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Novel Copolymers of 4-Fluorostyrene. 3. Some Ring-Substituted 2-Phenyl-1,1-dicyanoethylenes

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Novel copolymers of trisubstituted ethylene monomers, ring-substituted 2-phenyl-1,1-dicyanoethylenes, $RC_6H_4CH{=}C(CN)_2$ (where R is 4-dimethylamino, 4-diethylamino, 3-phenoxy, 3-benzyloxy, 4-benzyloxy, 4-acetoxy, 2-cyano, 3-cyano, and 4-cyano) and 4-fluorostyrene 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. The order of relative reactivity ($1/r_1$) for the monomers is 3-benzyloxy (2.9) $>$ 4-cyano (2.7) $>$ 3-phenoxy (1.9) $>$ 4-acetoxy (1.8) $>$ 3-cyano (1.7) $>$ 2-cyano (1.6) $>$ 4-benzyloxy (0.6) $>$ 4-dimethylamino (0.4) = 4-diethylamino (0.4). High T_g of the copolymers, in comparison with that of poly (4-fluorostyrene) indicates a substantial decrease in chain mobility of the copolymer due to the high dipolar character of the trisubstituted ethylene monomer unit. Decomposition of the copolymers in nitrogen occurred in two steps, first in the 290–400°C range with residue, which then decomposition in 400–800°C range.

Keywords: Trisubstituted ethylenes, radical copolymerization, 4-fluorostyrene 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). Dielectric properties and α–relaxation phenomena of two copolymers of vinylidene methyl cyanide with 4-fluorostyrene and 4-chlorostyrene have been studied (11). The values of dielectric increment $\Delta\varepsilon$ have been calculated and compared to those of similar copolymers synthesized from vinylidene cyanide with various substituted styrenes. The low values of the increment were related to the steric effect of the bulky aromatic rings. The low values of the increment were related to the steric effect of the bulky aromatic rings.

Recently we have described synthesis and characterization of copolymers of 2-phenyl-1,1-dicyanoethylene with 4-fluoro- and pentafluorostyrene (12). In continuation of our studies of the monomer structure-reactivity correlation in the radical copolymerization of electrophilic trisubstituted ethylene monomers, we have prepared copolymers of 4-fluorostyrene (4FST) with some ring-substituted 2-phenyl-1,1-dicyanoethylenes, $RC_6H_4CH{=}C(CN)_2$ (where R is 4-dimethylamino, 4-diethylamino, 3-phenoxy,

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3-benzyloxy, 4-benzyloxy, 4-acetoxy, 2-cyano, 3-cyano, and 4-cyano).

2 Experimental

2.1 General Procedures

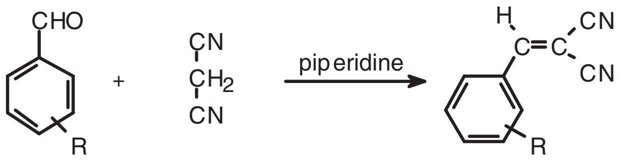
Infrared spectra of the TSE monomers and polymers (KBr plates) were determined with a Nicolet Avatar 360 FT-IR spectrometer. The melting points of the monomers, the glass transition temperatures (T_g) of the copolymers were measured with a TA (Thermal Analysis, Inc.) Model Q10 differential scanning calorimeter (DSC). The thermal scans were performed in the 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 a thermogravimetric analyzer TA Model 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 G4000HHR column at 25°C, 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

4-Dimethylamino, 4-diethylamino, 3-phenoxy, 3-benzyloxy, 4-benzyloxy, 4-acetoxy, 2-cyano, 3-cyano, and 4-cyanobenzaldehyde, 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 details of the synthesis and characterization of 4-dimethylamino, 4-diethylamino, 3-phenoxy, 3-benzyloxy, 4-benzyloxy, 4-acetoxy, 2-cyano, 3-cyano, and 4-cyano 2-phenyl-1,1-dicyanoethylenes were previously reported (13,14).

