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Novel Copolymers of Halogen Ring Substituted 2-Cyano-3-Phenyl-2-Propen- Amides and Styrene

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NOTES

NOVEL COPOLYMERS OF HALOGEN RING SUBSTITUTED 2-CYANO-3-PHENYL-2-PROPENAMIDES AND STYRENE

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ABSTRACT

Electrophilic trisubstituted ethylene monomers, halogen ring substituted 2-cyano-3-phenyl-2-propenamides, $RC_6H_4CH=C(CN)CONH_2$ (where R is *o*-Cl, *m*-Cl, *p*-Cl, *p*-Br, and *p*-F) were prepared by Knoevenagel condensation. Novel copolymers of the propenamides and styrene were prepared at equimolar monomer feed composition by solution copolymerization in the presence of a radical initiator at 80°C. The order of reactivity ($1/r_1$) for the monomers (M_1 =styrene) was *o*-Cl (1.42) > *p*-F (1.19) > *p*-Cl (0.70) > *m*-Cl (0.60) > *p*-Br (0.44).

INTRODUCTION

Trisubstituted ethylene (TSE) monomers containing substituents larger than fluorine exhibit no tendency to undergo radical polymerization due to kinetic consid-

erations superimposed on the thermodynamic factor responsible for the difficulty with 1,2-disubstituted ethylenes polymerize [1]. 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 electron-deficient TSE monomers having a double bond substituted with cyano, halo, and/or carbonyl groups via copolymerization with electron rich monosubstituted ethylenes [2]. In our studies of the monomer structure-monomer reactivity correlations in radical copolymerization of TSE monomers, it was of interest to prepare ring substituted 2-cyano-3-phenyl-2-propenamides, $RC_6H_4CH=C(CN)CONH_2$ (where R is *o*-Cl, *m*-Cl, *p*-Cl, *p*-Br, and *p*-F), and explore the feasibility of their copolymerization with styrene.

EXPERIMENTAL

General Procedures

Infrared spectra (KBr) were determined with a Perkin Elmer 1600 FT-IR spectrometer. Melting points of the monomers and Tg's 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 by GPC using a Waters Model 510 pump at an elution rate of 1.0 mL/min, a Model 410 refractive index detector, a linear ultrastyrigel column and Millenium software. 1H and ^{13}C NMR spectra of 4-10% $CDCl_3$ solutions of monomers were obtained on a Bruker AC-200 spectrometer. Elemental analyses were performed by Quantitative Technologies Incorporated (New Jersey).

Synthesis of Monomers

The preparation procedure was essentially the same for all the monomers. In a typical synthesis, equimolar amounts of 2-cyanoacetamide and an appropriate aldehyde were mixed with a small amount of DMF in an Erlenmeyer flask. Piperidine was added as a catalyst. The product was isolated and purified by crystallization from 2-propanol.

(*E*)-2-cyano-3-(2-chlorophenyl)-2-propenamide

Yield 47.8%; mp 169.6°C; 1H NMR d (ppm) 6.0 (s, 1H, amide), 6.3 (s, 1H, amide), 7.3-8.1 (m, 4H, phenyl), 8.8 (s, 1H, CH=); ^{13}C NMR d (ppm) 161.2 (C=O), 150.3 (CH=), 136.5, 133.4, 130.4, 130.3, 129.5, 127.4 (Ph), 116.3 (CN), 106.6 (C=); IR (KBr) 3478 (m, N-H), 3155 (m, C-H phenyl), 2217 (s, CN), 1702

(s, C=O). Anal. Calcd for $C_{10}H_7N_2OCl$: C, 58.13; H, 3.41; N, 13.56. Found: C, 57.46; H, 3.52; N, 13.35.

(E)-2-cyano-3-(3-chlorophenyl)-2-propenamide

Yield 18.5%; mp 208.5°C; 1H NMR d (ppm) 3.9 (s, 2H, amide), 7.4-7.9 (m, 4H, phenyl), 8.3 (s, 1H, CH=); ^{13}C NMR d 152.3 (CH=), 132.8, 131.9, 130.5, 129.7, 128.5 (phenyl); IR (KBr) 3472 (m, N-H), 3218 (m, C-H phenyl), 2211 (s, CN), 1700 (s, C=O). Anal. Calcd for $C_{10}H_7N_2OCl$: C, 58.13; H, 3.41; N, 13.56. Found: C, 58.05; H, 3.47; N, 12.96.

(E)-2-cyano-3-(4-chlorophenyl)-2-propenamide

Yield 65.9%; mp 208.7°C; 1H NMR d (ppm) 2.7 (s, 1H, amide), 2.9 (s, 1H, amide), 7.7-7.9 (q, 4H, phenyl), 8.3 (s, 1H, CH=); ^{13}C NMR d (ppm) 131.9, 129.7 (Ph), 95.1 (C=); IR (KBr) 3455 (m, N-H), 3161 (m, C-H phenyl), 2211 (s, CN), 1705 (s, C=O). Anal. Calcd for $C_{10}H_7N_2OCl$: C, 58.13; H, 3.41; N, 13.56. Found: C, 58.00; H, 3.49; N, 13.02.

