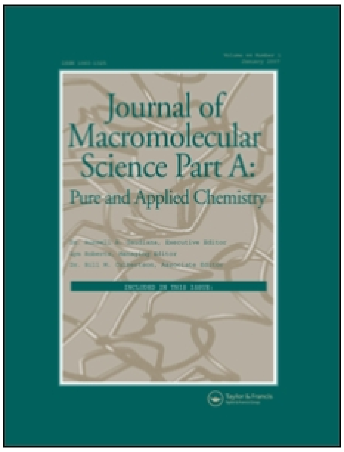

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SYNTHESIS AND RADICAL COPOLYMERIZATION OF TRISUBSTITUTED ETHYLENES WITH STYRENE. 6. ALKOXY, PHENOXY, AND CYANO RING-SUBSTITUTED METHYL-2-CYANO-3-PHENYL-2-PROPENOATES

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SYNTHESIS AND RADICAL COPOLYMERIZATION OF TRISUBSTITUTED ETHYLENES WITH STYRENE. 6. ALKOXY, PHENOXY, AND CYANO RING-SUBSTITUTED METHYL-2-CYANO-3-PHENYL-2-PROPENOATES

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Key Words: Trisubstituted Ethylenes, Radical Copolymerization, Styrene Copolymers

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 4-C_2H_5O, 4-C_3H_7O, 4-C_4H_9O, 3-C_6H_5O, and 3-CN), were prepared and copolymerized with styrene. The monomers were synthesized by the piperidine catalyzed

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Knoevenagel condensation of ring-substituted benzaldehydes and methyl cyanoacetate, and characterized by CHN elemental analysis, IR, ^{1}H- and ^{13}C-NMR. All the propenoates were copolymerized with styrene (M_1) in solution with radical initiation (AIBN) at 70°C. The compositions of the copolymers were calculated from nitrogen analysis and the structures were analyzed by IR, ^{1}H- and ^{13}C-NMR. The order of relative reactivity ($1/r_1$) for the monomers is 3-CN (1.21) > 3-C_6H_5O (1.16) > 4-C_2H_5O (0.94) > 4-C_3H_7O (0.8305) > 4-C_4H_9O (0.616). The high T_g's of the copolymers (> 130°C) in comparison with that of polystyrene indicate a substantial decrease in the chain mobility of the copolymers due to the high dipolar character of the trisubstituted monomer unit. Gravimetric analysis indicated that the copolymers decompose in the range 300-400°C.

INTRODUCTION

Trisubstituted ethylenes (TSE, $R^1CH=CR^2R^3$) containing substituents larger than fluorine exhibit no tendency to undergo polymerization via double bond, apparently because of kinetic considerations superimposed on the thermodynamic factor responsible for the difficulty with which 1,1- and 1,2-disubstituted ethylenes polymerize [1]. Radical copolymerization provides the most general method of overcoming problems encountered in homopolymerization of TSE monomers. This approach has been particularly successful in preparing copolymers from electophilic TSE monomers having double bonds substituted with halo, cyano, and carbonyl groups. These electron-poor TSE monomers copolymerize readily with monosubstituted electron-rich monomers like styrene, vinyl acetate, vinyl ethers, *N*-vinyl carbazole, and *N*-vinyl pyrrolidone [2-4].

In continuation of our studies of the monomer structure-reactivity correlations in the radical copolymerization of TSE monomers [5-8], it was of interest to prepare phenyl-substituted methyl 2-cyano-3-phenyl-2-propenoates, $RC_6H_4CH=C(CN)CO_2CH_3$ where R is 4-C_2H_5O, 4-C_3H_7O, 4-C_4H_9O, 3-C_6H_5O, and 3-CN), and explore the feasibility of their copolymerization with styrene.

EXPERIMENTAL

General Procedures

Infrared spectra of the TSE monomers (NaCl plates) and copolymers (KBr pellets) were determined with a 1710 Perkin Elmer FT-IR spectrometer.

