log_{10}(1/r_1) = 1.1\sigma + 0.36$$

The correlation coefficient is 0.7. A positive value of $\rho = 1.1$ indicates that $1/r_1$ increases by electron-withdrawing substituents. The ρ value was reported to be 0.51, 0.83, 0.83, and 0.48 for the attack of ring-substituted styrenes [16], α -substituted acrylates [27], α -substituted acrylonitrile [27], and *p*-substituted cinnamionitriles [25], respectively.

It was noted that the polarographic half-wave potential of reduction of some vinyl and diene monomers was related to the Alfrey-Price parameters Q and e [28]. The cyclic voltammetric reduction potentials of a number of electron-poor trisubstituted and tetrasubstituted ethylenes were correlated with Hammett substituent constants [29]. The E_p values, which are a measure of ΔG° or ΔG^\ddagger between the olefin and the olefin anion-radical, constitute a parameter related to the propagation reactions in the copolymerization of electron-poor and electron-rich olefins. A typical cyclic voltammogram of a ring-substituted TSE monomer (3CCP) is presented in Fig. 4. Relative reactivity of the phenyl-substituted TSE monomers upon copolymerization was correlated with their cyclic voltammetric reduction potentials E_p (Table 3, Fig. 5). The reduction potentials plot well against relative reactivity. Most likely, an electron transfer occurs in the reactions of the electron-accepting TSE monomers with styrene as evidenced by the parallel increasing order of the relative reactivities with increasing reduction potentials (increasing ease of one electron reduction).

Similarly, the relative reactivity can be correlated with molecular orbital properties of the TSE monomers, such as charge distribution on the olefinic carbons (Table 3, Fig. 6). The atomic charges were calculated at the planar optimized geometries (AM1). The relative reactivity, $\log_{10} 1/r_1$, correlates well with the charges on both olefinic carbons, C_α and C_β . A linear regression analysis gives

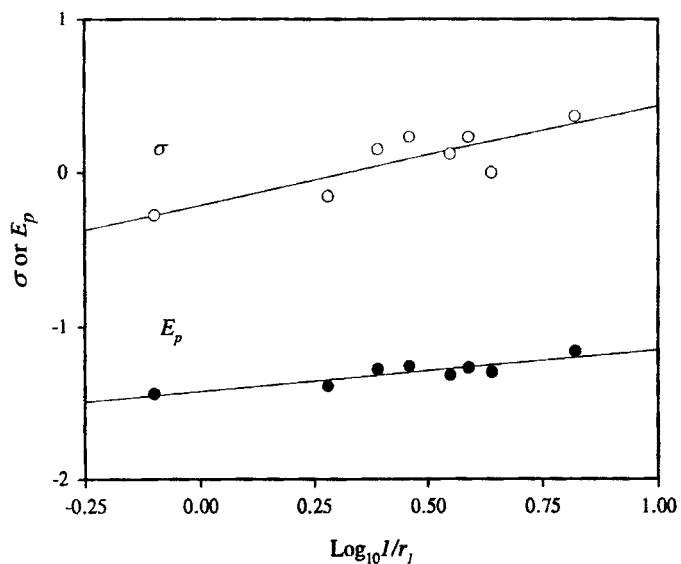


FIG. 5. Plot of relative reactivity, $\log_{10} 1/r_1$, against the Hammett constants σ and the cyclic voltammetric reduction potentials E_p of the TSE monomers.

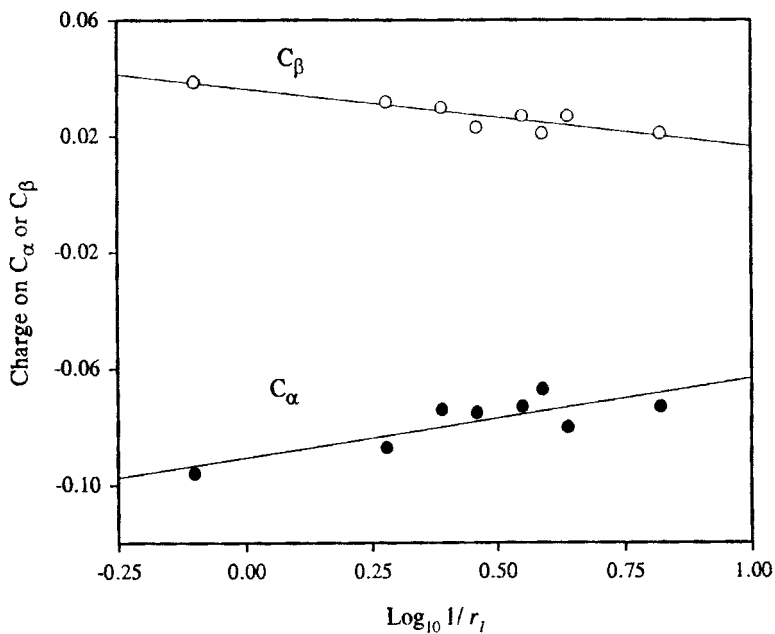


FIG. 6. Plot of relative reactivity, $\log_{10} 1/r_1$, against the calculated charges on olefinic carbons of the TSE monomers.

$$\log_{10} 1/r_1 = -0.09 + 0.03 \times (\text{charge on } C_\alpha)$$

and

$$\log_{10} 1/r_1 = 0.04 + 0.02 \times (\text{charge on } C_\beta)$$

The correlation coefficients are 0.67 and 0.81, respectively. These equations provide a means to estimate relative reactivity of the phenyl-substituted TSE from MO calculations and illustrates that polar properties of the monomers correlate with their reactivity.

