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Novel Copolymers of Styrene and Some Halogen Ring-substituted 2-Phenyl-1,1-dicyanoethylenes

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Novel copolymers of trisubstituted ethylene monomers, ring-substituted 2-phenyl-1,1-dicyanoethylenes, $RC_6H_3CH{=}C(CN)_2$ (where R is 2-bromo,3-bromo, 3-chloro, 2,3-dichloro, 2-chloro-6-fluoro, 2,6-difluoro, 3,4-difluoro, and 3,5-difluoro) 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 200–800°C range.

Keywords: Trisubstituted ethylenes, radical copolymerization, styrene copolymers

1. Introduction

Trisubstituted ethylenes (TSE, $CHR^1{=}CR^2R^3$) continue to attract attention of polymer chemists as reactive comonomers and models for mechanistic studies. It was shown that electrophilic tri- and tetrasubstituted olefins are particularly useful in delineating the transition from radical chemistry to ionic chemistry (1). Previous studies showed that TSE 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 (2). Copolymerization of TSE having double bonds substituted with halo, cyano, and carbonyl groups and electron-rich monosubstituted ethylenes such as styrene, *N*-vinylcarbazole, and vinyl acetate (3–5) show a tendency toward the formation of alternating copolymers.

Ring–unsubstituted 2-phenyl-1,1-dicyanoethylene was copolymerized with styrene (6), vinyl ethers (7), methyl methacrylate (8), and *N*-vinyl-2-pyrrolidone (9). In relation to applications, piezoelectric activity was observed in a copolymer of 1,1-dicyanoethylene (vinyledene cyanide) and vinyl acetate (10). Unlike fluoropolymers, this copolymer is amorphous with high T_g of 178°C and has an alternating monomer unit structure. The copolymer has an impedance similar to that of the human body and has been suggested for medical applications as an ultrasonic transducer (11). When a high electric field is imposed to the copolymer film near its glass transition temperature, a thin fiber-like assembly about 10 nm thick appears on the surface (12). This behavior in electrical field (piezoelectrical and dielectrical) has been attributed to a strong dipole moment of nitrile groups and the presence of free volume which is able to abate electrostatic interactions between vinyl acetate dipoles and facilitating orientation of these dipoles in the direction of the applied field (13).

In continuation of our studies of the monomer structure-reactivity correlation in the radical copolymerization of ring-substituted 2-phenyl-1,1-dicyanoethylene monomers (14,15) we have prepared halogen ring-substituted 2-phenyl-1,1-dicyanoethylenes, $RC_6H_3CH{=}C(CN)_2$ (where R is 2-bromo, 3-bromo, 3-chloro, 2,3-dichloro, 2-chloro-6-fluoro, 2,6-difluoro, 3,4-difluoro, and 3,5-difluoro), and explore the feasibility of their copolymerization with styrene (ST).

2. Experimental

2.1. *General procedures*

Infrared spectra of the TSE monomers (NaCl plates) and polymers (KBr pellets) were determined with a Nicolet

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Avatar 360 FT-IR spectrometer. The melting points of the monomers and the glass transition temperatures (T_g) of the copolymers were measured with TA (Thermal Analysis, Inc.) Models 2010 and Q10 differential scanning calorimeters (DSC). The thermal scans were performed in a 25 to 200°C range at a heating rate of 10°C/min. T_g was taken as a midpoint of a straight line between the inflection of the peak's onset and endpoint. The thermal stability of the copolymers was measured by thermogravimetric analyzers TA Models 2090 and Q50 from ambient temperature to 800°C at 20°C/min. 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 (GPC) using a Altech 426 pump at an elution rate of 1.0 mL/min; TSK – GEL G4000H_{HR} column at 25°C, and Viscotek 302 and Viscotek UV 2501 detector. ^{1}H- and ^{13}C-NMR spectra were obtained on 10–25% (w/v) monomer or polymer solutions in $CDCl_3$ at ambient temperature using a Bruker Avance 300 MHz spectrometer. Elemental analyses were performed by Quantitative Technologies Inc. (NJ).

