NOVEL COPOLYMERS OF SOME RING-SUBSTITUTED 2-PHENYL-1,1-DICYANOETHYLENES WITH 4-FLUOROSTYRENE

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Introduction

Trisubstituted ethylenes (TSE, $CHR^1= CR^2R^3$) continue to attract the attention of polymer chemists as reactive comonomers and as models for mechanistic studies. It was shown that electrophilic TSE and tetrasubstituted olefins are particularly useful in delineating the transition from radical 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 TSE 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. 2-Phenyl-1,1-dicyanoethylene (PDE) was copolymerized with styrene (6), vinyl acetate (7), vinyl ethers (8), methyl methacrylate (9), and *N*-vinyl-2-pyrrlidone (10).

In continuation of our studies of the monomer structure-reactivity correlation in the radical copolymerization of electrophilic TSE monomers, we have prepared novel copolymers of 4-fluorostyrene (4FST) with 2-(R-Ph)-1,1-dicyanoethylenes (where R is 3-bromo, 3-bromo-4-methoxy, 2,3-dichloro, 2,6-dichloro, and 6-bromo-3,4-dimethoxy).

Experimental

Materials. 3-Bromo, 3-bromo-4-methoxy, 2,3-dichloro, 2,6-dichloro, and 6-bromo-3,4-dimethoxybenzaldehydes, malononitrile, DMF, and piperidine, 1,1'-azobis(cyclohexanecarbonitrile) (ABCN), 4-fluorostyrene (4FST), and toluene supplied from Aldrich Chemical Co., were used as received.

Instrumentation. Infrared spectra were determined with a Nicolet Avatar 360 FT-IR spectrometer. The glass transition temperatures (T_g) of the polymers were measured with a TA (Thermal Analysis, Inc.) Model Q10 differential scanning calorimeter (DSC). The thermal scans were performed in 25 to 300 ºC range at a heating rate of 10ºC/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 (TGA) TA Models 2090 and Q50 from ambient temperature to 800 ºC at 20 ºC/min. The molecular weights of the polymers were determined relative to polystyrene standards in $CHCl_3$ 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 (EA) were performed by Quantitative Technologies Inc. (New Jersey).

Monomer synthesis. The TSE monomers were synthesized by a condensation of a ring-substituted benzaldehyde with malononitrile, catalyzed by base, piperidine.

$$\text{R-PhCHO} + \text{NCCH}_2\text{CN} \rightarrow \text{R-PhCH=C(CN)}_2$$

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 3-bromo (11), 3-bromo-4-methoxy (12), 2,3-dichloro, and 2,6-dichloro (13) ring-substituted PDEs were reported previously. 2-(6-Bromo-3,4-dimethoxyphenyl)-1,1-dicyanoethylene was prepared and characterized by DSC, FT-IR, ^{1}H-, ^{13}C-NMR spectra, and EA analysis. Yield 65%; mp 162°C; ^{1}H-NMR δ 8.2 (s, 1H, =CH), 7.9, 7.1 (d, 2H, Ph), 3.8, 3.1 (d, 6H, CH_3O); ^{13}C-NMR δ 157 (HC=), 149 (O-Ph), 121, 118, 113, 112 (Ph), 82 (>C=), 114 (CN), 56 (OCH_3); IR cm^{-1}, 3115 (Ar-H stretch), 2940 (C=CH), 2220 (CN), 1601, 1580 (Ar C=C), 835 (Ph); Anal. Calc. for $C_{12}H_9N_2O_2$: C 49.17%, H 3.09%, N 9.56%; Found: C 49.05%, H 2.65%, N 9.10%.

Results and Discussion

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 TSE polymerize is associated with steric difficulties encountered in homopolymerization of 1,1- and 1,2-disubstituted ethylenes (2). Homopolymerization of 4FST under conditions identical to those in the copolymerization experiments yielded homopolymer, P4FST (Table 1).

Copolymerization. Copolymers of PDEs and 4FST were prepared in 25-ml glass screw cap vials at 4FST/PDE = 1/1 molar ratio of the monomer feed in 20 ml of toluene. The copolymerization (**Figure 1**) was conducted at 70ºC. 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. Then copolymers were dried in a vacuum oven at 70ºC until constant weight. Conversions were determined gravimetrically. The composition of the copolymers was determined based on the nitrogen content (**Table 1**).