Studies of linear-free-energy relationships suggest the use of NMR chemical shifts, especially ^{13}C values, as a semiempirical measure of substituent effects in the styrene series [30]. Calculation of Alfrey-Price $Q-e$ values from ^{13}C -NMR data was attempted for a number of vinyl monomers [31]. For the TSE-ST copolymerizations the relative reactivity correlates well (the correlation coefficient is 0.88) to the ^{13}C -NMR chemical shift of the olefinic α -carbon [$=\text{C}(\text{CN})\text{CO}_2\text{CH}_3$] of the monomers, rather than β -carbon ($\text{ArCH}=\text{}$) (Table 3), as shown in Fig. 7. Based on the correlation of the relative reactivity and the chemical shift of the α -carbon, it was suggested that the attack of ST propagating radicals occurs at the site of the olefinic α -carbon of cinnamionitriles ($=\text{CH}-\text{CN}$) [25]. The influence of the substitution on the stability of TSE free radical is not obvious, since apparently the attack of a styrene-ended radical on both sides of the TSE monomer is possible. Thus, Boberly demonstrated that both head-to-tail and head-to-head structures of styrene-methyl 2-cyano-3-phenyl-2-propenoate dyads exist in the copolymer [10]. NMR microstructure analysis suggested that styrene-ended radical attacks 2-phenyl-1,1-dicyanoeth-

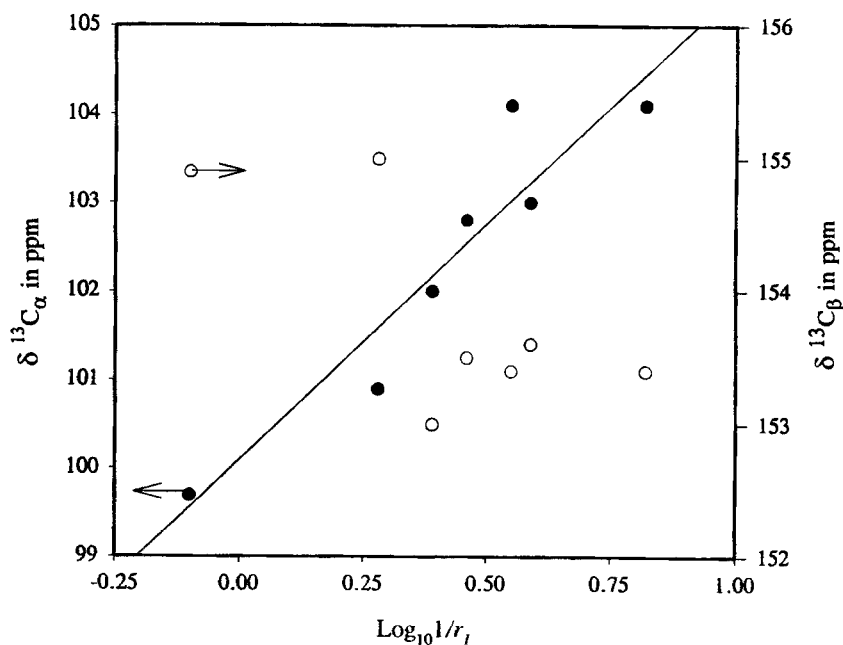


FIG. 7. Dependence of relative reactivity, $\log_{10} 1/r_1$, on ^{13}C NMR chemical shift of olefinic carbons of the TSE monomers.

ene about 60% at α -carbon [$=C(CN)_2$] and 40% at β -carbon ($ArCH=$) [32]. More detailed information on the microstructure of the TSE-ST copolymers is necessary to confirm that addition occurs at either end of the ring-substituted TSE monomer.

CONCLUSIONS

Radical copolymerization of the ring-substituted methyl 2-cyano-3-phenyl-2-propenoates with styrene in broad ranges of comonomer ratios produces copolymers with various compositions of monomer units. Deviations from the terminal model of the copolymerization of the trisubstituted ethylene monomers are attributed to the influence of penultimate units. The penultimate kinetic model predicts well the copolymer composition. The Alfrey-Price Q and e parameters calculated for the monomers correlate with the relative reactivity ($1/r_1$). The relative reactivity showed a tendency to increase with increasing Hammett constant σ , cyclic voltammetric reduction potential, E_p , calculated atomic charge, and ^{13}C -NMR chemical shift on the olefinic α -carbon of the ring-substituted monomers.

ACKNOWLEDGMENTS

We are grateful to acknowledge that the project is partly supported by a research and equipment grant from the Coatings Industry Education Foundation (CIEF), Office of Sponsored Programs and Research, and University Research Council of DePaul University. J.M.E. was supported by a CIEF graduate fellowship.

