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Novel Copolymers of 2-Phenyl-1,1-dicyanoethylene with 4-Fluoro- and Pentafluorostyrene

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Copolymerization of 2-phenyl-1,1-dicyanoethylene (PDE) with 4-fluorostyrene and pentafluorostyrene in solution with radical initiation (ABCN) at 70°C yielded random copolymers with PDE alternating units. The composition of the copolymers was calculated from nitrogen analysis and the structure was analyzed by IR, ^{1}H and ^{13}C-NMR. The order of relative reactivity ($1/r_1$) and the tendency toward alternation of monomer units in the copolymer for these two monomers, is 4-fluorostyrene (1.96) > pentafluorostyrene (0.51). Higher glass transition temperature of the copolymers in comparison with that of homopolymers indicates a decrease in chain mobility of the copolymer due to the high dipolar character of the trisubstituted ethylene monomer unit.

Keywords: Trisubstituted ethylenes, radical copolymerization, 4-fluorostyrene and pentafluorostyrene 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). Dielectric properties and αtrelaxation phenomena of two copolymers of vinylidene methyl cyanide with 4-fluorostyrene and 4-chlorostyrene have been studied (14). 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.

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) and pentafluorostyrene (PFST) with 2-phenyl-1,1-dicyanoethylene (PDE).

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Table 1. Copolymerization of 4-Fluorostyrene (M_1) and 2-phenyl-1,1-dicyanoethylene (M_2)

M_1 in feed, mol %	*Yield, %*	*Nitrogen, wt %*	*m_2 in polymer, mol%*	*T_g, °C*	*Onset of decomp. (TGA), °C*	*MW, KDa*
100	12.9	n/a	n/a	108	340	38.0
90	28.1	3.43	15.6	112	332	40.7
80	21.5	5.16	23.9	127	308	41.2
70	16.8	5.86	27.4	136	319	38.1
60	24.4	6.59	31.1	146	315	36.1
50	10.1	7.09	33.7	149	300	43.6
40	19.2	7.82	37.5	159	297	35.2

2 Experimental

2.1 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 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 Monomer Synthesis

2-Phenyl-1,1-dicyanoethene (PDE) was prepared via a Knoevenagel condensation in 90% yield by method of Carson and Stoughton (15). Equimolar amounts of malononitrile and benzaldehyde were mixed with 2 mL 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, purified by recrystallization from 2-propanol, and dried till a constant weight in a vacuum oven at ambient temperature. The product was characterized by DSC, FT-IR, ^{1}H-, ^{13}C-NMR spectra, and EA analysis. Yield: 85%; mp 83°C; ^{1}H-NMR δ 7.7 (=CH), 7.6–7.6; ^{13}C-NMR δ 82 (C=), 161 (HC=), 130, 131, 135 (Ph), 114 (CN); IR cm^{-1}, 3432 (Ar-H stretch), 3053 (C=CH), 2224 (CN), 1603, 1580 (Ar C=C), 755 (Ph); Anal. Calcd. for $C_{10}H_6N_2$: C 77.91%, H 3.92%, N 18.2%; Found: C 77.62%, H 4.12%, N 18.14%.

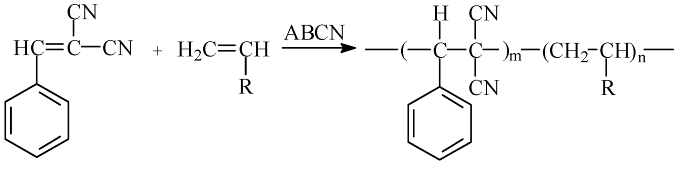
3 Results and Discussion

3.1 Homopolymerization

An attempted homopolymerization of the PDE monomers in the presence of ABCN did not produce any polymer as indicated by the lack of a precipitate in methanol. Inability of PDE to polymerize is associated with steric difficulties encountered in homopolymerization of 1,1- and 1,2-disubstituted ethylenes (2). Homopolymerization of 4FST and PFST under conditions identical to those in the copolymerization experiments yielded homopolymers (Tables 1 and 2).

