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Novel Copolymers of Styrene and Halogen Ring-Substituted 2-Cyano-*N,N*-Dimethyl-3-Phenyl-2-Propenamides

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Electrophilic trisubstituted ethylene monomers, halogen ring-substituted 2-cyano-*N,N*-dimethyl-3-phenyl-2-propenamides, $RC_6H_4CH{=}C(CN)CON(CH_3)_2$ (where R is 2-Br, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 2-F, 3-F, 4-F), were synthesized by potassium hydroxide catalyzed Knoevenagel condensation of ring-substituted benzaldehydes and *N,N*-dimethyl cyanoacetamide, and characterized by CHN elemental analysis, IR, ^{1}H- 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, ABCN at 70°C. The composition of the copolymers was calculated from nitrogen analysis, and the structures were analyzed by IR, ^{1}H 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 300–450°C range.

Keywords: trisubstituted ethylenes; radical copolymerization; styrene copolymers

1 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. In continuation of our studies of the monomer structure-reactivity correlation in the radical copolymerization of TSE monomers (4–6), we have prepared novel halogen ring-substituted 2-cyano-*N,N*-dimethyl-3-phenyl-2-propenamides, $RC_6H_4CH{=}C(CN)CON(CH_3)_2$, where R is 2-Br, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 2-F, 3-F, 4-F, and explore the feasibility of their copolymerization with styrene.

2 Experimental

2.1 General Procedures

Infrared spectra of the TSE monomers (KBr 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 TA Instruments model DSC 2010. 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 THF solutions with sample concentrations about 3–5 mg/ml by gel permeation chromatography (GPC) using a Alltech Model 426 HPLC pump at an elution rate of 1.0 ml/min, a Viscotek TDA 302 detector, a Viscotek Model 2501 UV detector, a linear ultrastyragel column and OminiSEC software. ^{1}H- and ^{13}C-NMR spectra of 4–10% $CDCl_3$ solutions of monomers and polymers were obtained on a Bruker Avance 300 MHz spectrometer. Elemental analyses were performed by Quantitative Technologies Inc., NJ.

2.2 Synthesis of Monomers

2-Br, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 2-F, 3-F, and 4-F-substituted benzaldehydes, *N,N*-dimethyl cyanoacetamide, supplied from

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Aldrich Chemical Co., were used for monomer synthesis as received. The preparation procedure was essentially the same for all of the TSE monomers. In a typical synthesis, equimolar amounts of *N,N*-dimethyl cyanoacetamide and an appropriate ring-substituted benzaldehyde were mixed in a vial with a screw-on top. The vial was heated in a hot water bath until the mixture formed a solution followed by the addition of about one drop of a KOH solution. The crystalline product of the reaction was isolated by filtration and purified by recrystallization from 2-propanol.

2.3 2-Cyano-N,N-dimethyl-3-(2-bromophenyl)-2-propenamide

Yield: 67%; mp 132°C; ^{1}H-NMR δ 3.2 (s, 6H, ($N(CH_3)_2$), 7.3–7.5 (m, 4H, phenyl); 8.3 (s, 1H, CH=); ^{13}C-NMR δ 38, 39 ($N(CH_3)_2$), 107 (=$\underline{C}$(CN)CO), 115 (CN), 123, 128, 130, 131, 132, 138 (phenyl), 152 (CH=), 164 (C=O); IR (NaCl): 3059, 2944 (m, C-H), 2256 (w, CN), 1655 (s, C=O), 816, 739 (m, C-H out-of-plane bending). Anal. Calcd. for C, 51.64; H, 3.97; N, 10.04; Found: C, 46.45; H, 3.86; N, 9.93.

2.4 2-Cyano-N,N-dimethyl-3-(3-bromophenyl)-2-propenamide

Yield: 53%; mp 143; ^{1}H-NMR δ 3.1 (s, 6H, ($N(CH_3)_2$), 7.4, 7.5, 7.7 (m, 4H, phenyl); ^{13}C-NMR δ 38 ($N(CH_3)_2$), 107 (=$\underline{C}$(CN)CO), 116 (CN), 123, 130, 137 (phenyl), 151 (CH=), 164 (C=O); IR (NaCl): 2939 (m, C-H), 2256 (w, CN), 1660 (s, C=O), 736 (m, C-H out-of-plane bending). Anal. Calcd. for C, 51.64; H, 3.97; N, 10.04; Found: C, 48.78; H, 3.77; N, 9.88.