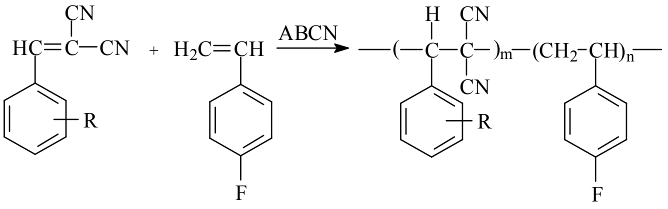

Figure 1. Copolymerization of 4-Fluorostyrene and Ring-substituted 2-Phenyl-1,1-dicyanoethenes (where R is 3-bromo, 3-bromo-4-methoxy, 2,3-dichloro, 2,6-dichloro, and 6-bromo-3,4-dimethoxy).

Table 1. Homo- and Copolymerization of 4-Fluorostyrene (M_1) with 2-(R-Ph-1,1-dicyanoethenes (M_2)

Polymers, R	Yield[a], (*wt%*)	N (*wt%*)	m_2 in copol. (*mol.%*)	M_W, (k*D*)	*Tg*[b], (°*C*)
P4FST	12.9	-	-	38.0	108
3-Br	16.3	6.32	36.78	18.0	199
3-Br, 4-OCH_3	46.0	5.75	27.78	7.9	137
2-Cl, 3-Cl	26	6.31	28.06	9.7	196
2-Cl, 6-Cl	20	5.01	20.40	8.7	166
6-Br, 3,4-$(OCH_3)_2$	63.4	6.51	38.59	7.8	161

[a] Polymerization time was 8 hours; [b] T_g transition was observed by DSC.

Copolymerization of the ring-substituted 2-phenyl-1,1-dicyanoethylenes and 4-fluorostyrene resulted in formation of copolymers (Table 1) with weight-average molecular masses 7.8 to 18.0 kD. According to elemental analysis, PDE co-monomer units are present in the copolymers, which is indicative of reactivity of PDE towards the fluorine-substituted styrenes. In an attempt to qualitatively correlate the observed monomer reactivities, we considered copolymer composition data obtained at $[M_1]/[M_2] = 1$ monomer feed. The relative reactivity of the 4FST in copolymerization with PDE can be estimated by assuming applicability of the copolymer composition of the terminal copolymerization model (1):

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

m_1 and m_2 are the mole fractions of 4FST and PDE monomer units in the copolymer, respectively; $[M_1]$ and $[M_2]$ are the concentrations of 4FST and PDEs in the monomer feed, respectively. In the absence of the self-propagation of PDEs ($k_{22}= 0$, $r_2 = 0$), and at the monomer feed ($[M_1] / [M_2] = 1$), the above equation yields:

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

Or the equation for the relative reactivity of fluorine-substituted styrene radical k_{12} / k_{11} with PDE monomers:

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

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 fluorine-substituted styrene 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 these two monomers is as follows, 6-bromo-3,4-dimethoxy (1.69) > 3-bromo (1.39) > 2,3-dichloro (0.64) > 3-bromo-4-methoxy (0.62), 2,6-dichloro (0.34). 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 properties. The structure of the copolymers was characterized by IR and NMR spectroscopy. A comparison of the spectra of the monomers, homopolymers, and copolymers shows that the reaction between 4FST and with the ring-substituted PDE is a copolymerization. The spectra of the copolymers show weak cyano group absorption of PDE monomer unit at 2230-2240 cm^{-1}. Benzene rings of both comonomers show stretching bands at 1650, 1524, and 1495 cm^{-1}, as well as a doublet 980, 870 cm^{-1}, associated with C-H out of plane deformations.

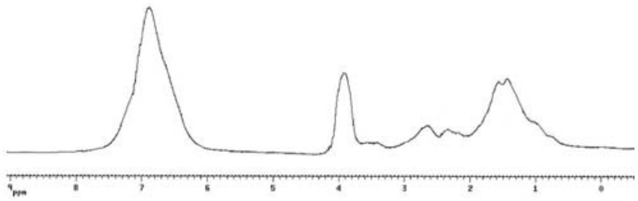

Figure 2. Proton NMR spectra of 4-fluorostyrene and 2-(3-bromo-4-methoxyphenyl)-1,1-dicyanoethylene.

The broadening of the NMR signals (Figure 2) in the spectra of the copolymers is apparently associated with head-to-head structures, which formed through the attack of a ST-ended radical on both sides of PDE monomer unit. All the ^{1}H-NMR spectra of the copolymers show a broad peak in the 6.0-8.0 ppm region corresponding to the phenyl ring protons of the monomers. The resonance in the range 3.2-4.3 ppm is assigned to 4FST backbone protons in ST-PDE dyads or PDE-4FST-PDE triads as well as of the methine and methoxy protons of PDE monomer units. Backbone 4FST protons, in 4FST-4FST dyads, removed from cyano groups give rise to the absorption in 0.6-2.9 ppm.

