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Novel Copolymers of Styrene and Alkyl and Alkoxy Ring-Trisubstituted Methyl 2-Cyano-3-phenyl-2-propenoates

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Novel Copolymers of Styrene and Alkyl and Alkoxy Ring-Trisubstituted Methyl 2-Cyano-3-phenyl-2-propenoates

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Electrophilic trisubstituted ethylene monomers, akyl and alkoxy ring-trisubstituted methyl 2-cyano-3-phenyl-2-propenoates, $RC_6H_2CH{=}C(CN)CO_2CH_3$, (where R is 2,3-dimethyl-4-methoxy, 2,5-dimethyl-4-methoxy-, 2,3,4-trimethoxy-, 2,4,5-trimethoxy, 2,4,6-trimethoxy, and 2,4-dimethoxy-3-methyl), were synthesized by the piperidine catalyzed Knoevenagel condensation of ring-substituted benzaldehydes and methyl cyanoacetate, and characterized by CHN elemental analysis, IR, ^1H- and ^{13}C-NMR. Novel copolymers of the ethylenes and styrene were prepared at equimolar monomer feed composition by solution copolymerization in the presence of a radical initiator (AIBN) at 70°C. The composition of the copolymers was calculated from nitrogen analysis, and the structures were analyzed by IR, ^1H and ^{13}C NMR, GPC, DSC, and TGA. High T_g 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 ethylene monomer unit. The gravimetric analysis indicated that the copolymers decompose in the 283–306°C range.

Keywords trisubstituted ethylenes, radical copolymerization, styrene copolymers

Introduction

Previous studies showed that trisubstituted ethylenes containing substituents larger than fluorine have very low reactivity in radical homopolymerization due to polar and steric reasons. Although steric difficulties preclude homopolymerization of most tri- and tetrasubstituted olefins, their copolymerization with a monosubstituted alkene makes it possible to overcome these steric problems (1). Copolymerization of trisubstituted ethylenes (TSE, $CHR^1 = CR^2R^3$) having double bonds substituted with halo, cyano, and carbonyl groups and electron-rich monosubstituted ethylenes such as styrene, *N*-vinylcarbazole, and vinyl acetate (2, 3) show a tendency toward the formation of alternating copolymers.

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In our studies of the monomer structure-reactivity correlation in the radical copolymerization of TSE monomers we have prepared styrene copolymers with a number of ring-substituted methyl 2-cyano-3-phenyl-2-propenoates (4–10). In this paper, we report on styrene copolymers with alkyl and alkoxy ring-trisubstituted methyl 2-cyano-3-phenyl-2-propenoates, $RC_6H_2CH{=}C(CN)CO_2CH_3$, (where R is 2,3-dimethyl-4-methoxy, 2,5-dimethyl-4-methoxy, 2,3,4-trimethoxy, 2,4,5-trimethoxy, 2,4,6-trimethoxy, and 2,4-dimethoxy-3-methyl).

Experimental

General Procedures

Infrared spectra of the TSE monomers (NaCl plates) and polymers (KBr pellets) were determined with a Nicolet Avatar 360 FT-IR spectrometer. The melting points of the monomers and the glass transition temperatures (T_g), of the copolymers were measured by using a Polymer Laboratories model DSC STA 625. Thermal stability of the copolymers was measured by using a TA Instruments model TGA 2090. 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, a Model 410 refractive index detector, a linear ultrastyragel column and Millenium software. ^1H and ^{13}C-NMR spectra of 4–10% $CDCl_3$ solutions of monomers and polymers were obtained on a Bruker Omega AC-200 spectrometer. Elemental analyses were performed by Quantitative Technologies Inc. (New Jersey).

