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

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

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Novel copolymers of trisubstituted ethylene monomers, alkyl ring-substituted 2-phenyl-1,1-dicyanoethylenes, $\text{RC}_6\text{H}_4\text{CH}=\text{C}(\text{CN})_2$ (where R is 2-methyl, 3-methyl, 4-methyl, 4-ethyl, 4-*i*-propyl, 4-butyl, 4-*i*-butyl, and 4-*t*-butyl) 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, ^1H and ^{13}C -NMR. The order of relative reactivity ($1/r_1$) for the monomers is 4-ethyl (42.6) > 4-butyl (29.4) > 4-*t*-butyl (26.7) > 4-*i*-butyl (1.6) > 4-*i*-propyl (1.29) > 3-methyl (1.26) > 2-methyl (0.8) > 4-methyl (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 183–500°C range with residue (5–30% wt.), which then decomposed in the 500–800°C range.

Keywords: Trisubstituted ethylenes, radical copolymerization, 4-fluorostyrene copolymers

1 Introduction

Trisubstituted ethylenes (TSE, $\text{CHR}^1=\text{CR}^2\text{R}^3$) 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 (vinylidene cyanide) and vinyl acetate (10). 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 α -relaxation phenomena of two copolymers of vinylidene methyl cyanide with 4-fluorostyrene and 4-chlorostyrene have been studied (14). The values of dielectric increment $\Delta\epsilon$ 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.

Recently we have described synthesis and characterization of copolymers of 2-phenyl-1,1-dicyanoethylene with 4-fluoro- and pentafluorostyrene (15). In continuation of our studies of the monomer structure-reactivity correlation

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in the radical copolymerization of electrophilic trisubstituted ethylene monomers, we have prepared copolymers of 4-fluorostyrene (4FST) with alkyl ring-substituted 2-phenyl-1,1-dicyanoethylenes, $\text{RC}_6\text{H}_4\text{CH}=\text{C}(\text{CN})_2$ (where R is 2-methyl, 3-methyl, 4-methyl, 4-ethyl, 4-*i*-propyl, 4-butyl, 4-*i*-butyl, and 4-*t*-butyl).

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. ^1H - 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-Methyl, 3-methyl, 4-methyl, 4-ethyl, 4-*i*-propyl, 4-butyl, 4-*i*-butyl, and 4-*t*-butylbenzaldehyde, 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 the alkyl ring-substituted 2-phenyl-1,1-dicyanoethylenes were reported previously, 2-methyl, 3-methyl, 4-methyl, 4-ethyl (16), 4-*i*-propyl, 4-butyl, and 4-*t*-butyl (17).

2.2.1 2-(4-*i*-Butylphenyl)-1,1-dicyanoethylene

Yield 74%; mp 74°C; ^1H -NMR δ 0.9 (m, 6H, CH_3), 1.9 (m, 1H, $\text{CH}(\text{CH}_3)_2$), 2.7 (d, 2H, CH_2), 7.3, 7.8 (m, 4H,

phenyl), 7.9 (s, 1H, $\text{CH}=\text{C}$); ^{13}C -NMR δ 22 (CH_3), 30 (CH), 42 (CH_2), 113 (CN), 115 ($=\text{CCN}$), 129, 130, 145 (phenyl), 160 ($\text{CH}=\text{C}$); IR 2960, 2929 (w, C–H phenyl), 2227 (s, CN), 1593 (C=C), 964, 848, 790 (C–H out-of-plane bending); Anal. Calc. for $\text{C}_{14}\text{H}_{14}\text{N}_2$: C 79.97%, H 6.71%, N 13.32%; Found: C 79.64%, H 6.75%, N 13.23%.

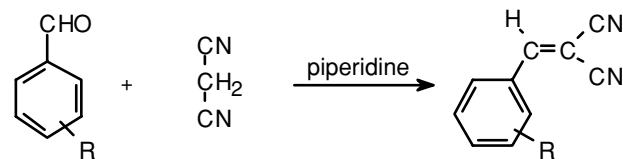
3 Copolymerization

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 composition of the copolymers was determined based on the nitrogen content.