3.2 Copolymerization

Copolymers of PDE and fluorine substituted styrenes, 4FST and PFST were prepared in 25-ml glass screw cap vials at various ratios of the monomer feed in 20 ml of toluene (Tables 1 and 2). The copolymerization (Scheme 1) was conducted at 70°C. After a predetermined time, the mixture was cooled to room temperature, and precipitated drop wise in methanol. The crude copolymers were purified by reprecipitation from chloroform solution into an excess of methanol. Then copolymers were dried in a vacuum oven at 70°C till constant weight. Conversions were determined gravimetrically. The composition of the copolymers was determined based on the nitrogen content (Tables 1 and 2). Radical copolymerization of PDE with the styrenes resulted in formation of PDE-4FST copolymers and PDE-PFST with weight-average molecular masses



Sch. 1. Copolymer synthesis (R is 4-fluorophenyl or pentafluorophenyl)

Table 2. Copolymerization of Pentafluorostyrene (M_1) and 2-Phenyl-1,1-dicyanoethylene (M_2)

M_1 in feed, mol %	*Yield, %*	*Nitrogen, wt %*	*m_2 in polymer, mol%*	*T_g, °C*	*Onset of decomp.(TGA) °C*	*MW, KDa*
100	13.0	n/a	n/a	103	280	23.2
90	14.4	0.78	5.35	82	269	12.2
80	14.3	1.10	7.51	86	264	12.6
70	15.3	1.42	9.65	90	254	10.4
60	19.5	1.49	10.11	92	260	10.8
50	11.5	1.75	11.84	105	253	12.9
40	9.91	1.98	13.35	109	258	10.7

35.2–43.6 kDa and 10.4–12.9 kDa, respectively. According to elemental analysis, a substantial amount of PDE is present in the PDE-4FST copolymers, which is indicative of relatively high reactivity of the monomer towards 4FST which is much lower in the case of PFST.

In an attempt to qualitatively correlate the observed monomer reactivities, we considered copolymer composition data obtained at various monomers feed. The relative reactivity of flurostyrene monomers (FST), 4FST and PFST in copolymerization with PDE 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 FST and PDE monomer units in the copolymer, respectively; $[M_1]$ and $[M_2]$ are the concentrations of FST and PDE in the monomer feed, respectively. Reactivity ratios, $r_1 = k_{11}/k_{12}$ and $r_2 = k_{22}/k_{21}$ define the relative trends of the monomer of M_1 (FST) and M_2 (PDE) to self-propagate or to cross-propagate. Fineman and Ross (16) rearranged Equation 1 to Equation 2:

$$G = r_1 F - r_2 \quad (2)$$

where $G = X(Y\text{-}1)/Y$, $F = X^2/Y$, $X = [M_1]/[M_2]$, and $Y = m_1/m_2$.

In the absence of the self-propagation of PDE monomer ($k_{22} = 0$, $r_2 = 0$), the Equation 2 yields Equation 3.

$$G = r_1 F \quad (3)$$

Thus, the plot of G against F yields a straight line with slope r_1 (Figure 1). In our case $r_{\mathrm{PFST}} = 1.97$, indicating that PFST tends to self-propagate, whereas for $r_{\mathrm{4FST}} = 0.51$, the copolymerization of 4FST and PDE is preferred. The figure shows also that reactivity of 4FST radical toward PDE is 3.9 times higher than that of PFST.

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 FST-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 PDE is 4FST (1.96) > PFST (0.51). Much lower PDE reactivity toward PFST limits significantly PDE content in the copolymers even at the high PDE monomer feed.