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Synthesis of Monomers

Monomer Synthesis. The TSE monomers were synthesized by Knoevenagel condensation (11) of a ring-substituted benzaldehyde with methyl cyanoacetate, catalyzed by base, piperidine.

$$RC_6H_2CHO + NCCH_2CO_2CH_3 \longrightarrow RC_6H_2CH{=}C(CN)CO_2CH_3$$

2,3-dimethyl-4-methoxy, 2,5-dimethyl-4-methoxy, 2,3,4-trimethoxy, 2,4,5-trimethoxy, 2,4,6-trimethoxy, and 2,4-dimethoxy-3-methylbezaldehydes, methyl cyanoacetate, and piperidine supplied from Aldrich Chemical Co., were used for monomer synthesis as received. The preparation procedure was essentially the same for all the 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 crystallization from 2-propanol. The preparation procedure and characterization of the TSE monomers, 2,4,5-trimethoxy, and 2,4,6-trimethoxy ring-substituted methyl (*E*)-2-cyano-3-phenyl-2-propenoates, was described earlier (12). The condensation reaction proceeded smoothly, yielding crystalline products, which were purified by conventional techniques.

Methyl (E)-2-cyano-3-(2,3-dimethyl-4-methoxyphenyl)-2-propenoate

Yield: 78%; mp 146°C; 1H-NMR δ 8.5 (s, 1H, CH=), 8.2, 6.7 (d, 2H, Ph), 3.8 (d, 6H, OCH_3), 2.1, 2.3 (d, 6H, CH_3); 13C-NMR δ 164 (CO), 162 (OPh), 154 (CH=), 139, 128, 123, 112, 111 (Ph), 116 (CN), 100 (>C=), 56 ($PhOCH_3$), 52 (OCH_3), 17, 11 (CH_3); IR (cm^{-1}) 3011 (m, C–H), 2214(m, CN), 1719 (s, C=O), 1650 (w, C=C), 1234 (w, C–O–CH_3), 798 (s, CH out of plane). Anal. calcd. for $C_{14}H_{15}NO_3$: C, 68.56%; H, 6.16%; N, 5.71%. Found: C, 69.70%; H, 6.26%; N, 5.84%.

Methyl (E)-2-cyano-3-(2,5-dimethyl-4-methoxyphenyl)-2-propenoate

Yield 64%; mp 113°C; 1H-NMR δ 8.6 (s, 1H, CH=), 7.3, 7.1 (d, 2H, Ph), 3.8 (d, 6H, OCH_3), 2.2, 2.3 (d, 6H, CH_3); 13C-NMR δ 164 (CO), 162 (OPh), 154 (CH=), 140, 129, 123, 112, 111 (Ph), 116 (CN), 100 (>C=), 56 ($PhOCH_3$), 52 (OCH_3), 20, 16 (CH_3); IR (cm^{-1}) 2940 (m, C–H), 2214 (m, CN), 1729 (s, C=O), 1650 (w, C=C), 1234 (w, C–O–CH_3), 758 (s, CH out of plane). Anal. Calcd. for $C_{14}H_{15}NO_3$: C, 68.56%; H, 6.16%; N, 5.71%. Found: C, 69.97%; H, 6.22%; N, 5.85%.

Methyl (E)-2-cyano-3-(2,3,4-trimethoxyphenyl)-2-propenoate

Yield 98%; mp 163°C; ^{1}H-NMR δ 8.4 (s, 1H, CH=), 3.8 (m, 3H, –OCH_3), 7.5, 6.9 (d, 2H, Ph); ^{13}C NMR δ 163 (C=O), 153 (Ph), 150 (HC=), 149, 142, 126, 113, 110 (Ph), 104 (C=), 116 (CN), 20, 17, 16 (CH_3); IR(KBr) 2966 (m, C-H), 2215 (m, CN), 1716 (s, C=O), 1263 (s, $COCH_3$), 769 (s, CH out of plane); Anal. Calcd. for $C_{14}H_{15}NO_5$: C, 60.64; H, 5.45; N, 5.05. Found: C, 62.08; H, 5.17; N, 5.16.

