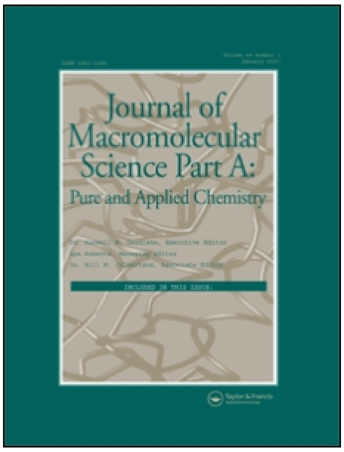

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Novel Copolymers of Trisubstituted Ethylenes with Styrene. II. Halogen Ring-Substituted Methyl 2-Cyano-3-Phenyl-2-Propenoates

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NOVEL COPOLYMERS OF TRISUBSTITUTED ETHYLENES WITH STYRENE. II. HALOGEN RING-SUBSTITUTED METHYL 2-CYANO-3-PHENYL-2-PROPENOATES

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ABSTRACT

Electrophilic trisubstituted ethylene monomers, ring-substituted methyl 2-cyano-3-phenyl-2-propenoates, $RC_6H_4CH=C(CN)CO_2CH_3$ (where R is *o*-Cl, *m*-Cl, *p*-Cl, *p*-Br, and *p*-F) were prepared and copolymerized in solution with styrene at equimolar monomer feed composition in the presence of a radical initiator, AIBN at 80°C. The order of reactivity ($1/r_1$) for the trisubstituted ethylene monomers was *p*-Cl (3.0) > *m*-Cl (2.9) > *p*-Br (2.3) > *o*-Cl (2.0) > *p*-F (1.4). High T_g's of the copolymers in comparison with that of polystyrene indicates substantial decrease in chain mobility of the copolymer due to high dipolar character of the trisubstituted monomer units.

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INTRODUCTION

Previous studies showed that trisubstituted ethylenes (TSE) have very low reactivity in radical homopolymerization due to polar and steric reasons (1). However, the steric problems observed in the homopolymerization can be overcome when electron-deficient trisubstituted alkenes carrying two cyano, halo, and/or carboalkoxy substituents are copolymerized with electron rich monosubstituted ethylenes, like styrene, vinyl acetate and N-vinylcarbazole (2-4). The copolymerization of the TSE monomers at equimolar comonomer feed ratios results in formation of copolymers with nearly 1:1 composition (A); copolymerization of monomer mixtures with low contents of a TSE monomer gives statistical copolymers (B):

$$-(R^1R^2C\text{-}CHR^3)_{x=0.5} - (CH_2\text{-}CHR^4)_{y=0.5} -$$

(A)

$$R^1R^2C{=}CHR^3 + CH_2{=}CHR^4 \text{ ---> }$$

$$-(R^1R^2C\text{-}CHR^3)_{x<0.5} - (CH_2\text{-}CHR^4)_{y>0.5} -$$

(B)

Copolymerization of the TSE monomers and vinyl ethers, which do not undergo radical homopolymerization led to equimolar alternating copolymers (5). The enhancement of reactivity of substituted ethylenes has been explained by considering the interaction between an electron-donor radical and an electron-acceptor monomer (or vice versa) (6) or homopolymerization of monomer donor-acceptor complexes (7).

In continuation of our studies of the monomer structure - monomer reactivity correlations in radical copolymerization of TSE monomers (8), it was of interest to prepare halogen ring-substituted methyl 2-cyano-3-phenyl-2-propenoates, $RC_6H_4CH{=}C(CN)CO_2CH_3$ (where R is *o*-Cl, *m*-Cl, *p*-Cl, *p*-Br, and *p*-F), and explore the feasibility of their copolymerization with an electron-rich olefin like styrene. This paper presents results on synthesis and copolymerization of novel trisubstituted ethylene monomers.

EXPERIMENTAL

General Procedures: Infrared spectra were determined with a Perkin Elmer 1710 FT-IR spectrometer. Samples in CH_2Cl_2 solution were cast on a NaCl plates followed by evaporation in a vacuum oven. Melting points of the monomers and glass transition temperatures of the copolymers were measured by using a DSC module of STA 625 thermal analyzer (Polymer Laboratories, Inc.). The molecular weight of polymers was determined relative to polystyrene standards in chloroform solutions with sample concentrations 0.8% (wt/vol) by gel permeation chromatography (GPC) using a Waters Model 510 pump at an elution rate of 1.0 mL/min through 500, 1000 and 10000 Å Phenogel (Phenomenex) columns at 35°C, and a Model 410 refractive index detector.