2.5 2-Cyano-N,N-dimethyl-3-(4-bromophenyl)-2-propenamide

Yield: 67%; mp 143°C; ^{1}H-NMR δ 3.1 (d, 6H, ($N(CH_3)_2$), 7.5, 7.6 (m, 4H, phenyl), 8.2 (s, 1H, CH=); ^{13}C-NMR δ 38 ($N(CH_3)_2$), 107 (=$\underline{C}$(CN)CO), 116 (CN), 131, 132 (phenyl), 151 (CH=), 163 (C=O); IR (NaCl): 2938 (m, C-H), 2216 (w, CN), 1655 (s, C=O), 823 (m, C-H out-of-plane bending). Anal. Calcd. for C, 51.64; H, 3.97; N, 10.04; Found: C, 49.83; H, 3.66; N, 9.93.

2.6 2-Cyano-N,N-dimethyl-3-(2-chlorophenyl)-2-propenamide

Yield: 73%; mp 109°C; ^{1}H-NMR δ 2.9 (s, 6H, ($N(CH_3)_2$), 7.1, 7.2, 7.4, 8.0 (m, 4H, phenyl), 8.3 (s, 1H, CH=); ^{13}C-NMR δ 36, 38 ($N(CH_3)_2$), 107 (=$\underline{C}$(CN)CO), 116 (CN), 127, 130, 132, 135 (phenyl), 149 (CH=), 164 (C=O); IR (NaCl): 2937 (m, C-H), 2220, (w, CN), 1657 (s, C=O), 756 (m, C-H out-of-plane bending). Anal. Calcd. for C, 61.42; H, 4.72; N, 11.94; Found: C, 56.73; H, 4.58; N, 11.52.

2.7 2-Cyano-N,N-dimethyl-3-(3-chlorophenyl)-2-propenamide

Yield: 64%; mp 112°C; ^{1}H-NMR δ 3.0, 3.2 (d, 6H, ($N(CH_3)_2$), 7.3, 7.8 (m, 4H, phenyl), 8.3 (s, 1H, -CH=); ^{13}C-NMR δ 36, 38 (N-$(CH_3)_2$), 106 (=$\underline{C}$(CN)CO), 116 (CN), 129, 130, 131, 138 (phenyl), 151 (-CH=), 164 (C=O); IR (NaCl): 2940 (m, C-H), 2255 (w, CN), 1695 (s, C=O), 788, 735 (m, C-H out-of-plane bending). Anal. Calcd. for C, 61.42; H, 4.72; N, 11.94; Found: C, 55.36; H, 4.05; N, 10.37.

2.8 2-Cyano-N,N-dimethyl-3-(4-chlorophenyl)-2-propenamide

Yield: 68%; mp 132°C; ^{1}H-NMR δ 3.0, 3.2 (d, 6H, ($N(CH_3)_2$), 7.3, 7.9 (m, 4H, phenyl), 8.2 (s, 1H, CH=); ^{13}C-NMR δ 38 ($N(CH_3)_2$), 107 (=C(CN)CO), 116 (CN), 127, 129, 131, 137 (phenyl), 151 (CH=), 164 (C=O); IR (NaCl): 2936 (m, C-H), 2211, 2242 (w, CN), 1653 (s, C=O), 822 (m, C-H out-of-plane bending). Anal. Calcd. for C, 61.42; H, 4.72; N, 11.94; Found: C, 59.68; H, 4.43; N, 10.2.

2.9 2-Cyano-N,N-dimethyl-3-(2-fluorophenyl)-2-propenamide

Yield: 84%; mp 78°C; ^{1}H-NMR δ 3.1 (d, 6H, ($N(CH_3)_2$), 7.2, 7.8 (m, 4H, phenyl), 8.1 (s, 1H, CH=); ^{13}C-NMR δ 38 ($N(CH_3)_2$), 108 (=$\underline{C}$(CN)CO), 116 (CN), 129, 131, 132, 133 (phenyl), 151 (CH=), 165 (C=O); IR (NaCl): 2941 (m, C-H), 2249 (w, CN), 1663 (s, C=O), 765 (m, C-H out-of-plane bending). Anal. Calcd. for C, 66.05; H, 5.08; N, 12.84; Found: C, 61.97; H, 4.38; N, 12.32.