2.3 Copolymerization

4-Fluorostyrene (4FST) and toluene (Aldrich) were used as received. 1,1′-Azobis(cyclohexanecarbonitrile) (ABCN) (Aldrich) was recrystallized twice from ethyl alcohol and then dried under reduced pressure at room temperature. Copolymers of the 4FST and the TSE monomers were prepared in 25-ml glass screw cap vials at 4FST/TSE = 1/1 (mol) the monomer feed using 0.12 mol/l of ABCN at an overall monomer concentration 2.44 mol/L in 10 ml of toluene. The copolymerization was conducted at 70°C. After a predetermined time, the mixture was cooled to room temperature, and precipitated drop wise in methanol/petroleum ether mixture. The crude copolymers were purified by reprecipitation from chloroform solution into an excess of petroleum ether. The composition of the copolymers was determined based on the nitrogen content.



Sch. 1. Monomer synthesis (where R is 3-dimethylamino, 4-diethylamino, 3-phenoxy, 3-benzyloxy, 4-benzyloxy, 4-acetoxy, 2-cyano, 3-cyano, 4-cyano).

3 Results and Discussion

3.1 Monomer Synthesis

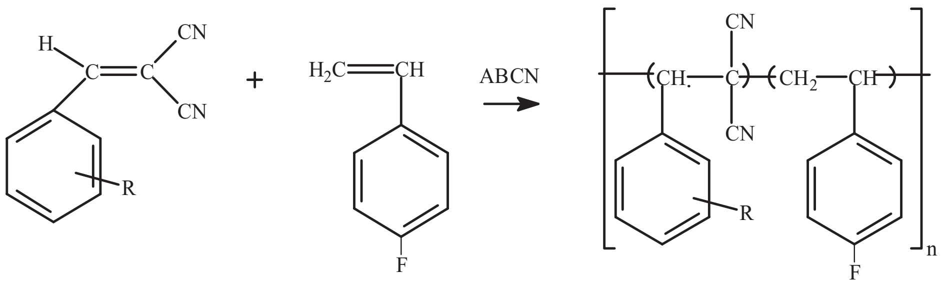
The TSE monomers were synthesized by Knoevenagel condensation (15) of a ring substituted benzaldehyde with an active hydrogen compound, malononitrile, catalyzed by a base, piperidine (Sch. 1). The condensation reaction proceeded smoothly, yielding crystalline products, which were purified by conventional techniques.

3.2 Homopolymerization

An attempted homopolymerization of the TSE monomers in the presence of ABCN 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. Homopolymerization of 4FST under conditions identical to those in the copolymerization experiments yielded 12.9% of poly(4-fluorostyrene), when polymerized for 30 min (12).

3.3 Copolymerization

Copolymerization (Sch. 2) of 4FST and the ring-substituted 1,1-dicyanoethylenes resulted in formation of copolymers (Table 1) with weight-average molecular masses 16.9 to 23.5 kD. According to elemental analysis, between 22.1 and 42.7 mol% of TSE monomer is present in the copolymers, which is indicative of high reactivity of the monomers in cross-propagation reactions.



Sch. 2. Copolymer synthesis (where R is 3-dimethylamino, 4-diethylamino, 3-phenoxy, 3-benzyloxy, 4-benzyloxy, 4-acetoxy, 2-cyano, 3-cyano, and 4-cyano).

In an attempt to qualitatively correlate the observed monomer reactivities, we considered copolymer composition data obtained at equimolar monomer feed. The relative reactivity of 4FST in copolymerization with these monomers can be estimated by assuming applicability of the copolymer composition equation (Eq. 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 4FST and TSE monomer units in the copolymer, respectively; $[M_1]$ and $[M_2]$ are the concentrations of 4FST 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 4-fluorostyrene 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 4FST-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 TSE monomers is 3-benzyloxy (2.9) > 4-cyano (2.7) > 3-phenoxy (1.9) > 4-acetoxy (1.8) > 3-cyano (1.7) > 2-cyano (1.6) > 4-benzyloxy (0.6) > 4-dimethylamino (0.4) ~ 4-diethylamino (0.4). 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 Spectral Properties

A comparison of the spectra of the monomers, copolymers and poly(4-fluorostyrene) shows, that the reaction between the TSE monomers and 4FST is a copolymerization. The structure of TSE-4FST copolymers was characterized by IR and NMR spectroscopy. IR spectra of the copolymers show overlapping bands in the 3125–2800 cm^{-1} region corresponding to C– H stretching vibrations. The spectra of