^1H and ^{13}C NMR spectra of 4-10% $CDCl_3$ solutions of monomers and polymers were obtained on a Bruker Omega 400WB spectrometer with 9.4T 89 mm bore magnet at room temperature. Parameters for the proton spectra were 3 us pulse width ($\approx$30°), pulse delay 2s, 16384 acquisition points, 32 scans; for the carbon spectra: 6.5 us pulse width ($\approx$30°), pulse delay 3s, 16384 acquisition points, 128 scans, with broadband proton decoupling. Elemental analyses were performed by Quantitative Technologies Incorporated (New Jersey).

Synthesis of Monomers: 2-chlorobenzaldehyde (98%), 3-chlorobenzaldehyde (97%), 4-chlorobenzaldehyde (97%), 4-bromobenzaldehyde (97%), and 4-fluorobenzaldehyde (97%) supplied from Pfaltz and Bauer, methyl cyanoacetate (99%), and piperidine (99%) supplied from Aldrich Chemical Co., were used for monomer synthesis as received, without additional purification. The preparation procedure was essentially the same for all the monomers. In a typical synthesis, equimolar amounts of methyl cyanoacetate and an appropriate aldehyde were mixed with a small amount of *N,N*-dimethylformamide in an Erlenmeyer flask. A few drops of piperidine were added with stirring. The product of the reaction was isolated and purified by recrystallization from 2-propanol.

Methyl (*E*)-2-cyano-3-(4-chlorophenyl)-2-propenoate. Yield 90.9%; mp 127.8°C; ^{1}H NMR δ 3.9 (s, 3H, -OCH$_3$), 7.5-7.9 (d, Ph-H), 8.2 (s, -CH=); ^{13}C NMR δ 162.6 (C=O), 153.5 (CH=), 139.5, 132.1, 129.6, 129.5 (Ph), 1 5.1 (C≡N), 102.8 (C=), 53.4 (CH$_3$); IR 2227 (m, C≡N), 1735 (s, C=O), 1271 (s, -OCH$_3$). Anal. Calcd for $C_{11}H_8O_2NCl$: C, 59.61; H, 3.64; N, 6.32; Cl, 15.99. Found: C, 59.54; H, 3.53; N, 6.24; Cl, 15.96.

Methyl (*E*)-2-cyano-3-(3-chlorophenyl)-2-propenoate. Yield 83.8%; mp 113.5°C; ^{1}H NMR δ 3.99 (s, 3H, -OCH$_3$), 7.0-7.6 (m, Ph-H), 8.2(s,-CH=); ^{13}C δ NMR 162.4 (C=O), 153.4 (CH=), 135.2, 133.0, 132.8, 130.7, 130.5, 128.6 (Ph), 114.8 (C≡N), 104 (C=), 53.5 (CH$_3$); IR 2228 (m, C≡N), 1734 (s, C=O), 1272 (s, -OCH$_3$). Anal. Calcd for $C_{11}H_8O_2NCl$: C, 59.61; H, 3.64; N, 6.32; Cl, 15.99. Found: C, 59.60; H, 3.64; N, 6.26; Cl, 15.99.

Methyl (*E*)-2-cyano-3-(2-chlorophenyl)-2-propenoate. Yield 85.4%; mp 108.9 °C; ^{1}H NMR δ 3.99 (s, 3H, -OCH$_3$), 7.3-7.6 (m, Ph-H), 8.2(d,-CH=); ^{13}C NMR δ 161.9 (C=O), 150.8 (CH=), 136.3, 133.7, 130.2, 129.7, 129.6, 127.3 (Ph), 114.4 (C≡N), 105.4 (C=), 53.3 (CH$_3$); IR (NaCl) 2226 (m, C≡N), 1730(s, C=O), 1268 (s, -OCH$_3$). Anal. Calcd for $C_{11}H_8O_2NCl$: C, 59.61; H, 3.64; N, 6.32; Cl, 15.99. Found: C, 59.62; H, 3.61; N, 6.40; Cl, 15.89.