2.10 2-Cyano-N,N-dimethyl-3-(3-fluorophenyl)-2-propenamide

Yield: 71%; mp 127°C; ^{1}H-NMR δ 3.1 (d, 6H, ($N(CH_3)_2$), 7.1, 7.2, 7.4, 7.6 (m, 4H, phenyl), 7.9 (s, 1H, CH=); ^{13}C-NMR δ 35, 38 ($N(CH_3)_2$), 107 (=$\underline{C}$(CN)CO), 117 (CN), 127, 131, 140, 144 (phenyl), 152 (CH=), 164 (C=O); IR (NaCl): 2939 (m, C-H), 2257 (w, CN), 1664 (s, C=O), 787 (m, C-H out-of-plane bending). Anal. Calcd. for 66.05; H, 5.08; N, 12.84; Found: C, 64.97; H, 4.58; N, 11.02.

2.11 2-Cyano-N,N-dimethyl-3-(4-fluorophenyl)-2-propenamide

Yield: 85%; mp 124°C; ^{1}H-NMR δ 3.1 (d, 6H, ($N(CH_3)_2$), 7.1, 7.8 (m, 4H, phenyl), 8.2 (s, 1H, CH=); ^{13}C-NMR δ 38 ($N(CH_3)_2$), 109 (=$\underline{C}$(CN)CO), 115 (CN), 117, 126, 131, 144 (phenyl), 151 (CH=), 164 (C=O); IR (NaCl): 2936 (m, C-H), 2213 (w, CN), 1649 (s, C=O), 838 (m, C-H out-of-plane bending). Anal. Calcd. for 66.05; H, 5.08; N, 12.84; Found: C, 65.05; H, 4.61; N, 11.83.

2.12 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. 1,1′-Azobis(cyclohexanecarbonitrile) (ABCN) (Aldrich) was recrystallized twice from ethyl alcohol and then dried under reduced pressure at ambient temperature. Copolymers of the TSE monomers and ST were prepared in 25-ml Pyrex screw cap ampoules at equimolar ratio of the monomer feed using 0.0045 mole/L of ABCN at an overall monomer concentration 2 mole/L in 20 ml of ethyl acetate. The copolymerization was conducted at 70°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.

3 Results and Discussion

3.1 Monomer Synthesis

The TSE monomers were synthesized by Knoevenagel condensation (7) of a ring-substituted benzaldehyde with *N,N*-dimethyl cyanoacetamide, catalyzed by a base, KOH.

$$RC_6H_4CHO + NCCH_2CON(CH_3)_2 \longrightarrow RC_6H_4CH{=}C(CN)CON(CH_3)_2 + H_2O$$

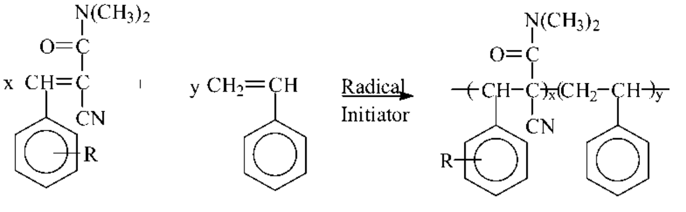
The condensation reaction proceeded smoothly, yielding crystalline or liquid products, which were purified by conventional techniques.

3.2 Homopolymerization

An attempted homopolymerization of the TSE monomers in the presence of ACBN 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 min.

3.3 Copolymerization

Copolymerization (Scheme 1) of halogen ring-substituted 2-cyano-*N,N*-dimethyl-3-phenyl-2-propenamides with ST resulted in formation of copolymers (Table 1) with weight-average molecular masses 11×10^3 to 17×10^3 daltons. According to elemental analysis, a significant amount of TSE monomer is present in the copolymers, which is indicative of relatively high reactivity of the monomers towards ST.



Sch. 1. ST-TSE copolymer synthesis. R = 2-Br, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 2-F, 3-F, 4-F.

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):

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

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 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 ($[M]_1/[M_2] = 1$), the above equation yields:

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

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

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

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 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 seven TSE monomers is 4-Br (0.45) > 3-Cl (0.40) > 2-Cl (0.39) > 2-F (0.38) > 3-Br (0.37) > 4-Cl (0.34) = 3-F (0.34) > 4-F (0.33) > 2-Br (0.20). 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.