The melting points of the monomers, the glass transition temperatures (T_g) and the thermal stability of the copolymers were measured by using a STA 625 thermal analyzer (Polymer Laboratories, Inc.). The molecular weights of the polymers were determined relative to polystyrene standards in THF 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; a Model 410 refractive index detector; styragel columns in series: 10^6, 10^5, 10^4, 10^3, and 500 Å; and Millennium 2010 software. ^{1}H and ^{13}C NMR spectra of 4-10% $CDCl_3$ solutions of monomers and polymers were obtained on a Bruker AC-200 spectrometer. Atomic charge distributions were calculated (AM1) by using HYPERCHEM software (AUTODESK, Inc.). Elemental analyses were performed by Quantitative Technologies Inc., New Jersey.

Synthesis of Monomers

4-ethoxybenzaldehyde, 4-propoxybenzaldehyde, 4-butoxybenzaldehyde, 3-phenoxybenzaldehyde, 3-cyanobenzaldehyde, methyl cyanoacetate, DMF, and piperidine were supplied by Aldrich Chemical Co. The preparation procedure was essentially the same for all of the TSE monomers. In a typical synthesis, equimolar amounts of methyl cyanoacetate and an appropriate ring-substituted benzaldehyde were mixed with a small amount of DMF in an Erlenmeyer flask. A few drops of piperidine were added with stirring. The crystalline product of the reaction was isolated by filtration and purified by recrystallization from 2-propanol.

Methyl (*E*)-2-cyano-3-(4-ethoxyphenyl)-2-propenoate

Yield 63.8%; mp 113ºC; ^{1}H NMR δ 1.2 (t, 3H, $OCH_2C\underline{H}_3$), 3.9 (s, 3H, CH_3), 4.0-4.2 (q, 2H, OCH_2) 6.9-7.9 (q, 4H, Ph-H), 8.1 (s, HC=); ^{13}C NMR δ 163 (C=O), 154 (HC=), 134, 124, 115 (Ph), 116 (CN), 98 (C=), 64 (OCH_2), 53 ($OCH_2\underline{C}H_3$), 15 (CH_3); IR 3020 (m, CH), 2222 (m, CN), 1726 (s, C=O), 1216 (s, C-O-CH_3), 758 (s, CH out of plane). Anal. Calcd. for $C_{13}H_{13}NO_3$: C, 67.53%; H, 5.62%; N, 6.06%. Found: C, 67.32%; H, 5.75%; N, 6.13%.

Methyl (*E*)-2-cyano-3-(4-propoxyphenyl)-2-propenoate

Yield 58.2%; mp 118°C; ^{1}H NMR δ 0,9 (t, 3H, $OCH_2CH_2C\underline{H}_3$), 1.7 (m, 2H, $OCH_2C\underline{H}_2CH_3$), 3.8 (s, 3H, $CO_2C\underline{H}_3$), 3.9 (t, 2H, $OC\underline{H}_2CH_2CH_3$), 6.7-7.9 (q, 4H, Ph-H), 8.0 (s, HC=); ^{13}C NMR δ 163 (C=O), 154 (HC=), 133, 124,115, (Ph), 116 (CN), 98 (C=), 70 ($O\underline{C}H_2CH_2CH_3$), 53 ($CO_2\underline{C}H_3$), 22 ($OCH_2\underline{C}H_2CH_3$), 10 ($OCH_2CH_2\underline{C}H_3$); IR 2990 (m, C-H), 2220 (m, CN), 1715 (s, C=O), 1267 (s, C-O-CH_3), 840 (s, C-H out of plane). Anal. Calcd. for $C_{14}H_{15}NO_3$: C, 68.57%; H, 6.12%; N, 5.71%. Found: C, 68.41%; H, 6.17%; N, 5.70%.

