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Gregory B. Kharas[a]; Emi Hanawa[a]; Jamie Lachenberg[a]; Beata Brozek[a]; Patricia Miramon[a]; Audris C. Mojica[a]; Acheera C. Colbert[a]; Bridget T. Crowell[a]; Ashley Madison[a]; Amanda P. Martinez[a]
[a] Chemistry Department, DePaul University, Chicago, Illinois

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Novel Copolymers of Vinyl Acetate and Some Ring-Substituted 2-Phenyl-1,1-dicyanoethylenes

GREGORY B. KHARAS, EMI HANAWA, JAMIE LACHENBERG, BEATA BROZEK, PATRICIA MIRAMON, AUDRIS C. MOJICA, ACHEERA C. COLBERT, BRIDGET T. CROWELL, ASHLEY MADISON, and AMANDA P. MARTINEZ

Chemistry Department, DePaul University, Chicago, Illinois

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Electrophilic trisubstituted ethylene monomers, some ring-substituted 2-phenyl-1,1-dicyanoethylenes, $RC_6H_4CH{=}C(CN)_2$ (where R is 3-Br, 4-CH_3O; 5-Br, 2-CH_3O; 4-Cl, 3-NO_2; 5-Cl, 2-NO_2; 2-CN, 3-CN, 4-CN, and 4-$(CH_3)_2N$), were synthesized by piperidine catalyzed Knoevenagel condensation of ring-substituted benzaldehydes and malononitrile, and characterized by CHN elemental analysis, IR, ^{1}H- and ^{13}C-NMR. Novel copolymers of the ethylenes and vinyl acetate 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, GPC, DSC, and TGA. High T_g of the copolymers, in comparison with that of polyvinyl acetate, 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 190–800°C range.

Keywords: trisubstituted ethylenes; radical copolymerization; vinyl acetate copolymers

1 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 tri- and tetrasubstituted olefins are particularly useful in delineating the transition from radical to ionic chemistry (1). Previous studies showed that trisubstituted ethylenes 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 trisubstituted ethylenes, 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 acetate (7), vinyl ethers (8), methyl methacrylate (9), and *N*-vinyl-2-pyrrlidone (10).

In relation to applications, 1,1-dicyanoethylene (vinyledene cyanide) and its copolymer with vinyl acetate showed piezoelectric activity (11). Unlike fluoropolymers, this copolymer is amorphous with high T_g of 178°C and has alternating monomer unit structure. The copolymer has impedance similar to that of human body and has been suggested for medical applications as an ultrasonic transducer (12). 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 (13). 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 capable to abate electrostatic interactions between vinyl acetate dipoles and facilitating orientation of these dipoles in the direction of the applied field (14).

In continuation of our studies of the monomer structure-reactivity correlation in the radical copolymerization of ring-substituted 2-phenyl-1,1-dicyanoethylene monomers (15–17), we have prepared some ring-substituted 2-phenyl-1,1-dicyanoethylenes, $RC_6H_4CH{=}C(CN)_2$ (where R is 3-Br, 4-CH_3O; 5-Br, 2-CH_3O; 4-Cl, 3-NO_2; 5-Cl, 2-NO_2; 2-CN, 3-CN, 4-CN, and 4-$(CH_3)_2N$), and explore the feasibility of their copolymerization with vinyl acetate.

Address correspondence to: Gregory B. Kharas, Chemistry Department, DePaul University, Chicago, IL 60614-3214. Fax: 773-325-7421; E-mail: gkharas@depaul.edu

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 a TA (Thermal Analysis, Inc.) Model 2010 differential scanning calorimeter (DSC). The thermal scans were performed in the 25 to 200°C range at a heating rate of 10°C/min. Tg 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 2090 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*

The TSE monomers were synthesized by Knoevenagel condensation (18) of a ring-substituted benzaldehyde with malononitrile, catalyzed by base, piperidine. 3-Br, 4-CH_3O; 5-Br, 2-CH_3O; 4-Cl, 3-NO_2; 5-Cl, 2-NO_2; 2-CN, 3-CN, 4-CN, and 4-$(CH_3)_2N$ ring-substituted aldehydes, 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.

2.2.1 *2-(3-Bromo-4-methoxyphenyl)-1,1-dicyanoethylene*

Yield: 80%; mp 156°C; ^{1}H-NMR δ 3.9 (s, 3H, CH_3), 6.9, 7.7, 7.9 (m, 3H, Ph), 8.2 (s, 1H, CH=); ^{13}C-NMR δ 56 (OCH_3), 77 (=C<), 113 (CN), 127, 128, 130, 140 (Ph), 160 (CH=); IR (NaCl) 3046, 2962, 2930 (m, C-H, Ph), 2225 (s, CN), 1579, 1497 (s, C=C), 878, 827 (m, C-H out-of-plane bending). Anal. Calcd. for $C_{11}H_7BrN_2O$; Calc. for C, 50.22; H, 2.68; N, 10.65; Found: C, 49.88; H, 2.23; N, 10.68.