2.2. *Synthesis of monomers*

2.2.1. *Monomer synthesis*

The TSE monomers were synthesized by Knoevenagel condensation (16) of a ring-substituted benzaldehyde with malononitrile, catalyzed by base, piperidine.

$$RC_6H_3CHO + NCCH_2CN \longrightarrow RC_6H_3CH{=}C(CN)_2$$

2-Bromo, 3-bromo, 3-chloro, 2,3-dichloro, 2-chloro-6-fluoro, 2,6-difluoro, 3,4-difluoro, 3,5-difluorobenzaldehydes, malononitrile, 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 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 crystallization from 2-propanol. The condensation reaction proceeded smoothly, yielding crystalline products, which were purified by conventional techniques. The details of the synthesis and characterization of the halogen ring-substituted 2-phenyl-1-dicyanoethylenes were reported previously, 2-bromo, 3-bromo, 3-chloro (14), 2,3-dichloro, 2-chloro-6-fluoro, 2,6-difluoro, 3,4-difluoro, and 3,5-difluoro (15).

2.3. *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 mol/l of AIBN at an overall monomer concentration 2 mol/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.

3. Results and discussion

3.1. *Copolymerization*

Copolymerization (Scheme 1) of halogen ring-substituted 2-phenyl-1,1-dicyanoethylenes with ST resulted in formation of copolymers (Table 1) with weight-average molecular masses 7.0×10^3 to 64×10^3 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 (2).

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

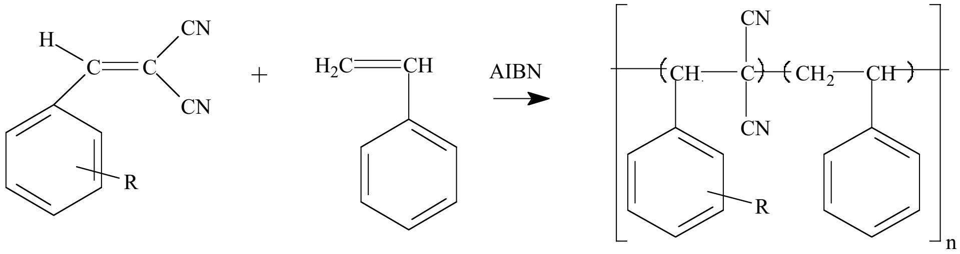
m_1 and m_2 are the mole fractions of ST and TSE monomer units in the copolymer, respectively; $[M_1]$ and $[M_2]$ are the concentrations of ST and TSE in the monomer feed, respectively. In the absence of the self-propagation of TSE monomers ($k_{22} = 0$, $r_2 = 0$) and at equimolar monomer feed ($[M_1]/[M_2] = 1$), Equation 1 yields.

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

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

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

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



Sch. 1. ST-TSE copolymer synthesis. R = is 2-bromo, 3-bromo, 3-chloro, 2,3-dichloro, 2-chloro-6-fluoro, 2,6-difluoro, 3,4-difluoro, and 3,5-difluoro.

for the TSE monomers is 3-chloro (2.78) > 3-bromo (2.40) > 3,4-difluoro (2.03) > 2-chloro-6-fluoro (1.98) > 3,5-difluoro (1.93) > 2-bromo (1.51) > 2,3-dichloro (1.00) > 2,6-difluoro (0.54).

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.

3.2. *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 the 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 2235–2246 cm^{-1} (2222–2230 cm^{-1} in the monomer). Benzene rings of both monomers show ring stretching 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 (17) and *N*-vinyl-2-pyrrolidone (18).

^{1}H-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 (19). 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. 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), 35–58 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 ^{1}H and ^{13}C-NMR spectra of 2-phenyl-1,1-dicyanoethylene-ST copolymers (19). 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 (Figure 1). 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.

Table 1. Copolymerization of Styrene (M_1) and Halogen Ring-Substituted 2-Phenyl-1,1-Dicyanoethylenes, $RC_6H_3CH{=}C(CN)_2$ (M_2)

R	*Yield*[a], *Wt%*	*Nitrogen (wt%)*	m_2 *in pol., mol%.*	$M_W \times 10^{-3}$, *D*	T_g, °*C*	*Onset of Decomp. (TGA)*, °*C*
2-bromo	15.2	6.90	0.38	12.3	188	261
3-bromo	13.1	7.36	0.41	8.4	180	291
3-chloro	18.6	8.50	0.42	19.6	212	260
2,3-dichloro	15.6	6.50	0.33	7.0	144	263
2-chloro-6-fluoro	12.7	7.69	0.40	64.9	217	274
2,6-difluoro	13.8	5.74	0.26	43.6	192	260
3,4-difluoro	18.1	8.11	0.40	40.7	190	263
3,5-difluoro	17.1	7.76	0.38	53.9	188	261

[a] Polymerization time was 8 h.