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Methyl (E)-2-cyano-3-(2,4-dimethoxy-3-methylphenyl)-2-propenoate

Yield 42.91%; mp 105°C; ^{1}H-NMR δ 8.5 (s, 1H, CH=), 6.8, 8.2 (d, 2H, Ph), 3.7–3.9 (d, 9H, –OCH_3), 2.1 (s, 3H, CH_3); ^{13}C-NMR δ 162, (C=O), 148 (HC=), 161, 160, 128, 120, 119, 107 (Ph), 98 (C=), 62, 59 (OCH_3), 8 (CH_3); IR(KBr) 2950 (m, C–H), 2214(m, CN), 1719 (s, C=O), 1200 (s, $COCH_3$), 794 (s, CH out of plane). Anal. Calcd. for $C_{14}H_{15}NO_4$: C, 64.36; H, 5.79; N, 5.36. Found: C, 64.24; H, 5.95; N, 5.29.

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 ambient temperature. Copolymers of the TSE and ST were prepared in 50-mL Pyrex screw-cap ampoules at an equimolar ratio of the monomer feed using 0.0045 mole/l of AIBN at an overall monomer concentration 2 mole/l in ethyl acetate (total volume 20 ml). The copolymerization was conducted at 70°C. After a predetermined time, the mixture was cooled to ambient temperature and precipitated dropwise in methanol. The crude copolymers were purified by reprecipitation from solution into an excess of methanol. Then, the copolymers were dried under reduced pressure at 60°C until constant weight. The composition of the copolymers was determined based on the nitrogen content.

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Results and Discussion

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 the 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 copolymerization experiments yielded 18.3% of polystyrene, when polymerized for 30 min.

Copolymerization

Copolymerization (Scheme 1) of the alkyl and methoxy ring-trisubstituted methyl 2-cyano-3-phenyl-2-propenoates with ST resulted in formation of copolymers (Table 1) with weight-average molecular masses 33.7×10^3 to 42.6×10^3 daltons. According to elemental analysis, 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 (Equation 1) of the terminal copolymerization model (1).

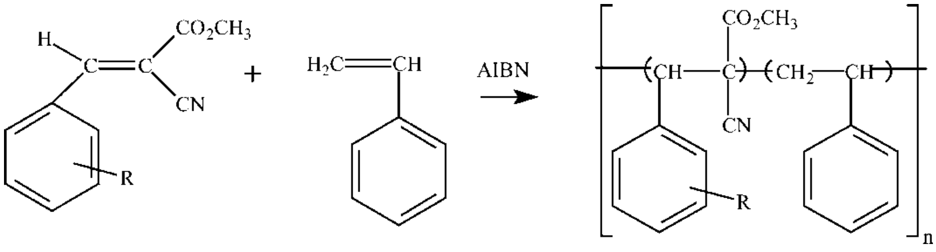
$$m_1/m_2 = [M_1](r_1[M_1] + [M_2])/[M_2]([M_1] + r_2[M_2]) \qquad (1)$$

m_1 and m_2 are the mole fractions of ST and TSE monomer units in the copolymer, respectively; $[M_1]$ and $[M_2]$ are the concentrations of ST and 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 (2) yields:

$$r_1 = m_1/m_2 - 1 \qquad (2)$$

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

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



Scheme 1. ST-TSE copolymer synthesis.

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Table 1
Copolymerization of styrene (M_1) and methyl 2-cyano-3-phenyl-2-propenoates $RC_6H_2CH{=}C(CN)CO_2CH_3$ (M_2)

R	Yield,[a] wt%	N wt%	m_2 in pol., mol%	$M_W \times 10^{-3}$, D	T_g, °C	Onset of, decomp. TGA, °C
2,3-Dimethyl-4-methoxy	20.4	1.67	14.91	35.1	140	283
2,5-Dimethyl-4-methoxy	20.7	1.95	18.03	33.7	157	289
2,3,4-Trimethoxy	30.2	2.00	19.73	42.6	135	302
2,4,5-Trimethoxy	20.1	1.65	15.42	35.4	146	293
2,4,6-Trimethoxy	20.5	1.18	10.23	38.6	118	295
2,4-Dimethoxy-3-methyl	34.6	2.14	20.92	41.2	134	306

[a] Polymerization time was 8 h.