Methyl (E)-2-cyano-3-(4-butoxyphenyl)-2-propenoate

Yield 54.9%; mp 112°C; ^{1}H NMR δ 0,9 (t, 3H, $OCH_2CH_2CH_2C\underline{H}_3$), 1.4 (m, 2H, $OCH_2CH_2C\underline{H}_2CH_3$), 1.7 (m, 2H, $OCH_2C\underline{H}_2CH_2CH_3$), 3.8 (s, 3H, $CO_2C\underline{H}_3$), 3.9 (t, 2H, $OC\underline{H}_2CH_2CH_3$), 6.7-7.9 (q, 4H, Ph-H), 8.0 (s, HC=); ^{13}C NMR δ 163 (C=O), 154 (HC=), 133, 124,115, (Ph), 116 (CN), 98 (C=), 68 ($O\underline{C}H_2CH_2CH_2CH_3$), 52 ($CO_2\underline{C}H_3$), 31 ($OCH_2\underline{C}H_2CH_2CH_3$), 29 ($OCH_2CH_2\underline{C}H_2CH_3$), 14 ($OCH_2CH_2CH_2\underline{C}H_3$); IR 2956 (m, C-H), 2222 (m, CN), 1703 (s, C=O), 1263 (s, C-O-CH_3), 798 (s, C-H out of plane). Anal. Calcd. for $C_{15}H_{17}NO_3$: C, 69.50; H, 6.56; N, 5.41. Found: C, 69.20; H, 6.60; N, 5.41.

Methyl (*E*)-2-cyano-3-(3-phenoxyphenyl)-2-propenoate

Yield 42.9%; mp 105°C; ^{1}H NMR δ 3.9 (s, 3H, -CO_2CH_3), 7.0-7.7 (m, Ph-H), 8.2 (s, HC=); ^{13}C NMR δ 162 (C=O), 157 (HC=), 155, 153, 133, 130, 125, 124, 123, 120, 119 (Ph), 115 (CN), 103 (C=), 54 (CH_3); IR 2955 (m, C-H), 2219 (m, CN), 1735 (s, C=O), 1240 (s, C-O-CH_3), 794 (s, C-H out of plane). Anal. Calcd. for $C_{17}H_{13}NO_3$: C, 73.12%; H, 4.66%; N, 5.02%. Found: C, 73.01%; H, 4.73%; N, 5.07%.

Methyl (*E*)-2-cyano-3-(3-cyanophenyl)-2-propenoate

Yield 51.2%; mp 128°C; ^{1}H NMR δ 3.9 (s, 3H, OCH_3), 7.2, 7.6-8.3 (m, Ph-H), 8.2 (s, CH=); ^{13}C NMR δ 162 (C=O), 152 (HC=), 136, 134,133, 130 (Ph), 117, 114, 115 (CN), 104 (C=), 54 (CH_3); IR 3052 (m, C-H), 2224 (m, CN), 1730 (s, C=O), 1289 (s, C-O-CH_3), 962 (s, C-H out of plane). Anal. Calcd. for $C_{12}H_8N_2O_2$: C, 67.92%; H, 3.77%; N, 13.21%. Found: C, 67.92%; H, 3.80%; N, 13.20%.

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'-Azobisisobutyronitrile (AIBN) (Aldrich) was twice recrystallized from ethyl alcohol and then dried under reduced pressure at room temperature. Copolymers of the TSE monomers and styrene were prepared in 25-ml Pyrex screw cap ampoules at equimolar ratio 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 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.