REFERENCES

- [1] G. Odian, *Principles of Polymerization*, 3rd ed., Wiley, New York, NY, 1991.
- [2] E. T. Borrows, R. N. Haward, J. Porges, and J. Street, *J. Appl. Chem.*, **5**, 379 (1955).
- [3] M. Kreisel, U. Garbatski, and D. H. Kohn, *J. Polym. Sci.*, **A2**, 105 (1964).
- [4] H. K. Hall Jr. and R. S. Dally, *Macromolecules*, **8**, 22 (1975).
- [5] G. K. Noren and H. K. Hall Jr., *J. Polym. Sci., Polym. Chem. Ed.*, **10**, 3183 (1972).
- [6] G. B. Kharas and D. H. Kohn, *Ibid.*, **21**, 1457 (1983).
- [7] G. B. Kharas and H. Ajbani, *J. Polym. Sci. Part A: Polym. Chem. Ed.*, **31**, 2295 (1993).
- [8] G. B. Kharas and M. H. Litt, *Polym. Bull.*, **12**, 65 (1984).
- [9] A. Gilath, S. H. Ronel, M. Shmueli, and D. H. Kohn, *J. Appl. Polym. Sci.*, **14**, 1491 (1970).
- [10] R. Bednarski, D. Braun, J. Borberly, and T. Kelen, *Makromol. Chem.*, **191**, 773 (1990).
- [11] D. Braun, W. K. Czerwinski, R. Bednarski, T. Kelen, and F. Tüdös, *Ibid.*, **193**, 465 (1992).

- [12] J. M. Eaker, B. C. Dian, M. E. Elenteny, M. Kamenetsky, L. M. Provenza, G. B. Kharas, and G. R. Quinting, *J. Macromol. Sci.—Macromol. Rep.*, **A32**, 13 (1995).
- [13] G. B. Kharas, T. S. Wheeler, J. M. Eaker, S. A. Armatys, J. A. Fehringer, R. M. Gehant, E. C. Glaser, K. A. Johnson, P. S. Moy, and G. R. Quinting, *Ibid.*, **A32**, 405 (1995).
- [14] T. Hayashi, *J. Org. Chem.*, **31**, 3253 (1966).
- [15] G. D. Green, J. I. Weinschenk, J. E. Mulvaney, and H. K. Hall Jr., *Macromolecules*, **10/11**, 71 (1987).
- [16] C. Walling, E. R. Briggs, K. B. Wolfstern, and F. R. Mayo, *J. Am. Chem. Soc.*, **70**, 1537 (1948).
- [17] N. G. Gaylord, *J. Macromol. Sci.—Chem.*, **A6**, 259 (1972).
- [18] T. Sato, M. Abe, and T. Otsu, *Makromol. Chem.*, **178**, 1061 (1971).
- [19] F. R. Mayo and F. M. Lewis, *J. Am. Chem. Soc.*, **66**, 1594 (1944).
- [20] E. Merz, T. Alfrey Jr., and G. Goldfinger, *J. Polym. Sci.*, **1**, 75 (1946).
- [21] J. A. Seiner and M. H. Litt, *Macromolecules*, **4**, 308 (1971).
- [22] T. Alfrey Jr. and C. C. Price, *J. Polym. Sci.*, **2**, 101 (1947).
- [23] R. Z. Greenley, in *Polymer Handbook* (J. Brandrup and E. H. Immergut, Eds.), Wiley-Interscience, New York, NY, 1989, p. 267.
- [24] T. Otsu, B. Yamada, and T. Nozaki, *Nippon Kagaku Zasshi*, **70**, 1941 (1967).
- [25] H. Tanaka, M. Sakaguchi, Y. Kikukawa, T. Sato, and T. Ota, *Macromol. Chem. Phys.*, **195**, 2083 (1994).
- [26] T. H. Lowry and K. S. Richardson, *Mechanism and Theory in Organic Chemistry*, 2nd ed., Harper and Row, New York, NY, 1987, Chap. 2.
- [27] B. Yamada and T. Otsu, *J. Macromol. Sci.—Chem.*, **A3**, 1551 (1969).
- [28] S. A. Voronov, V. A. Puchin, L. A. Kosik, V. S. Tokarev, and E. M. Kiselev, *Vysokomol. Soedin., Ser. B*, **20**, 577 (1978).
- [29] J. E. Mulvaney, R. J. Cramer, and H. K. Hall Jr., *J. Polym. Sci., Polym. Chem. Ed.*, **21**, 309 (1983).
- [30] A. Corneliws, S. Lambert, P. Laszlo, and P. Schaus, *J. Org. Chem.*, **46**, 2130 (1981).
- [31] J. K. Borchardt and E. D. Dalrymple, *J. Polym. Sci., Polym. Chem. Ed.*, **20**, 1745 (1982).
- [32] G. B. Kharas, P. A. Mirau, K. Watson, and H. J. Harwood, *Polym. Int.*, **28**, 67 (1992).

Received May 10, 1996

Revision received July 30, 1996