Methyl (*E*)-2-cyano-3-(4-bromo)phenyl-2-propenoate. Yield 88.1%; mp 131.2°C; ^{1}H NMR δ 3.99 (s, 3H, -OCH$_3$), 7.7-7.9 (d, Ph-H), 8.2(s,-CH=); ^{13}C NMR δ 162.6 (C=O), 153.6 (CH=), 132.6, 132.2, 130.0, 128.3 (Ph), 115.1 (C≡N), 103.0 (C=), 53.4 (CH$_3$); IR 2224 (m, C≡N), 1732 (s, C=O), 1274 (s, -OCH$_3$), 1600 (s, C=C). Anal. Calcd for $C_{11}H_8O_2NBr$: C, 49.65; H, 3.03; N, 5.26; Br,30.04. Found: C, 49.65; H, 2.92; N, 5.21; Br, 29.99.

Methyl (*E*)-2-cyano-3-(4-fluorophenyl)-2-propenoate. Yield 78.6%; mp 128.4°C; ^{1}H NMR δ 3.98 (s, 3H, -OCH$_3$), 7.2-7.3 (m, Ph-H), 8.0-8.3 (m, Ph-

H), 8.2 (s,-CH=); ^{13}C NMR δ 166.6, 164.0, 162.8 (C=O), 153.6 (CH=), 133.6, 133.5, 127.6 (Ph), 116.7, 115.3 (C≡N), 102 (C=), 53.3 (CH_3); IR 2227 (m, C≡N), 1741 (s, C=O), 1262 (s, $-OCH_3$) Anal. Calcd for $C_{11}H_8O_2NF$: C, 64.39; H, 3.93; N, 6.83; F, 9.26. Found: C, 64.13; H, 3.89; N, 6.89; F, 9.22.

Copolymerization: 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'-Azobisisobutironitrile (AIBN) (Aldrich) was twice recrystallized from ethyl alcohol and then dried under reduced pressure at r.t. Copolymers of the TSE monomers and ST were prepared in 50-mL Pyrex screw cap ampules at an equimolar ratio of the monomer feed using 0.0045 mole/L of AIBN at an overall monomer concentration 2 mole/L in 20 ml of ethyl acetate. The copolymerization was conducted at 80°C. After a predetermined time the mixture was cooled to r.t. and precipitated dropwise in methanol. The crude copolymers were purified by reprecipitation from chloroform solution into an excess of methanol. The composition of the copolymers was determined based on the nitrogen content with precission of 0.1 wt%.

RESULTS AND DISCUSSION

Monomer Synthesis

The TSE monomers were prepared according to the general procedure of Knoevenagel condensation (9) by reacting an appropriate ring-substituted benzaldehyde with methyl cyanoacetate, as described in the experimental section.

$$RC_6H_4CHO + NCCH_2CO_2CH_3 \text{ ---> } RC_6H_4CH{=}C(CN)CO_2CH_3$$

The condensation reaction proceeded smoothly, yielding crystalline products, which were purified by conventional techniques. The ^{13}C 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 (10,11).

Homopolymerization

An attempted homopolymerization of the TSE monomers in the presence of AIBN did not produce any polymer on the precipitation 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 extent as to favor the occurrence of chain transfer or termination step instead. Homopolymerization of styrene under conditions identical to those in copolymerization experiments yielded 18.3% of polystyrene, when polymerized for 30 min.

Copolymerization

The TSE monomers were copolymerized with styrene at equimolar feed ratios in ethyl acetate at 80°C in the presence of AIBN. Copolymerization of the halogen ring-substituted methyl 2-cyano-3-phenyl-2-propenoates with styrene resulted in formation of copolymers (Table 1). According to elemental analysis of the copolymers, a substantial amount of trisubstituted ethylene monomer is present in the copolymers, which is indicative of relatively high reactivity of the monomers towards styrene.

In an attempt to qualitatively correlate the observed monomer reactivities, we considered copolymer composition data obtained at equimolar monomer feed. The relative reactivity of styrene in copolymerization with these monomers can be estimated by assuming applicability of the copolymer composition equation (I) of the terminal copolymerization model (1),

$$m_1/m_2 = [M_1](r_1[M_1] + [M_2])/[M_2]([M_1] + r_2[M_2]) \qquad \text{(I)}$$

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 a

TABLE 1.

Copolymerization of styrene (M_1) and halogen ring-substituted methyl 2-cyano-3-phenyl-2-propenoates, $R\text{-}C_6H_4CH{=}C(CN)COOCH_3$ (M_2).