RESULTS AND DISCUSSION

Monomer Synthesis

TSE monomers were synthesized by Knoevenagel condensation [9] of a ring-substituted benzaldehyde with an active hydrogen compound, methyl cyanoacetate, catalyzed by a base, piperidine.

$$RC_6H_4CHO + NCCH_2CO_2CH_3 \rightarrow RC_6H_3CH{=}C(CN)CO_2CH_3$$

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, 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 as indicated by the lack of a precipitate in methanol. The inability of the monomers to polymerize is associated with steric difficulties encountered in homopolymerization of 1,1- and 1,2-disubstituted ethylenes. 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

Copolymerization of the ring-substituted methyl 2-cyano-3-phenyl-2-propenoates with ST resulted in formation of copolymers (Table 1) with weight-

TABLE 1. Copolymerization of Styrene (M_1) and Ring-Substituted Methyl 2-cyano-3-phenyl-2-propenoates, $RC_6H_3CH{=}C(CN)CO_2CH_3$ (M_2)

R (M_2)	Yield[a] (wt%)	Nitrogen (wt%)	m_2 (mol%)	$M_W \times 10^{-3}$ (daltons)	Tg ((C)
4-C_2H_5O	17.8	3.14	32.60	48	179
4-C_3H_7O	12.6	2.95	27.70	5	131
4-C_4H_9O	8.1	2.63	27.60	177	147
3-C_6H_5O	9.2	2.96	34.93	18	187
3-CN	10.5	6.96	35.37	116	>300[b]

[a] Polymerization time was 8 hours.
[b] No T_g transition was observed by DSC.

average molecular weights of 5.0×10^3 to 177×10^3. According to elemental analysis of the copolymers, a substantial amount of TSE monomer is present in the copolymers, which is indicative of relatively high reactivity of the monomers towards ST.

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

$$m_1 / m_2 = [M_1](r_1 [M_1] + [M_2]) / [M_2]([M_1] + r_2 [M_2]) \tag{1}$$

m_1 and m_2 are the 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 TSE in the monomer feed, respectively. In the absence of the self-propagation of TSE monomers ($k_{22} = 0$, $r_2 = 0$), and at equimolar monomer feed ($[M_1]/[M_2] = 1$), Equation 1 yields:

$$r_1 = m_1 / m_2 - 1 \tag{2}$$

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

$$1 / r_1 = 1/[(m_1 / m_2) - 1] \qquad (3)$$

Consideration of monomer reactivities according to Equation 3 also involves 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 TSE monomers is:

3-CN (1.21) > 3-C_6H_5O (1.16) > 4-C_2H_5O (0.94) > 4-C_3H_7O (0.83) > 4-C_4H_9O (0.62)

The significant TSE content in the copolymers indicates a relatively high reactivity of the monomers in cross-propagation reactions.

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 β-carbon, to which only two hydrogen atoms are 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. These ring-substituted TSE monomers were less reactive than the ring unsubstituted methyl 2-cyano-3-phenyl-2-propenoate with $1/r_1 = 1.3$ [12]. With such bulky substituents, steric hindrance could be a reasonable explanation. Based on information on the effect of substituents on electrophilic aromatic substitution, alkoxy and phenoxy groups are moderately activating *ortho* or *para* positions thus decreasing (lowering electrophilicity) reactivity of the TSE monomer. In an attempt to correlate relative reactivity, $1/r_1$ with polarity of the TSE double bond, the charge distribution on the olefinic carbons was calculated at the planar geometries (AM1) for C_α(=C(CN)CO_2CH_3), 3-CN (-0.032) > 3-C_6H_5O (-0.039) > 4-C_4H_9O (-0.076) > 4-C_3H_7O (-0.083) > 4-C_2H_5O (-0.099) and C_β (PhHC=), > 3-CN (0.034) > 3-C_6H_5O (0.040) > 4-C_4H_9O (0.068) > 4-C_3H_7O (0.072) > 4-C_2H_5O (0.080); C_α and C_β for unsubstituted methyl 2-cyano-3-phenyl-2-propenoates were -0.080 and

0.027, respectively. The relative reactivity, $1/r_1$, correlates well with charges on both olefinic carbons, although slightly better with C_α than with the one on C_β (the correlation coefficients are 0.98 and 0.94, respectively) which is suggestive of the fact that the attack of a polystyryl radical occurs preferentially at the site of the α-carbon. 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.