3.4 Structure and Thermal Properties

The structure of copolymers was characterized by IR and NMR spectroscopy. A comparison of the spectra of the copolymers, TSE and polystyrene shows that the reaction between

Table 1. Copolymerization of styrene (M_1) and 2-cyano-*N,N*-dimethyl-3-(R-phenyl)-2-propenamides, $RC_6H_4CH{=}C(CN)CON(CH_3)_2$ (M_2)

						TGA			
R	Yield[a], wt%	Nitrogen, wt%	M_2 in copol., mol%	$M_w \times 10^{-3}$, D	T_g, °C	Onset of decom., °C	10 wt% loss, °C	50% wt loss, °C	Residue, wt%
2-Br	13	3.12	31.1	15	147	300	311	350	6
3-Br	18	4.20	41.9	14	148	293	300	335	8
4-Br	19	4.55	45.4	17	168	288	304	337	11
2-Cl	21	4.64	38.9	12	164	292	305	334	7
3-Cl	12	4.69	39.3	11	169	300	309	335	4
4-Cl	21	4.37	36.6	17	164	298	307	336	4
2-F	18	4.69	36.6	15	166	300	309	336	7
3-F	16	4.48	34.9	14	148	292	303	329	4
4-F	22	4.37	34.1	17	148	297	306	334	4

[a] Polymerization time was 7 h.

ST and TSE monomers is a copolymerization. IR spectra of copolymers show overlapping bands in 2800–3100 cm^{-1} region corresponding to C-H vibrations, weak cyano group absorption in 2218–2230 cm^{-1}, strong absorption of carbonyl group in 1640–1642 cm^{-1}, and strong doublet absorptions around 698–699, 757–759 cm^{-1} associated with benzene ring out-of-plane bending. Polystyrene shows absorptions at 2927 cm^{-1} (C-H) and 758, 699 cm^{-1} (out-of-plane bending).

All NMR spectra show broad resonance signals. Broadening of the NMR signals in the spectra of the copolymers is associated with head-to-tail and head-to-head structures, which are formed through the attack of a styrene-ended radical to both sides of the TSE monomers. It was demonstrated that both head-to-head and head-to-tail structures of ST-TSE dyads exist in the structure of copolymers of styrene and 2-phenyl-1,1-dicyanoethene (8). In all ^{1}H-NMR spectra of copolymers, a broad signal region at 6.0–6.7 ppm is assigned with the phenyl ring protons of TSE, an adjacent higher broad signal region at 6.7–7.5 ppm is assigned with the phenyl ring protons of ST. The broad resonance in 3.5–2.2 ppm region is assigned to the overlapping resonances of the methine of TSE monomer unit in head–to-tail and head-to-head ST methine protons in TSE-ST dyads. The TSE $N(CH_3)_2$ protons absorb in 2.9–3.2 ppm range. A broad overlapping signals in 0.8–2.4 ppm are corresponding to ST methylene and methine protons in ST-ST dyads.

The ^{13}C-NMR spectra also support the suggested skeletal structure of copolymers. The assignments of the peaks are as follows (ppm): 170–173 (C=O), 145, 120–134 (aromatic carbons), 116 (CN), 68–70 (C-O), 42–49 (methine, methylene and quaternary carbons), 36 ($N(CH_3)_2$). The IR and NMR data showed that these are true copolymers, composed with both ST and TSE monomer units.

The copolymers prepared in the present work are all soluble in acetone, methylene chloride and insoluble in methanol, petroleum ether. High T_g of the copolymers (Table 1) in comparison with that of polystyrene ($T_g = 95°C$) indicates a substantial decrease of chain mobility of the copolymer due to high dipolar character of the structural unit. Information on the decomposition of the copolymers was obtained from thermogravimetric analysis. The decomposition of all copolymers in nitrogen occurs rapidly in a one-step degradation in the 300–450°C range. The decomposition products were not analyzed in this study, and the mechanism has yet to be investigated.

4 Conclusions

Halogen ring-substituted 2-cyano-*N,N*-dimethyl-3-phenyl-2-propenamides were prepared via a base-catalyzed condensation of appropriate substituted benzaldehydes and *N,N*-dimethyl cyanoacetamide. The copolymerization of TSE with styrene resulted in statistical copolymers, with the TSE mole percent in the range 31–45%. 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 300–450°C.

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