3.3 Structure and Thermal Properties

The structure of FST-TSE copolymers was characterized by IR and NMR spectroscopy. IR spectra of the copolymers show overlapping bands in the 3300–2800 cm^{-1} region corresponding to C-H stretching vibrations. The spectra of the copolymers show weak cyano group absorption of PDE monomer unit at 2237–2246 cm^{-1} (2222–2230 cm^{-1} in the monomer). Benzene rings of both monomers show ring stretching bands at 1500, 1456, and 830 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 various copolymers of 2-phenyl-1,1-dicyanoethylene with vinyl acetate (17) and *N*-vinyl-2-pyrrolidone (18).

NMR spectra of both FST-PDE copolymers show similar spectroscopic features. Figure 2 shows proton NMR spectra of 4FST-PDE copolymer and poly-(4-fluostyrene) for comparison. The broadening of the NMR signals in the spectra of the copolymers is apparently associated with head-to-head structure, which formed through the attack of a FST-ended radical on both sides of PDE monomer unit.

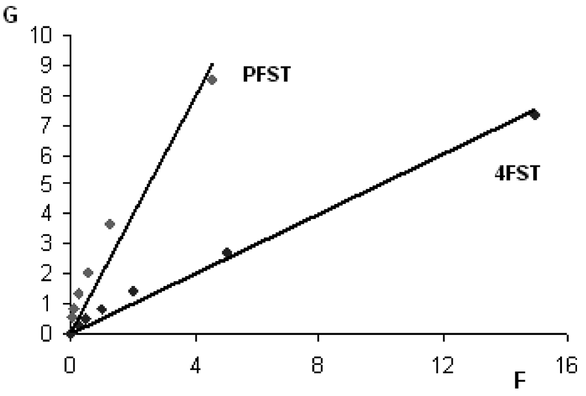


Fig. 1. Fineman-Ross plot of composition data from Tables 1 and 2.

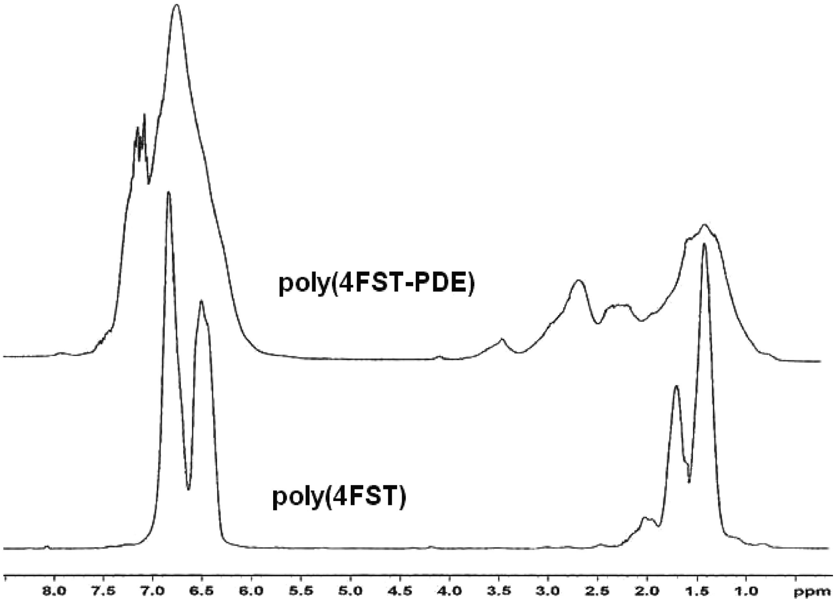


Fig. 2. ^{1}H-NMR spectra of 4FST-PDE (37.5 mol% PDE) copolymer and poly(4-fluostyrene).

All the ^{1}H-NMR spectra show a broad peak 6.0–8.0 ppm region corresponding to the phenyl protons of the FST and PDE monomer units.

Overlapping resonances at 2.2–3.7 ppm are assigned to FST backbone protons, methylene and methane, which are in close proximity to cyano groups in FST-PDE dyads or in ST centered PDE-FST-PDE triads. The overlapping low and high field components of the 2.2–3.0 ppm resonances are assigned to the PDE's methine protons in head-to-tail and head-to-head structures (19). Backbone ST protons removed further from cyano groups give rise to the absorption in 0.5–2.5 ppm like in styrenic homopolymers.