2.2.2 *2-(5-Bromo-2-methoxyphenyl)-1,1-dicyanoethylene*

Yield 90%; mp 141°C (Lit. 137–139°C (19)); ^{1}H-NMR δ 3.8 (s, 3H, CH_3), 7.3, 7.9 (m, 3H, Ph), 8.2 (s, 1H, CH=); ^{13}C-NMR δ 56 (OCH_3), 81 (=C<), 113 (CN), 129, 130, 146 (Ph), 153 (CH=); IR 2981, 2941 (m, C-H, Ph), 2220 (s, CN), 1581, 1477 (m, C=C), 818 (m, C-H out-of-plane bending); Anal. Calcd. for $C_{11}H_7BrN_2O$: C 50.22%, H 2.68%, N 10.65%; Found: C 50.09%, H 2.51%, N 10.64%.

2.2.3 *2-(4-Chloro-3-nitrophenyl)-1,1-dicyanoethylene*

Yield 94%; mp 144°C; ^{1}H-NMR δ 7.8, 8.2 (m, 3H, Ph), 8.3 (s, 1H, =CH); ^{13}C-NMR δ 84 (=C<), 113 (CN), 125, 130, 135, 148 (Ph), 160 (=CH); IR 3090, 3045 (m, C-H, Ph), 2232 (m, CN), 1594 (m, C=C), 1538, 1350 (s, NO_2), 831 (m, C-H out-of-plane bending); Anal. Calcd. for $C_{10}H_4ClN_3O_2$: C 51.41%, H 1.73%, N 17.99%; Found: C 51.00%, H 1.39%, N 17.90%.

2.2.4 *2-(5-Chloro-2-nitrophenyl)-1,1-dicyanoethylene*

Yield 66%; mp 139°C; ^{1}H-NMR δ 7.8, 8.3 (m, 3H, Ph), 8.4 (s, 1H, =CH); ^{13}C-NMR δ 87 (=C<), 113 (CN), 126, 130, 133, 140 (Ph), 160 (=CH); IR 3050 (m, C-H, Ph), 2235 (s, CN), 1589 (m, C=C), 1520, 1341 (s, NO_2), 920, 848 (m, C-H out-of-plane bending); Anal. Calcd. for $C_{10}H_4ClN_3O_2$: C 51.41%, H 1.73%, N 17.99%; Found: C 51.12%, H 1.34%, N 17.83%.

2.2.5 *2-(2-Cyanophenyl)-1,1-dicyanoethylene*

Yield 69%; mp 124°C; ^{1}H-NMR δ 8.2 (s, 1H, =CH), 7.8–8.0, 8.4 (m, 4H, Ph); ^{13}C-NMR δ 87 (=C<), 113 (CN), 116 (Ph-CN), 158 (=CH), 139, 133, 129 (Ph), 160 (=CH); IR 2920 (m, C-H, Ph), 2230, 2214 (s, CN), 1598, 1587 (m, C=C), 830 (m, C-H out-of-plane bending); Anal. Calcd. for $C_{11}H_5N_3$: C 73.74%, H 2.83%, N 23.45%; Found: C 68.03%, H 3.22%, N 22.41%.

2.2.6 *2-(3-Cyanophenyl)-1,1-dicyanoethylene*

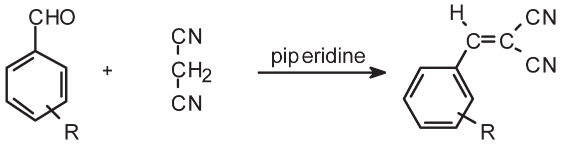
Yield 76%; mp 150°C; ^{1}H-NMR δ 8.1 (s, 1H, =CH), 7.6–7.8, 8.2 (m, 4H, Ph); ^{13}C-NMR δ 83 (=C<), 113 (CN), 119 (Ph-CN), 160 (=CH), 137, 129, 113 (Ph); IR 3036 (m, C-H, Ph), 2230 (s, CN), 1599, 1572 (m, C=C), 960, 800 (m, C-H out-of-plane bending); Anal. Calcd. for $C_{11}H_5N_3$: C 73.74%, H 2.83%, N 23.45%; Found: C 73.25%, H 2.65%, N 22.56%.

2.2.7 *2-(4-Cyanophenyl)-1,1-dicyanoethylene*

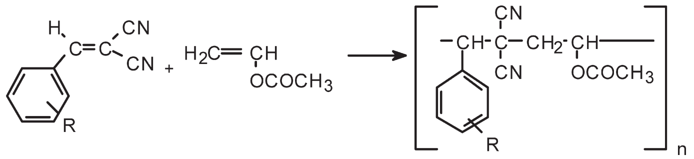
Yield 52%; mp 157°C; ^{1}H-NMR δ 8.1 (s, 1H, =CH), 7.6–8.2 (m, 4H, Ph); ^{13}C-NMR δ 83 (=C<), 113 (CN), 160 (=CH), 137, 129, 113 (Ph); IR 3031, 2966, (m, C-H, Ph), 2230 (s, CN), 1591 (m, C=C), 940, 835 (m, C-H out-of-plane bending); Anal. Calcd. for $C_{11}H_5N_3$: C 73.74%, H 2.83%, N 23.45%; Found: C 73.37%, H 2.62%, N 23.41%.