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 non-rigorous kinetic treatment nevertheless allows estimation of the reactivity of a ST-ended polymer radical in reaction with electrophilic monomer. Thus the order of relative reactivity ($1/r_1$) and the tendency toward alternation of monomer units in the copolymer for the five TSE monomers is 2,4-dimethoxy-3-methyl (0.36) > 2,3,4-trimethoxy (0.33) > 2,5-dimethyl-4-methoxy (0.28) > 2,4,5-trimethoxy (0.22) > 2,3-dimethyl-4-methoxy (0.21) > 2,4,6-trimethoxy (0.13). 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.

Structure and Thermal Properties

The structures of ST-TSE copolymers were characterized by IR and NMR spectroscopy. IR spectra of the copolymers show overlapping bands in the 3200-2700 cm^{-1} region corresponding to C–H stretching vibrations. The spectra of the copolymers show weak cyano group absorption of the TSE monomer unit at 2235–2245 cm^{-1} (2220–2230 cm^{-1} in the monomer). Benzene rings of both monomers show ring stretching bands at 1497 and 1458 cm^{-1}, as well as a doublet 780, 690 cm^{-1}, associated with C–H out of plane deformations. Carbonyl groups show bands at 1742-1739 (C=O) and 1180-1180 cm^{-1} (C–O). ^{1}H-NMR spectra of the ST-TSE copolymers show a broad double peak in a 5.5–7.6 ppm region corresponding to phenyl ring protons. The resonance at 4.2-3.4 ppm is assigned to methoxy protons. The low and high field components of the 3.5-2.2 ppm peak is assigned to the overlapping resonances of the methine and methoxy protons of the TSE monomer unit in head-to-tail and head-to-head structures. Backbone ST protons removed further from cyano groups give rise to the absorption in 1.8–2.3 ppm with a maximum at 2.2 ppm overlapping with TSE methyl protons. The strong absorption in the 0.7–2.1 ppm range corresponds to ST backbone protons in ST-ST diads. The ^{13}C-NMR spectra also support the suggested skeletal structure of the copolymers. Thus, the assignment of the peaks as follows: 170-168 (C=O) 135–145 ppm (quarternary carbons of both phenyls), 120–145 ppm (phenyl carbons), 110–120 ppm (CN), 55-65 ppm (methine carbons of TSE and ST, and ST methylene). Methoxy group carbons are at 60 ppm, whereas methyl groups are at 10–15 ppm (CH_3). The IR and NMR data showed that these are true copolymers, composed of ST and TSE monomer units.

The copolymers prepared in the present work are all soluble in ethyl acetate, DMF, $CHCl_3$ and insoluble in methanol, ethyl ether, and heptane. They are amorphous and show no crystalline DSC endotherm. 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 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. The decomposition of all copolymers in nitrogen occurs rapidly in one stage in the 283–306°C range.

Conclusions

Electrophilic trisubstituted ethylene monomers, alkyl and alkoxy ring-trisubstituted methyl 2-cyano-3-phenyl-2-propenoates, were prepared via a piperidine-catalyzed condensation of appropriate trisubstituted benzaldehydes and methyl cyanoacetate. The copolymerization of the monomers with styrene resulted in copolymers, with the trisubstituted ethylene mole percent in the range 10–21 mol%. The compositions of the copolymers were calculated from nitrogen analysis and the structures were analyzed by IR, ^{1}H- and ^{13}C-NMR. High glass transition temperatures of the copolymers, 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 ethylene monomer unit. The gravimetric analysis indicated that the copolymers decompose in the range 283–306°C.

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