The ^{13}C-NMR spectra of 4FST-PDE copolymer (Fig. 3) also support the suggested skeletal structure of the copolymers. Thus, the assignment of the peaks as follows: 158–168 ppm (quarternary carbons of both phenyls), 120–140 ppm (phenyl carbons), 110–120 ppm (CN), 55–65 (quaternary carbon of PDE and methine carbon 4FST in proximity to cyano groups) 35–52 ppm (methine and methylene backbone carbons of 4FST and PDE). 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 (Fig. 4). Glass

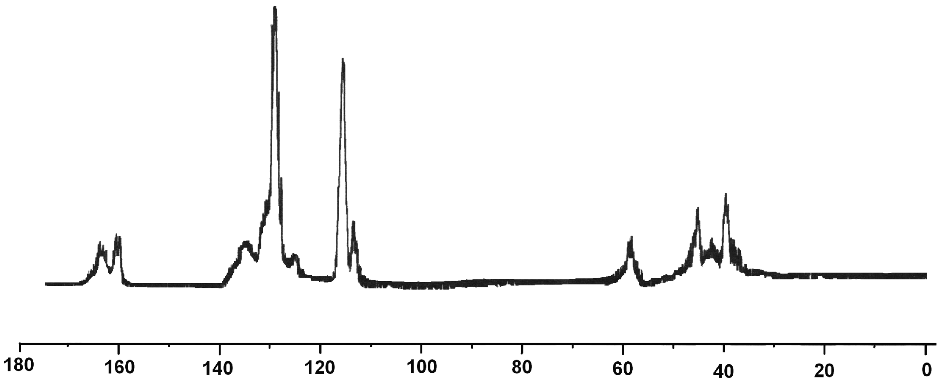


Fig. 3. ^{13}C-NMR spectra of 4FST-PDE (37.5 mol% PDE) copolymer.

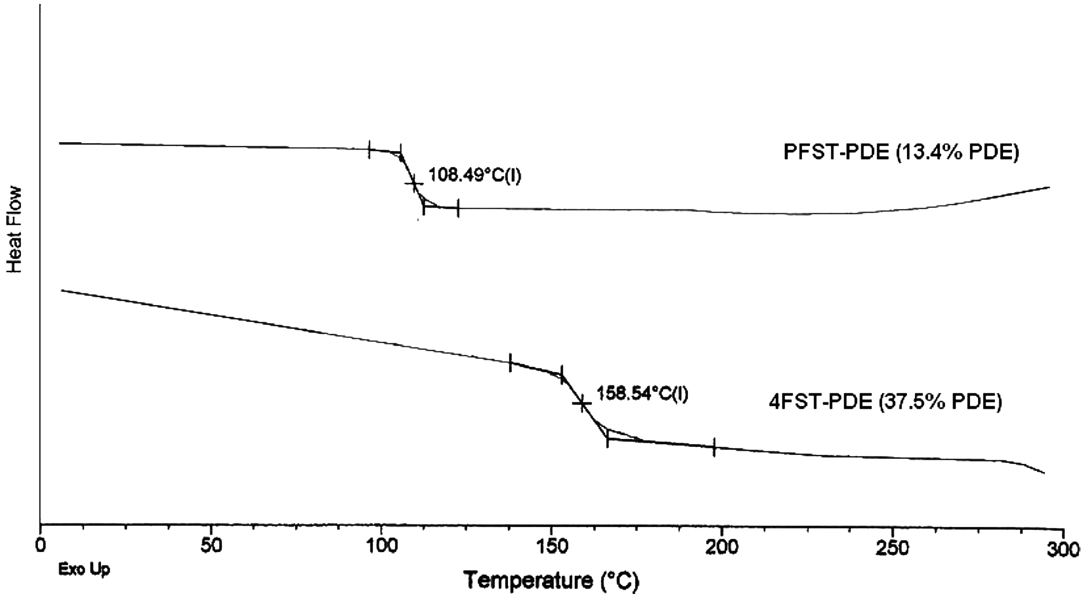


Fig. 4. DSC traces of PDE copolymers with 4-fluorostyrene and pentafluorostyrene.

