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NOVEL COPOLYMERS OF TRISUBSTITUTED ETHYLENES WITH STYRENE. I. 2-HALOPHENYL-1,1-DICYANOETHYLENES

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ABSTRACT

Electrophilic trisubstituted ethylene monomers, 2-halophenyl-1,1-dicyanoethylenes, $\text{RC}_6\text{H}_4\text{CH}=\text{C}(\text{CN})_2$ (where R is *o*-Cl, *m*-Cl, *p*-Cl, *p*-Br, and *p*-F) were prepared and copolymerized with styrene. The monomers were synthesized by the piperidine catalyzed Knoevenagel condensation of ring-substituted benzaldehydes and malononitrile, and characterized by CHN elemental analysis, IR, ¹H and ¹³C-NMR. All the ethylenes 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, ¹H and ¹³C-NMR. The order of relative reactivity ($1/r_1$) for the monomers is *p*-Cl (14.8) > *m*-Cl (2.67) > *o*-Cl (1.82) > *p*-Br (1.52) > *p*-F (1.36). High T_g 's of the copolymers (> 150°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.

Key Words: Trisubstituted ethylenes; Radical copolymerization; Styrene copolymers.

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INTRODUCTION

Trisubstituted ethylenes (TSE, $R^1CH=CR^2R^3$) containing substituents larger than fluorine exhibit no tendency to undergo radical polymerization via double bond. This is 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. Hall *et al.*, in pioneering studies on copolymerization of electron-poor TSE monomers showed that they copolymerize readily with monosubstituted electron-rich monomers like styrene, vinyl acetate, vinyl ethers, and *N*-vinylcarbazole [2]. 2-Phenyl-1,1-dicyanoethene (PDE) was copolymerized by the radical initiation with styrene, vinyl acetate, vinyl ethers, and *N*-vinylpyrrolidone [3]. Monomer reactivity of 1,1-dicyanoethenes, *b*-substituted with 3-cyclohexenyl, 5-norbornenyl, 1-naphthyl, 3-pyridinyl, was estimated in radical copolymerization with styrene at equimolar monomer feed [4].

In continuation of our studies of the monomer structure-reactivity correlation in the radical copolymerization of TSE monomers [5, 6], we have prepared 2-(halophenyl)-1,1-dicyanoethylenes, $RC_6H_4CH=C(CN)_2$ (where R is *o*-Cl, *m*-Cl, *p*-Cl, *p*-Br, and *p*-F), and explore the feasibility of their copolymerization with styrene (ST).

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, the glass transition temperatures (T_g), and the thermal stability of the copolymers were measured by using a DSC-TGA module of a STA 625 thermal analyzer (Polymer Laboratories, Inc.). 1H and ^{13}C NMR were obtained on a Bruker WP270SY spectrometer operating at 200.13 MHz for 1H and 50.33 MHz for ^{13}C . All NMR spectra were obtained on 10% solutions in $CDCl_3$ at ambient temperature. 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 using a Waters Model 510 pump at an elution rate of 1.0 ml/min; a Model 410 refractive index detector; phenogel columns in series: 500, 10^3 , and 10^4 Å; and Millennium software. Elemental analyses were performed by Quantitative Technologies Inc., New Jersey.

Synthesis of Monomers

2-Chlorobenzaldehyde (98%), 3-chlorobenzaldehyde (97%), 4-chlorobenzaldehyde (97%), 4-bromobenzaldehyde (97%), 4-fluorobenzaldehyde (97%), malononitrile (99%), DMF, and piperidine (99%) supplied from 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 malononitrile 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.

2-(2-Chlorophenyl)-1,1-dicyanoethylene

Yield: 79.0%; mp 96°C, lit. 96 [7]; ^1H NMR δ 8.3 (s, CH=), 8.2–7.2 (m, 4H, Ph); ^{13}C NMR δ 158-125 (Ph), 115-110 (CN), 86 (=C(CN)₂), 77 (CH=); IR 3048 (m, C-H, Ph), 2227 (m, CN), 1650 (m, C=C), 757 (s, CH out of plane). Anal. Calcd. for C₁₀H₅N₂Cl: C, 63.68%; H, 2.67%; N, 14.85. Found: C, 63.50%; H, 2.65%; N, 14.87.

2-(3-Chlorophenyl)-1,1-dicyanoethylene

Yield: 51.8%; mp 120°C, lit. 117 [7]; ^1H NMR δ 8.3 (s, CH=), 8.2–7.2 (m, Ph); ^{13}C NMR δ 158-125 (Ph), 115-110 (CN), 86 (=C(CN)₂), 77 (CH=); IR 3066 (m, C-H, Ph), 2226 (s, CN), 1650 (m, C=C), 760 (s, CH out of plane). Anal. Calcd. for: C₁₀H₅N₂Cl: C, 63.68%; H, 2.67%; N, 14.85%. Found: C, 63.50%; H, 2.85%; N, 14.86%.

2-(4-Chlorophenyl)-1,1-dicyanoethylene

Yield: 90.3%; mp 163°C, lit. 163 [7]; ^1H NMR δ 8.3 (s, CH=), 8.2–7.2 (m, phenyl); ^{13}C NMR δ 158-125 (phenyl), 115-110 (CN), 86 (=C(CN)₂), 77 (CH=); IR 3034 (m, C-H phenyl), 2226 (m, CN), 1650 (m, C=C), 779 (s, CH out of plane). Anal. Calcd. for C₁₀H₅N₂Cl: C, 63.68%; H, 2.67%; N, 14.85%. Found: C, 63.64%; H, 2.63%; N, 14.86%.

