

Synthesis and copolymerization of halogen phenyl-substituted methyl 2-cyano-3-phenyl-2-propenoates with styrene

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Received: 9 February 1998/Revised version: 5 March 1998/Accepted: 5 March 1998

Summary

Halogen phenyl-substituted methyl 2-cyano-3-phenyl-2-propenoates, $\text{RC}_6\text{H}_4\text{CH}=\text{C}(\text{CN})\text{CO}_2\text{CH}_3$ (R= 2-fluoro, 3-fluoro, 2-bromo, and 3-bromo), were prepared by the piperidine catalyzed Knoevenagel condensation of corresponding substituted benzaldehydes and methyl cyanoacetate. Novel copolymers of the propenoates and styrene were prepared at equimolar monomer feed by solution copolymerization in the presence of a radical initiator. The order of relative reactivity ($1/r_1$) was $3\text{Br} (3.02) > 2\text{Br} (2.63) > 3\text{F} (1.84) > 2\text{F} (1.66)$. High glass transition temperatures of the copolymers compared that of polystyrene indicates a substantial decrease in chain mobility of the copolymers due to the high dipolar character of the trisubstituted ethylene monomer unit.

Introduction

Trisubstituted ethylenes (TSE) containing substituents larger than fluorine exhibit no tendency to undergo radical polymerization, due to 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 electrophilic 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).

In continuation of our studies of the monomer structure-reactivity correlation in radical copolymerization of TSE monomers (3–5), we prepared monohalogenated phenyl-substituted methyl 2-cyano-3-phenyl-2-propenoates, $\text{RC}_6\text{H}_4\text{CH}=\text{C}(\text{CN})\text{CO}_2\text{CH}_3$ where R is 2-fluoro (2F), 3-fluoro (3F), 2-bromo (2Br), and 3-bromo (3Br), and explored the feasibility of their copolymerization with styrene (ST).

Experimental

General procedures

Infrared spectra of the TSE monomers were obtained with a 1710 Perkin Elmer FT-IR spectrometer. Melting points of monomers and glass transition temperatures of the copolymers were measured using a DSC module of an STA 625 thermal analyzer (Polymer Laboratories, Inc.). ^1H and ^{13}C NMR were obtained on a Bruker WP270SY spectrometer. All NMR spectra were obtained on 10% solutions in CDCl_3 at ambient

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temperature. The molecular weights of polymers were determined relative to polystyrene standards in chloroform solution with sample concentrations 0.8% (wt/vol) by gel permeation chromatography 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, a Model 410 refractive index detector, and Millennium software. 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:

2-Fluorobenzaldehyde, 3-fluorobenzaldehyde, 2-bromobenzaldehyde, and 3-bromobenzaldehyde, 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 appropriately substituted benzaldehyde were mixed with N,N-dimethylformamide in an Erlenmeyer flask. A few drops of piperidine were added at the start of the reaction with stirring at room temperature. The product was isolated by filtration and purified by repeated recrystallizations from 2-propanol.

Methyl (*E*)-2-cyano-3-(2-fluorophenyl)-2-propenoate. Yield 57.00 %; m.p. 96°C; ¹H NMR δ 3.9 (s, 3H, -OCH₃), 7.1–7.7 (m, Ph-H), 8.3–8.5 (s, -CH=); ¹³C NMR δ 165 (C=O), 159 (HC=), 148,135,129,125,120,115 (Ph), 113 (CN), 105 (C=), 52 (CH₃); IR (NaCl) 2960 (m, C-H), 2223(m, CN), 1736 (s, C=O), 1234 (s, C-O-CH₃), 764 (s, C-H out of plane). Anal. Calcd for C₁₁H₈FNO₂: C, 64.44; H, 3.93; N, 6.83. Found: C, 65.12; H, 4.1; N, 7.21.

Methyl (*E*)-2-cyano-3-(3-fluorophenyl)-2-propenoate. Yield 86.33 %; m.p. 109°C; ¹H NMR δ 3.9 (s, 3H, -OCH₃), 7.2–7.7 (m, Ph-H), 8.2 (s, -CH=); ¹³C NMR δ 162 (C=O), 153 (HC=), 134, 131, 128, 120,116, 115 (Ph), 114 (CN), 104 (C=), 54 (CH₃); IR (NaCl): 2990 (m, C-H), 2234 (m, CN), 1740 (s, C=O), 1242 (s, C-O-CH₃), 969 (s, C-H out of plane). Anal. Calcd for C₁₁H₈FNO₂: C, 64.44; H, 3.9; N, 6.83. Found: C, 66.5; H, 3.9; N, 7.12.