R	Time, hr	Yield, wt%	m_2 in copolymer mol. fr.	M_w x 10^{-3}	T_g*) °C
o-Cl	1.5	15.6	0.40	86.2	198
m-Cl	1.2	44.29	0.42	93.1	177
p-Cl	1.5	14.3	0.43	82.0	192
p-Br	2.0	16.0	0.41	93.4	187
p-F	8.0	12.3	0.37	81.4	155

*) The T_g values are reported for the copolymers containing 68-71 mol% of styrene units.

TSE in the monomer feed, respectively. In the absence of the TSE monomer self-propagation ($k_{22} = 0$, $r_2 = 0$) and at equimolar monomer feed ($[M_1]/[M_2] = 1$), eq I yields

$$r_1 = m_1/m_2 - 1 \qquad \text{(II)}$$

or the equation for the relative reactivity of styrene radical k_{12}/k_{11} with trisubstituted ethylene monomers:

$$1/r_1 = 1/[(m_1/m_2) - 1] \qquad \text{(III)}$$

Consideration of monomer reactivities according to eq III involves also the assumption of minimal copolymer compositional drift at equimolar monomer feed and given conversion. This nonrigorous kinetic treatment nevertheless allows estimation of the reactivity of a styrene-ended polymer radical in reaction with electrophilic monomer (1). The order of reactivity ($1/r_1$) for the five TSE monomers is *p*-Cl (3.0) > *m*-Cl (2.9) > *p*-Br (2.3) > *o*-Cl (2.0) > *p*-F (1.4).

In general, the reactivity of a monomer in a copolymerization reaction depends on: (i) the polarity of the double bond; (ii) the stability of the free radical formed by addition of a growing chain to the monomer; and (iii) steric hindrance in the transition state (1). Styrene has a high electron-availability at the double bond as measured by its *e*-value of -0.80. 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 ß-carbon, to which only two hydrogen atoms attached. The significant conclusion from the early copolymerization studies (1) is that the $1/r_1$ and the tendency toward alternation of monomer units in the copolymer increases as the difference in polarity between two monomers increases. In the ring-halogenated TSE monomers, electron-withdrawing halogens increase the positive charge on the double bond. Indeed, all of the ring-substituted monomers were more reactive than the ring unsubstituted methyl 2-cyano-3-phenyl-2-propenoate with $1/r_1 = 1.3$ (12). In an attempt to correlate relative reactivity, $1/r_1$ with polarity of the TSE double bond, we have calculated the charge distribution by using HYPERCHEM™ (AutoDesk) PC-based software for C_α (=C(CN)CO_2CH_3), *o*-Cl (-0.056) > *p*-Br (-0.067) > *m*-Cl (-0.073) > *p*-F (-0.074) > *p*-Cl (-0.075), and $C_ß$ (PhC=), *o*-Cl (0.012) < *m*-Cl (0.021) = *p*-Br (0.021) < *p*-Cl (0.023) < *p*-F (0.03); C_α and $C_ß$ for unsubstituted methyl 2-cyano-3-phenyl-2-propenoate were -0.080 and 0.027, respectively. Except for *p*-F ring-substituted TSE, the relative reactivity, $1/r_1$ correlates better with the charge on $C_ß$ than with the one on C_α which is suggestive of the attack of a polystyryl radical at the site of the olefinic ß-carbon of the TSE monomer, since sterically C_α is more hindered. The influence of the substitution on the stability of the free radical is not obvious, since apparently the attack of a styrene-ended polymer radical on both sides of the trisubstituted ethylene monomer is possible. Thus, Borberly (12) has 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. More detailed information on the copolymer composition at different monomer feed ratios would be necessary for the application of copolymerization models that would allow prediction of copolymer composition.

Physical Properties

The copolymers prepared in the present work (M_w of $8.1 \cdot 10^4$-$9.3 \cdot 10^4$ are all amorphous powders, soluble in DMF, $CHCl_3$ and insoluble in methanol and in heptane, and petroleum ether. IR and NMR data showed that these are true copolymers, composed of both trisubstituted ethylene and styrene monomer unit. High T_g of the copolymers (Table 1) in comparison with that of polystyrene (T_g=95°C) indicates substantial decrease of chain mobility of the copolymer due to high dipolar character of the propenoate structural unit.

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