transition of the copolymers increases with increase of PDE units in the copolymer. Higher T_g of the copolymers in comparison with that of homopolymers, poly(4-flurostyrene), $T_g = 108°C$ and poly(pentafuorostyrene), $T_g = 103°C$ 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 in nitrogen. The decomposition products were not analyzed in this study, and the mechanism has yet to be investigated. Figure 5 shows the results of thermogravimetric analysis of 4FST- and PFST-PDE copolymers in nitrogen. The 4FST-PDE copolymer with 37.5% of PDE monomer unit content decomposed rapidly in one stage in the 280–430°C range with no residue, whereas the PFST-PDE copolymer with much smaller content loses weight on heating in two stages (Fig. 5) with rapid decomposition of 95% of the sample in the 250–440°C range followed by a much slower second stage decomposition in the 440–600°C range.

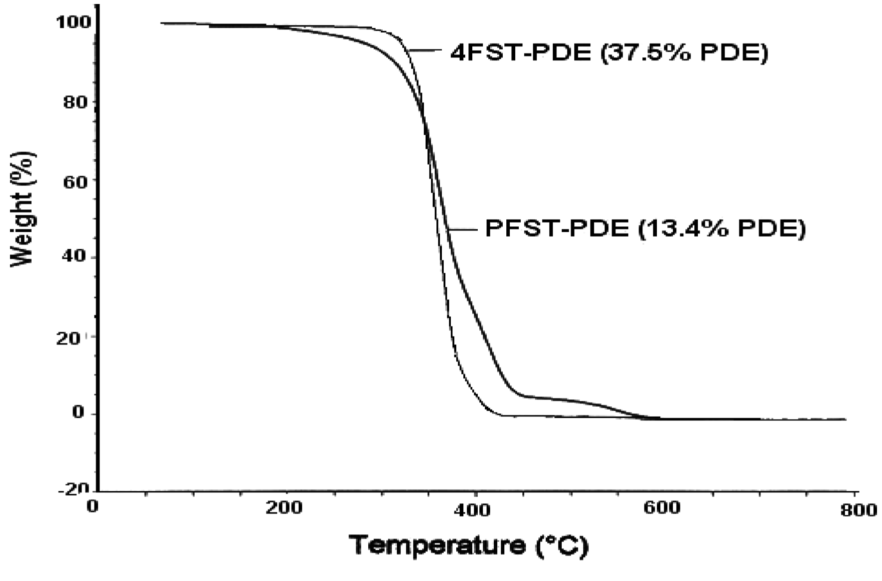


Fig. 5. TGA traces of PDE copolymers with 4-fluorostyrene and pentafluorostyrene.

4 Conclusions

Copolymerization of 2-phenyl-1,1-dicyanoethylene (PDE) with 4-fluorostyrene and pentafluorostyrene in solution with radical initiation (ABCN) at 70°C yielded random copolymers with PDE alternating units. The composition of the copolymers was calculated from nitrogen analysis and the structure was analyzed by IR, ^{1}H and ^{13}C-NMR. The order of relative reactivity ($1/r_1$) and the tendency toward alternation of monomer units in the copolymer for these two monomers, is 4-fluorostyrene (1.96) > pentafluorostyrene (0.51). Higher glass transition temperature of the copolymers in comparison with that of homopolymers indicates a decrease in chain mobility of the copolymer due to the high dipolar character of the trisubstituted ethylene monomer unit. The 4FST-PDE copolymers decompose rapidly in one stage in the 280–430°C range, whereas the PFST-PDE copolymers lose weight on heating in two stages with rapid decomposition in the 250–440°C range followed by a much slower second stage decomposition in the 440–600°C range.

Acknowledgments

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