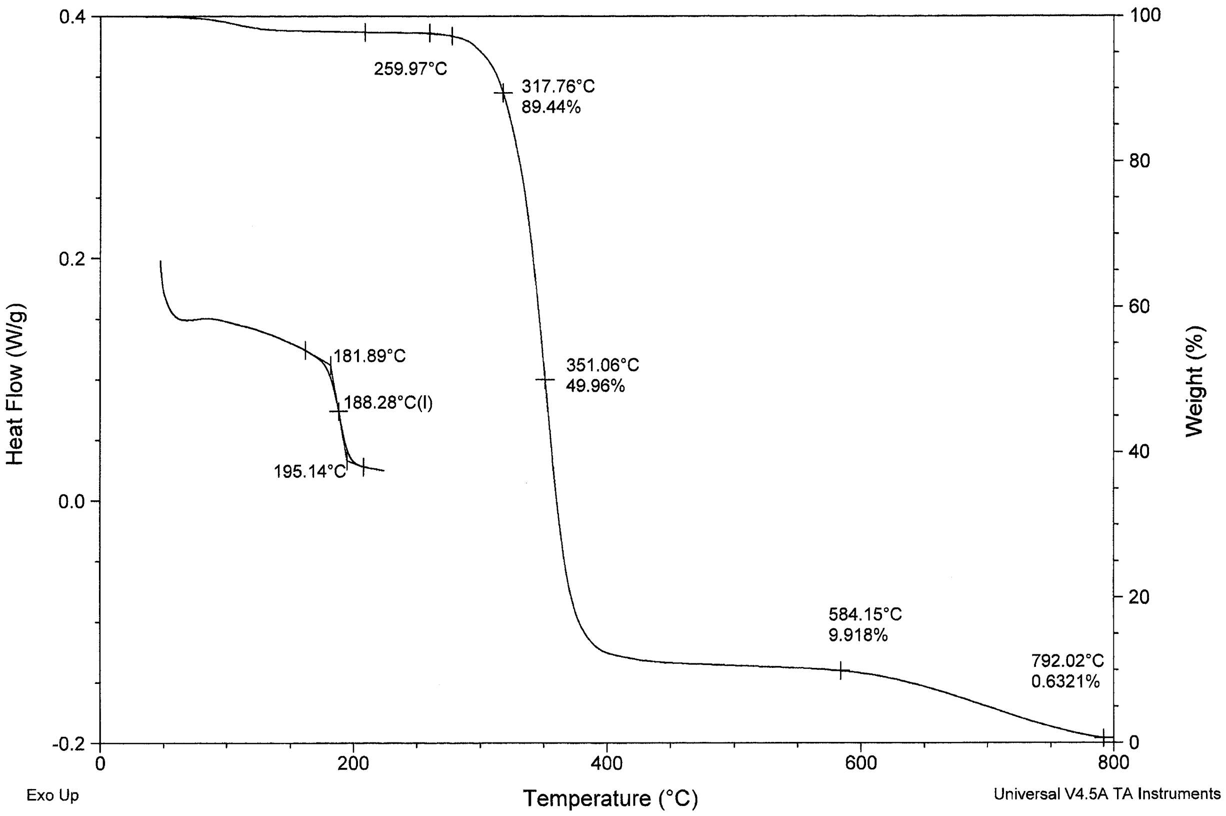


Fig. 1. DSC and TGA data for styrene copolymer with 2-(2-bromophenyl)-1,1-dicyanoethylene.

The decomposition of all copolymers in nitrogen occurs in two stages (Figure 1) with rapid decomposition in the 270–380°C range followed by second stage in 600–800°C.

4. Conclusions

Electrophilic trisubstituted ethylene monomers, halogen ring-substituted 2-phenyl-1,1-dicyanoethylenes, were prepared via a base-catalyzed condensation of appropriate substituted benzaldehydes and malononitrile. The copolymerization of the ethylenes with styrene resulted in statistical copolymers, with the ethylene mole percent in the range 26–42%. 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 270–800°C.

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