4 Results and Discussion

4.1 Monomer Synthesis

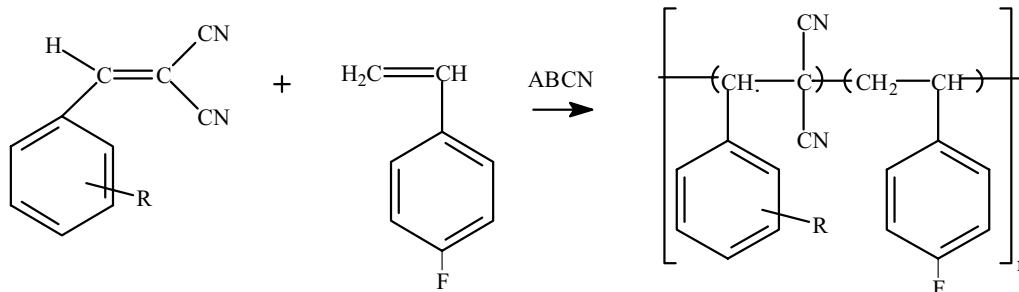
The TSE monomers were synthesized by Knoevenagel condensation (18) of a ring-substituted benzaldehyde with an active hydrogen compound, malononitrile, catalyzed by a base, piperidine (Scheme 1). The condensation reaction proceeded smoothly, yielding crystalline products, which were purified by conventional techniques.



Sch. 1. Monomer synthesis (where R = 2-methyl, 3-methyl, 4-methyl, 4-ethyl, 4-*i*-propyl, 4-butyl, 4-*i*-butyl, and 4-*t*-butyl).

4.2 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



Sch. 2. Copolymer synthesis (where R is 2-methyl, 3-methyl, 4-methyl, 4-ethyl, 4-*i*-propyl, 4-butyl, 4-*i*-butyl, and 4-*t*-butyl).

experiments yielded 12.9% of poly(4-fluorostyrene), when polymerized for 30 min (15).

equimolar monomer feed ($[M_1]/[M_2] = 1$), equation (1) yields.

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

4.3 Copolymerization

Copolymerization (Scheme 2) of 4FST and the alkyl ring-substituted 1,1-dicyanoethylenes resulted in formation of copolymers (Table 1) with weight-average molecular masses 5.6 to 21.6 kD. According to elemental analysis, between 23.1 and 49.4 mol% of TSE monomer is present in the copolymers, which is indicative of high reactivity of the monomers in cross-propagation reactions.

or the equation for the relative reactivity of 4-fluorostyrene radical k_{12}/k_{11} with TSE monomers:

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

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 (Equation (1)) of the terminal copolymerization model (2).

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 4-ethyl (42.6) > 4-*t*-butyl (29.4) > 4-*t*-butyl (26.7) > 4-*i*-butyl (1.6) > 4-*i*-propyl (1.29) > 3-methyl (1.26) > 2-methyl (0.8) > 4-methyl (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.

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

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

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

R	Yield ^a , wt%	N wt%	m_2 in pol., mol%	M_w , kD	T_g^b , °C	TGA			
						Onset of decomp., °C	10% wt. loss, °C	50% wt. loss, °C	Residue at 500°C, wt%
2-methyl	6.6	6.91	30.5	11.8	168	225	307	337	5
3-methyl	30.3	7.89	35.8	21.6	135	228	297	344	7
4-methyl	18.2	5.45	23.1	5.6	156	230	285	343	9
4-ethyl	15.7	9.70	49.4	11.1	138	226	292	351	12
4- <i>i</i> -propyl	18.0	7.35	36.0	15.0	146	223	309	350	15
4-butyl	26.7	8.81	49.2	13.1	123	221	307	364	23
4- <i>t</i> -butyl	25.0	8.80	49.1	7.2	118	194	272	335	30
4- <i>i</i> -butyl	49.4	7.37	38.0	5.4	124	183	248	337	10

^aPolymerization time was 24 h. ^b T_g transition was observed by DSC.

4.4 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 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 2230–2248 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 (5) and *N*-vinyl-2-pyrrolidone (9).