Table 1. Copolymerization of 4-Fluorostyrene (M_1) and ring-substituted 1,1-dicyanoethylenes, $RC_6H_4CH=C(CN)_2$ (M_2)

						TGA			
R	*Yield*[a]*, wt%*	*N wt%*	*m_2 in pol., mol%*	*M_W, kD*	*T_g^b, °C*	*Onset of decomp., °C*	*10% wt loss, °C*	*50% wt loss, °C*	*Residue at 500°C, wt%*
4-$(CH_3)_2N$	5.1	6.70	22.1	18.8	155	290	312	353	7
4-$(C_2H_5)_2N$	15.4	6.45	22.3	20.2	151	301	308	339	5
3-C_6H_5O	17.1	6.60	39.5	23.5	146	281	314	350	12
3-$C_6H_5CH_2O$	5.7	4.81	42.7	16.9	142	302	317	359	18
4-$C_6H_5CH_2O$	23.6	6.96	27.5	20.4	157	283	310	345	17
4-CH_3CO_2	13.3	11.12	39.1	20.2	152	298	304	344	8
2-CN	27.3	11.19	38.1	18.3	146	307	323	351	11
3-CN	10.1	12.09	38.4	17.8	149	287	302	340	11
4-CN	15.4	6.45	42.1	19.0	148	289	312	376	13

[a] Polymerization time was 24 h.
[b] T_g transition was observed by DSC.

the copolymers show weak cyano group absorption of the TSE monomer unit at 2222–2236 cm^{-1} (2205–2230 cm^{-1} in monomers). Benzene rings of both monomers show ring stretching bands around 1600, 1500, and 1450 cm^{-1}, as well as a doublet 740, 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 (5) and *N*-vinyl-2-pyrrolidone (9).

^{1}H-NMR spectra of the 4FST-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 4FST backbone protons in the close proximity of in 4FST-TSE dyad or in 4FST centered TSE-4FST-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 4FST 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 4FST backbone protons in 4FST-4FST diads. The ^{13}C-NMR spectra also support the suggested skeletal structure of the copolymers. Thus, the assignment of the peaks as follows: 160–168 carbonyl, 138–148 (quaternary phenyl carbons), 112–116 ppm (CN), 55–65 ppm (methine carbons of TSE and 4FST, and 4FST methylene), and at 40 ppm for N-methyl, CH_2 ethyl carbons, and 15 for ethyl CH_3 carbons, when present. 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-4FST copolymers (16). The IR and NMR data showed that these are true copolymers, composed of 4FST and TSE monomer units.

The copolymers prepared in the present work are all soluble in methyl ethyl ketone, acetone, benzene, THF, DMF and $CHCl_3$ and insoluble cyclohexane, and in ethyl and petroleum ether. They are amorphous and show no crystalline DSC endotherm. Relatively high T_g of the copolymers (Table 1) in comparison with that of poly(4-fluorostyrene) ($T_g = 108°C$) (15) indicates decrease of 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 TGA in nitrogen and air produce similar traces. The copolymers decomposed rapidly in one stage in the 290–400°C range followed by a more slow decomposition of the formed residue at 400–800°C. The decomposition products were not analyzed in this study, and the mechanism has yet to be investigated.

4 Conclusions

Trisubstituted ehtylenes, ring-substituted 2-phenyl-1,1-dicyanoethylene were prepared via a base catalyzed condensation of appropriate substituted benzaldehyde and malononitrile. The copolymerization of the monomers with 4-fluorostyrene results in copolymers. The composition of the copolymers was calculated from nitrogen analysis and the structure was analyzed by IR, ^{1}H and ^{13}C-NMR. Relatively high T_g of the copolymers (Table 1) in comparison with that of poly(4-fluorostyrene) ($T_g = 108°C$) indicates decrease of chain mobility of the copolymer due to the high dipolar character of the TSE structural units. The copolymers decomposed rapidly in one stage in the 290–400°C range followed by a more slow decomposition of the formed residue at 400–800°C.

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