The copolymers prepared in the present work are all soluble in methyl ethyl ketone, acetone, benzene, THF, DMF and $CHCl_3$ and insoluble cyclohexane, ethyl and petroleum ether, and methanol. They are amorphous and show no crystalline DSC endotherm (Figure 3). Relatively high T_g of the copolymers (**Table 1**) in comparison with that of P4FST indicates decrease of chain mobility of the copolymer due to the high dipolar character of PDE structural units.

Information on the degradation of the copolymers was obtained from TGA in nitrogen. The decomposition products were not analyzed in this study, and the mechanism has yet to be investigated. Figure 3 shows the results of TGA of 4-fluorostyrene copolymer with 2-(3-bromophenyl)-1,1-dicyanoethylene.

The copolymer loses weight on heating in two stages with rapid decomposition of 91% of the sample in the 290-400°C range followed by a slow decomposition in the 400-650°C range.

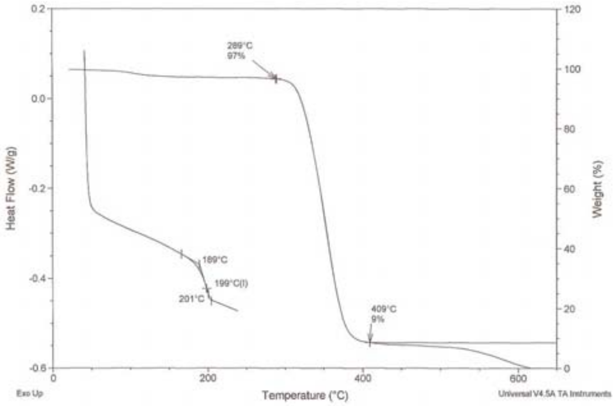

Figure 3. DSC and TGA traces of 4-fluorostyrene copolymer with 2-(3-bromophenyl)-1,1-dicyanoethylene.

Conclusions

The copolymerization of 4FST with the ring-substituted 2-phenyl-1,1-dicyanoethylenes results in random copolymers with PDE alternating units and weight-average molecular masses 7.8 to 18.0 kD. The composition of the coolymers 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 as follows, 6-bromo-3,4-dimethoxy (1.69) > 3-bromo (1.39) > 2,3-dichloro (0.64) > 3-bromo-4-methoxy (0.62), 2,6-dichloro (0.34). 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.

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References

(1) Hall, H.K., Jr. and Padias, A.B. *J. Polym. Sci. Part A: Polym. Chem.* **2004,** *42*, 2845.
(2) Odian, G. Principles of Polymerization, 3rd Ed.; Wiley: New York, 1991.
(3) Hall, H.K., Jr. and Daly, R.C. *Macromolecules* **1975**, *8*, 22.
(4) Hall, H.K., Jr, and Ykman, P. *Macromolecules*, **1977**, *10,* 464.
(5) Kharas, G.B. Trisubstituted Ethylene Copolymers. In Polymeric Materials Encyclopedia, edited by Salamone, J.C. CRC Press: Boca Raton, Vol. 11, 8405, 1996.
(6) Kreisel, M., Garbatski, U., and Kohn, D.H. *J. Polym. Sci.*, **1964**, *2(1;Pt A)* 105.
(7) Kharas, G.B. and Kohn, D.H. *J. Polym. Sci. Polym. Chem. Ed.*, **1984**, *22*, 583.
(8) Kharas, G.B., Ajbani, H. *J. Polym. Sci.*, **1993**, *A31*, 2295.
(9) Sayyah, S. M., El-Shafiey, Z. A., El-Sockary, M. A., Kandil, U. F. *Int. J. Polym. Mat.*, **2002**, *51(3)*, 225.
(10) Kharas, G.B. *J. Appl. Polym. Sci.* **1988**, *35*, 733, ibid., 2173.
(11) Kharas, G.B. Russell, S.M., Ward, D.R., Doshi, R.M., Hijazin, M.Y., Korkofigas, E., Kuzenkova, N., Leung, B. Martinez, H., Merchant, F.A., Meschbach, N.T., and Opiola. E.S. *J. Macromol. Sci.* **2008**, *A45* (2) 133.
(12) Kharas, G.B., Hanawa, E., Lachenberg, J., Brozek, B., Miramon, P., Mojica, A.C., Colbert, A.C., Crowell, B.T., Madison, A., Martinez, A.P. *J. Macromol. Sci.* **2008**, *A45* (6) 420.
(13) Kharas, G.B. Russell, S.M., Cisler, R., Capen, T.L., Chlupsa, E.A., DeBellis, L.A., Duke, J.T.A., Frazier, C.B., Gora, A., Kamenetsky, E., Kurani, A.S., Kuta, D.L., Madison, A., Miramon, P. *J. Macromol. Sci.* **2008**, *A45* (4) 261.