2-(4-Bromophenyl)-1,1-dicyanoethylene

Yield: 78.5%; mp 164°C; ^1H NMR δ 8.3 (s, CH=), 8.2–7.2 (m, phenyl); ^{13}C NMR δ 158-125 (phenyl), 115-112 (CN), 86 (=C(CN)₂), 77 (CH=); IR 3031 (m, C-H phenyl), 2227 (m, CN), 1651 (m, C=C), 775 (s, CH out of plane). Anal.

Calcd. for: C₁₀H₅N₂Br: C, 51.58%; H, 2.16%; N, 12.03%. Found: C, 51.39%; H, 2.13%; N, 11.90%.

2-(4-Fluorophenyl)-1,1-dicyanoethylene

Yield: 53.8%; mp 128°C, lit. 129 [8]; ¹H NMR δ 8.5 (s, CH=), 8.2–7.2 (m, phenyl); ¹³C NMR δ 158–125 (phenyl), 115–112 (CN), 86 (=C(CN)₂), 77 (CH=); IR 3041 (m, C-H phenyl), 2230 (m, CN), 1651 (m, C=C), 760 (s, CH out of plane). Anal. Calcd. for C₁₀H₅N₂F: C, 69.77%; H, 2.93%; N, 16.27%. Found: C, 69.77%; H, 3.17%; N, 16.13%.

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 ethanol and then dried under reduced pressure at ambient 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 of 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

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



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

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

Copolymerization

Copolymerization of the 2-halophenyl-1,1-dicyanoethylenes with ST resulted in formation of copolymers (Table 1) with weight-average molecular weights of 5.0×10^3 to 118×10^3 . 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]:

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

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:

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

Table 1. Copolymerization of Styrene (M_1) and 2-Halophenyl-1,1-dicyanoethylenes, $RC_6H_4CH=C(CN)_2$ (M_2)

R (M_2)	Yield ^a (wt%)	Nitrogen (wt%)	m_2 in copolymer (mol%)	$M_w \times 10^{-3}$ (daltons)	T_g (°C)
o-Cl	16.3	8.05	39.5	37.7	162
m-Cl	19.6	8.44	42.1	57.6	202
p-Cl	26.6	9.34	48.4	62.5	201
p-Br	41.5	6.90	37.6	4.9	188
p-F	19.5	7.93	36.5	118	158

^aPolymerization time was 5 hours.

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 nonrigorous kinetic treatment nevertheless allows estimation of the reactivity of a styrene-ended polymer radical in reaction with electrophilic monomer [1]. The order of relative reactivity ($1/r_1$) for the five TSE monomers is p -Cl (14.8) > m -Cl (2.67) > o -Cl (1.82) > p -Br (1.52) > p -F (1.36). 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. In the halophenyl TSEs, electron-withdrawing halogens increase the positive charge on the double bond. Indeed, all of the TSE monomers were more reactive than the ring unsubstituted 2-phenyl-1,1-dicyanoethylene with $1/r_1 = 1.25$ [3]. 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. It has been demonstrated that both head-to-tail and head-to-head structures of styrene-(2-phenyl-1,1-dicyanoethylene) dyads exist in the copolymer [10]. 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 structure of ST-TSE copolymers was characterized by IR and NMR spectroscopy. IR spectra of the copolymers show overlapping bands in 3800-2800 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 2240 cm^{-1} (2230 cm^{-1} in the monomer). Benzene rings of both monomers show ring stretch-

ing bands at 1495 and 1456 cm^{-1} , as well as a doublet 770, 690 cm^{-1} , associated with C-H out of plane deformations. These bands were found also in copolymers of 2-phenyl-1,1-dicyanoethylene with vinyl acetate [3] and *N*-vinyl-2-pyrrolidone [11]. ^1H NMR spectra of the ST-TSE copolymers show a broad double peak in a 5.8-8.0 ppm region corresponding to phenyl ring protons. The resonance at 3.2-3.8 ppm is assigned to ST backbone protons in the close proximity of in ST-TSE dyad or in ST centered TSE-ST-TSE triads. The low and high field components of the 2.2-3.2 ppm peak is assigned to the overlapping resonances of the methine proton of the TSE monomer unit in head-to-tail and head-to-head structures [10]. Backbone ST protons removed further from dicyano groups give rise to the absorption in 1.8-2.3 ppm with a maximum at 2.2 ppm. 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: 137-147 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). The broad carbon resonances are due to presence of both head-to-tail and head-to-head dyads as discussed in more detailed assignment of ^1H and ^{13}C NMR spectra of 2-phenyl-1,1-dicyanoethylene-ST copolymers [10].

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 ($T_g = 95^\circ\text{C}$) indicates substantial decrease in chain mobility of the copolymer due to the high dipolar character of the TSE structural units. 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 copolymers of electrophilic trisubstituted 2-(halophenyl)-1,1-dicyanoethylenes and styrene were prepared by radical copolymerization at equimolar monomer feed. The composition of the copolymers was calculated from nitrogen analysis. IR and NMR data showed that these are true copolymers, composed of both TSE and ST monomer units. The order of relative reactivity ($1/r_1$) for the TSE monomers is *p*-Cl (14.8) > *m*-Cl (2.67) > *o*-Cl (1.82) > *p*-Br (1.52) > *p*-F (1.36).

High T_g of the copolymers indicates substantial decrease in chain mobility of the copolymer due to the high dipolar character of the TSE structural units. The thermal gravimetric analysis indicated that the copolymers decompose in 300-400°C range.

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