(E)-2-cyano-3-(4-bromo)phenyl-2-propenamide

Yield 40.8%; mp 220.9°C; 1H NMR d (ppm) 5.7 (s, 1H, amide), 6.3 (s, 1H, amide), 7.6-7.8 (d, 4H, phenyl), 8.3 (s, 1H, CH=); ^{13}C NMR d (ppm) 161.8 (C=O), 152.5 (CH=), 133.4, 133.2, 128.0 (Ph), 116.5 (CN), 102.8 (C=); IR (KBr) 3432 (m, N-H), 3160 (m, C-H phenyl), 2215 (s, CN), 1708 (s, C=O). Anal. Calcd for $C_{10}H_7N_2OBr$: C, 47.84; H, 2.81; N, 11.16. Found: C, 48.00; H, 2.76; N, 11.07.

(E)-2-cyano-3-(4-fluorophenyl)-2-propenamide

Yield 19.5%; mp 160.0°C; 1H NMR d (ppm) 3.9 (s, 2H, amide), 7.3-7.8 (m, 2H, phenyl), 7.9-8.4 (m, 2H, phenyl), 8.3 (s, 1H, CH=); ^{13}C d (ppm) 132.7, 132.0 (Ph), 95.1 (C=); IR (KBr) 3470 (m, N-H), 3160 (m, C-H phenyl), 2215 (s, CN), 1700 (s, C=O). Anal. Calcd for $C_{10}H_7N_2OF$: C, 63.18; H, 3.71; N, 14.73. Found: C, 62.90; H, 3.78; N, 13.94.

Copolymerization

Styrene (ST) (Aldrich) was purified by washing with aqueous sodium hydroxide, drying and subsequently distilling at reduced pressure. Ethyl acetate (Aldrich) were 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 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 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

Lieberson and Kohn [3] has reported radical copolymerization of (α -cyanocinnamide and styrene in solution. We found that halogen ring substituted (α -cyanocinnamides, 2-cyano-3-phenyl-2-propenamides also form copolymers when copolymerized with styrene at equimolar feed ratios in ethyl acetate at 80°C in the presence of AIBN. The results of the copolymerization experiments are presented in Table 1.

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 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 of the terminal copolymerization model [1] adapted for the absence of TSE self-propagation ($k_{22}=0$, $r_2=0$) and at equimolar monomer feed ($[M_1]/[M_2]=1$), $r_1=m_1/m_2-1$ (m_1 and m_2 are mole fractions of styrene and TSE monomer units in the copolymer, respectively), or the equation for the relative reactivity of styrene radical k_{12}/k_{11} with TSE monomers: $1/r_1 = 1/[(m_1/m_2) - 1]$.

This nonrigorous kinetic treatment nevertheless allows estimation of the reactivity of a styrene-ended polymer radical in reaction with an electrophilic monomer [1]. The order of reactivity ($1/r_1$) for the five trisubstituted ethylene monomers is o -Cl (1.42) > p -F (1.19) > p -Cl (0.70) > m -Cl (0.60) > p -Br (0.44). The early copolymerization studies [1] showed that the tendency toward alternation of monomer units in the copolymer ($1/r_1$) increases as the difference in polarity between two monomers increases. Styrene has an electron-rich double bond whereas the TSE monomers have electron-poor double bond due to two electron withdrawing substituents, cyano and amide groups. In the ring-halogenated trisubstituted ethylene monomers, electron-withdrawing halogens increase the

TABLE 1. Copolymerization of Styrene (M_1) and Ring Substituted 2-cyano-3-phenyl-2-propenamides, $R-C_6H_4CH=C(CN)CONH_2$ (M_2)

R	Time, hr	Yield, M_2 in wt%	M_w mol%	T_g $\times 10^{-3}$	$^{\circ}C$
<i>o</i> -Cl	168	20.0	37.0	65.6	147
<i>m</i> -Cl	28	11.8	27.2	36.2	178
<i>p</i> -Cl	28	11.7	29.2	28.2	164
<i>p</i> -Br	144	31.4	23.5	44.0	220
<i>p</i> -F	168	26.1	35.2	41.2	158

positive charge on the double bond thus leading to an increase in the difference in polarity between two monomers. In an attempt to correlate relative reactivity, $1/r_1$ with the polarity of the trisubstituted ethylene double bond we have calculated (AM1) the atomic charge distribution by using HYPERCHEM software (AUTODESK Inc) PC-based software for $C_a (=C(CN)CONH_2)$, m -Cl (-0.022) > o -Cl (-0.062) > p -Br (-0.072) > p -Cl (-0.077) > p -F (-0.078) and C_b (PhC=), m -Cl (-0.003) < o -Cl (0.016) < p -Br (0.022) < p -Cl (0.026) < p -F (0.027). The relative reactivity, $1/r_1$, correlates better with the charge on C_a and C_b of the *para*-substituted monomers than with those of the *ortho*- and *meta*-substituted monomers. The correlation of the relative reactivity of *p*-F, *p*-Cl, and *p*-Br monomers with the charge distribution on the double bond reflects on the direct relation between the monomer reactivity and halogen electronegativity.

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