Copolymer Structure

The structure of the copolymers was characterized by using IR and NMR spectroscopy. All IR spectra of the copolymers show overlapping bands in the 3300-2600 cm^{-1} region corresponding to C-H stretch vibrations. The bands for the TSE monomer unit are 2235-2245 (w, CN), 1740-1748 (s, C=O), and 1232-1238 cm^{-1} (m, C-O). Benzene rings of both monomers show ring-stretching bands at 1492-1499 and 1455-1561 cm^{-1} as well as a doublet 758-767, 690-675 cm^{-1}, associated with out of plane C-H bending motions. These bands can be readily identified in styrene copolymers with TSE ethylene monomers containing cyano and carbonyl groups [4-8]. Broadening of the NMR signals in the spectra of the copolymers is apparently associated with head-to-tail and head-to-head structures, which formed though the attack of a styrene-ended radical on both sides of TSE monomer. The ^1H NMR spectra of the ST-TSE copolymers show a broad double peak in a 6.0-8.0 ppm region corresponding to phenyl ring protons of TSE and styrene monomer unit. A broad resonance in a 3.5-4.5 ppm range is assigned to methoxy protons of the TSE monomer unit [12] and the methine protons of TSE monomer unit in head-to-head dyads. The broad resonance in 2.7-3.4 ppm range is assigned to the methine proton of the TSE monomer unit in the head-to-tail ST-TSE dyads. Broad, overlapping resonances in the 1.4-2.7 region are assigned to methine and methylene protons of ST monomer unit in the ST-TSE dyads, which are more subjected to deshielding than the ones in polystyrene. The overlapping resonances in 0.4-2.7 ppm range are attributed to methine and methylene protons of ST-ST diads. The alkoxy protons of the ring substituted TSEs absorb in the in the same regions as in alkoxy-substituted styrenes. Thus, in the 13C NMR spectra of the ST-TSE copolymers the assignment of the peaks is as follows: 165-170 ppm (C=O), 145-155 ppm (substituted aromatic carbons), 130-145 ppm (quaternary carbons of both phenyls), 120-145 ppm (phenyl carbons), 110-125 ppm (CN), 50-60 ppm (methine and quaternary carbons of TSE, methoxy carbon), 45 ppm (ST methine) and 40-43 ppm (ST methylene). The broad carbon resonances are most likely due to the presence of both head-to-tail and head-to-head dyads. IR and NMR data showed that these are true copolymers, composed of both TSE and ST monomer units.

Physical Properties

The copolymers prepared in the present work are all soluble in ethyl acetate, THF, DMF and $CHCl_3$, and insoluble in methanol, heptane, and petroleum ether. They are amorphous and show no crystalline DSC endotherm. This behavior is similar to that of the copolymers of ring-unsubstituted methyl 2-cyano-3-phenyl-2-propenoate [13]. 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. Information on the degradation of the copolymers was obtained from thermogravimetric analysis. The decomposition products were not analyzed in this study, and the mechanism has yet to be investigated. Decomposition of all copolymers in air occurs rapidly in one stage in 300-400°C range.

CONCLUSION

Novel electrophilic trisubstituted ethylenes, ring-substituted methyl 2-cyano-3-phenyl-2-propenoates were prepared via a base catalyzed condensation of appropriate substituted benzaldehyde and methyl cyanoacetate. The copolymerization of the propenoates with styrene at equimolar monomer feed results in copolymers. The composition of the copolymers was calculated from nitrogen analysis and the structure was analyzed by IR, ^{1}H and ^{13}C NMR. The order of relative reactivity ($1/r_1$) for the monomers is:

3-CN (1.21) > 3-C_6H_5O (1.16) > 4-C_2H_5O (0.94) > 4-C_3H_7O (0.8305) > 4-C_4H_9O (0.616)

High glass transition temperature of the copolymers in comparison with that of polystyrene indicates a substantial decrease in chain mobility of the copolymer due to the high dipolar character of the trisubstituted monomer unit. The gravimetric analysis indicated that the copolymers decompose in 300-400°C range.

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