^1H -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 protons of the TSE monomer unit in head-to-tail and head-to-head structures (19). Alkyl protons absorbances are overlapping with backbone resonances. 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: 137–147 ppm (quaternary carbons of both phenyls), 120–145 ppm (phenyl carbons), 110–120 ppm (CN), and 55–65 ppm (methine carbons of TSE and 4FST, and 4FST 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-4FST copolymers (19). 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) ($T_g = 108^\circ\text{C}$) (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. Decomposition of the copolymers in nitrogen occurred in two steps, first in 183–

500 $^\circ\text{C}$ range with residue (5–30% wt.), which then decomposed in the 500–800 $^\circ\text{C}$ range. The decomposition products were not analyzed in this study, and the mechanism has yet to be investigated.

5 Conclusions

Trisubstituted ethylenes, alkyl 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, ^1H and ^{13}C -NMR. Relatively high T_g of the copolymers (Table 1) in comparison with that of poly(4-fluorostyrene) ($T_g = 108^\circ\text{C}$) indicates decrease of chain mobility of the copolymer due to the high dipolar character of the TSE structural units. Decomposition of the copolymers in nitrogen occurred in two steps, first in 183–500 $^\circ\text{C}$ range with residue (5–30% wt.), which then decomposed in the 500–800 $^\circ\text{C}$ range.

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References

- Hall, H.K., Jr. and Padias, A.B. (2004) *J. Polym. Sci. Part A: Polym. Chem.* 42, 2845–2858.
- Odian, G. *Principles of Polymerization*, 3rd Ed.; Wiley: New York, 1991.
- Hall, H.K., Jr. and Daly, R.C. (1975) *Macromolecules*, 8, 22–31.
- Hall, H.K., Jr. and Ykman, P. (1977) *Macromolecules*, 10, 464–469.
- Kharas, G.B. (1996) Trisubstituted ethylene copolymers. In *Polymeric Materials Encyclopedia*, edited by Salamone, J.C., CRC Press: Boca Raton, Vol. 11, 8405–8409.
- Kreisel, M., Garbatski, U., and Kohn, D.H. (1964) *J. Polym. Sci.*, 2(1; Part A) 105–121.
- Kharas, G.B. and Ajbani, H. (1993) *J. Polym. Sci.*, A31, 2295–2303.
- Sayyah, S.M., El-Shafiey, Z.A., El-Sockary, M.A. and Kandil, U.F. (2002) *Int. J. Polym. Mat.*, 51(3), 225–242.
- Kharas, G.B. (1988) *J. Appl. Polym. Sci.*, 35, 733–741.
- Koizumi, S., Tanado, K., Tanaka, Y., Shimidzu, T., Kutsumizu, S., and Yano, S. (1992) *Macromolecules*, 95, 6563.
- Tasaka, S., Miyasato, K., Yoshikawa, M., Miyata, S., and Ko, M. (1984) *Ferroelectrics*, 57, 267.
- Seto, T. and Nozoye, H. (1997) *Chem. Lett.*, 141–142.
- Poulsen, M., Ducharme, S., Sorokin, A., Reddy, S., Takacs, J., Wen, Y., Kim, J., and Adenwalla, S. (2005) *Ferroelectrics Letters*, 32(3–4), 91–97.

14. Raihane, M., Montheard, J.P., and Boiteux, G. (2000) *Macromol. Chem. and Phy.* 201(17), 2365–2370.
15. Kharas, G.B., Hanawa, E., Hill, B.L., Atlas, S., and Raihane, M. (2009) *J. Macromol. Sci., Pure & Applied Chem.*, A46, 650–655.
16. Kharas, G.B., Adibu, E., Brusek, A., Vigdor, W., Dorth, D., Hallis, L., Chipman, H., Kaiser, K., and Watson, K. (2007) *J. Macromol. Sci., Pure & Applied Chem.*, A44(7), 675–678.
17. Kharas, G.B., Russell, S.M., Trickey, K., Baecher, D.P., Becker, J.H., Borgmeyer, S., Mancias, J., Delgado, A.M., and Hartmann, M.K. (2007) *J. Macromol. Sci., Pure & Applied Chem.*, A44(11), 1151–1154.
18. Smith, M.B. and March, J. (2001) Addition to Carbon-Hetero Multiple Bonds. In *March's Advanced Organic Chemistry*: J. Wiley & Sons: New York Ch. 16, 1225.
19. Kharas, G.B., Murau, P.A., Watson, K., and Harwood, H.J. (1992) *Polym. Int.*, 28, 67–74.