Methyl (*E*)-2-cyano-3-(2-bromophenyl)-2-propenoate. Yield 66.30 %; m.p. 96°C; ¹H NMR δ 3.9 (s, 3H, -OCH₃), 7.3–7.7 (m, Ph-H), 8.1–8.2 (s, CH=); ¹³C NMR δ 162 (C=O), 154 (CH=), 134 (d), 132, 129, 128, 126 (Ph), 114 (CN), 107 (C=), 54 (-CH₃); IR (NaCl) 3025 (m, C-H), 2228(m, CN), 1736(C=O), 1265 (s, C-O-CH₃), 929 (s, C-H out of plane). Anal. Calcd for C₁₁H₈BrNO₂: C, 49.65; H, 3.03; N, 5.26. Found: C, 49.72; H, 2.96; N, 5.14.

Methyl (*E*)-2-cyano-3-(3-bromophenyl)-2-propenoate. Yield 88.10%; m.p. 115–116°C; ¹H NMR δ 3.9 (s, 3H, -OCH₃), 7.3–7.8 (m, Ph-H), 8.2 (s, CH=); ¹³C NMR δ 163 (C=O), 153 (=CH), 136,133(d), 130,128,123 (Ph), 115 (CN), 104 (C=), 53 (-CH₃); IR (NaCl) 2983 (m, C-H), 2229 (m, CN), 1738 (C=O), 1220 (s, C-O-CH₃), 753 (s, C-H out of plane). Anal. Calcd for C₁₁H₈BrNO₂: C, 49.65; H 3.03; N, 5.26. Found: C, 49.74; H, 3.04; N, 5.40.

Copolymerization

Styrene (ST) (Aldrich) was purified by washing with aqueous sodium hydroxide, drying and subsequent 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 r.t. Copolymers of the TSE monomers and ST were prepared in 25-mL Pyrex screw cap ampules at an equimolar ratio of the monomer feed using 0.0045 mol/L of AIBN at an overall monomer concentration 2 mole/L in 20 mL, of ethyl acetate. The copolymerization was conducted at 70°C. After 6 hrs the mixture was cooled to r.t. and precipitated dropwise in methanol with stirring. 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 precision of 0.1 wt%.

Results and discussion

Monomer Synthesis

TSE monomers were synthesized by Knoevenagel condensation (6) of a ring substituted benzaldehyde with an active hydrogen compound, methyl cyanoacetate, catalyzed by a base, piperidine, $\text{RC}_6\text{H}_4\text{CHO} + \text{NCCH}_2\text{CO}_2\text{CH}_3 \rightarrow \text{RC}_6\text{H}_4\text{CH}=\text{C}(\text{CN})\text{CO}_2\text{CH}_3$. 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 (7,8).

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. 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 a number-average molecular weight of 5×10^3 to 1.23×10^5 daltons.

Table 1. Copolymerization of styrene and halogen ring-substituted methyl 2-cyano-3-phenyl-2-propenoates, $\text{RC}_6\text{H}_4\text{CH}=\text{C}(\text{CN})\text{CO}_2\text{CH}_3$.

R	Yield, wt%	TSE, mol %	MW, $\times 10^{-3}$	T _g , °C
2-fluoro	8.2	38.4	102.7	260
3-fluoro	7.0	39.3	64.0	247
2-bromo	8.3	42.0	29.4	297
3-bromo	8.8	42.9	59.2	269

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),

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

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

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

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

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

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 four TSE monomers is 3Br (3.02) > 2Br (2.63) > 3F (1.84) > 2F (1.66), which is similar to the order of reactivity for chloro ring-substituted methyl 2-cyano-3-phenyl-2-propenoates (5), 3-chloro (6.67) > 2-chloro (4.76).

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 the 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. In the ring-halogenated TSE monomers, electron-withdrawing halogens increase the positive charge on the double bond. All, except for 2F, of the ring-substituted monomers were more reactive than the ring-unsubstituted methyl 2-cyano-3-phenyl-2-propenoate with $1/r_1 = 1.3$ (9). In an attempt to correlate relative reactivity, $1/r_1$ with polarity of the TSE double bond, we have calculated the charge distribution on the olefinic carbons by using HYPERCHEM software. The order of the atomic charges calculated at the planar optimized geometries (AM1) for C_α ($=C(CN)CO_2CH_3$) is 3F (-0.043) > 3Br (-0.045) > 2F (-0.051) > 2Br (-0.076), and for C_β (RPhC=) is 3-F (0.041) < 3Br (0.042) < 2F (0.048) < 2Br (0.050);

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 the charges on both olefinic carbons, C_α and C_β . 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 TSE monomer is possible. Thus, Borberly (9) 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.

The copolymers prepared in the present work are all amorphous powders, soluble in DMF, CHCl_3 and insoluble in methanol, heptane, and petroleum ether. High T_g of the copolymers (Table 1) in comparison with that of polystyrene ($T_g = 95^\circ\text{C}$) indicates substantial decrease in chain mobility of the copolymer due to the high dipolar character of the TSE structural units.

Acknowledgments

We are grateful to acknowledge that the project is partly supported by the research and equipment grants from National Science Foundation's DUE Grant (No. 9455681), Coating Industry Education Fund (CIEF), Chicago Society of Coatings Technology, the DePaul University Research and Quality of Instruction Councils, and Office of Sponsored Programs and Research. NAL was supported by the CIEF graduate fellowship.

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