2.2.8 *2-(4-Dimethylaminophenyl)-1,1-dicyanoethylene*

Yield 50%; mp 186°C (Lit. 182–183°C (20)); ^{1}H-NMR δ 7.5 (s, 1H, =CH), 6.7, 7.8 (m, 4H, Ph), 3.0 (s, 6H, CH_3); ^{13}C-NMR δ 83 (=C<), 113 (CN), 160 (=CH), 136, 129, 113 (Ph); IR 2918, 2962 (m, C-H, Ph), 2208 (s, CN), 1611, 1563 (m, C=C), 944, 817 (m, C-H out-of-plane bending);



Sch. 1. Monomer synthesis (where R is 3-Br, 4-CH_3O; 5-Br, 2-CH_3O; 4-Cl, 3-NO_2; 5-Cl, 2-NO_2; 2-CN, 3-CN, 4-CN, and 4-$(CH_3)_2N$).



Sch. 2. Copolymer synthesis (where R is 3-Br, 4-CH_3O; 5-Br, 2-CH_3O; 4-Cl, 3-NO_2; 5-Cl, 2-NO_2; 2-CN, 3-CN, 4-CN, and 4-$(CH_3)_2N$).

Anal. Calcd. for $C_{12}H_{11}N_3$: C 73.07%, H 5.62%, N 21.30%; Found: C 72.83%, H 5.45%, N 21.30%.

2.3 *Copolymerization*

Vinyl acetate and ethyl acetate (Aldrich) were used as received. 1,1′Azobis(cyclohexane- carbonitrile) (ABCN) (Aldrich) was recrystallized twice from ethyl alcohol and then dried under reduced pressure at room temperature. Copolymers of the TSE monomers and vinyl acetate were prepared in 25-ml glass screw cap vials at TSE/VAC = 1/1 molar ratio of the monomer feed using 0.12 mol/l of ABCN at an overall monomer concentration 2.44 mol/L in 10 ml of ethyl acetate. The copolymerization was conducted at 70°C. After a predetermined time, the mixture was cooled to room temperature, and precipitated drop wise in petroleum ether. 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.

3 Results and Discussion

3.1 *Monomer Synthesis*

The TSE monomers were synthesized by Knoevenagel condensation 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.

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 VAC under conditions identical to those in the copolymerization experiments yielded 28.7% of poly(vinyl acetate), when polymerized for 30 min.

3.3 *Copolymerization*

Copolymerization (Scheme 2) of vinyl acetate and the ring-substituted 1,1-dicyanoethylenes resulted in formation of copolymers (Table 1) with weight-average molecular masses 1.2×10^3 to 7.3×10^3 daltons. According to elemental analysis, the copolymers have equimolar composition, which is indicative of high reactivity of the monomers in cross-propagation reactions.

Table 1. Copolymerization of vinyl acetate (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%	$M_W \times 10^{-3}$, D	T_g[b], °C	Onset of decomp., °C	10% wt. loss, °C	50% wt. loss, °C	Residue at 700 °C, wt.%
3-Br, 4-CH_3O	54	8.03	50.12	3.7	120	236	300	361	19
5-Br, 2-CH_3O	71	8.11	51.14	2.7	127	210	280	355	22
4-Cl, 3-NO_2	93	13.12	49.71	1.5	121	168	225	360	20
5-Cl, 2-NO_2	67	13.26	50.69	1.2	118	162	200	553	25
2-CN	56	15.86	50.14	1.7	123	206	260	435	22
3-CN	52	15.88	50.24	3.3	125	193	256	436	20
4-CN	36	15.76	49.65	7.3	125	77	250	346	15
4-$(CH_3)_2$	48	15.11	51.60	6.3	121	152	237	290	17

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

3.4 Structure and Properties

A comparison of the spectra of the copolymers and polyvinyl acetate shows that the reaction between the TSE monomers and VAC is a copolymerization. All the IR spectra of the copolymers show overlapping bands in the 3000–2800 cm^{-1} region corresponding to C-H vibrations. The absorptions of the VAC units appear at 1760–1750 cm^{-1} (carbonyl group), 1370 cm^{-1} (wagging CH_3), 1220 cm^{-1} (stretching COO), and 1010 and 1110 cm^{-1} (stretching C-C-C). The bands for the TSE monomer unit are 2225–2232 cm^{-1} (w, CN), 1610–1605, 1580–1570, 960–950, 840–830 for the phenyl group. The broadening of the NMR signals in the spectra of the copolymers is apparently associated with head-to-head structures, which formed through the attack of a VAC-ended radical on both sides of the TSE monomer unit (21). Thus the ^{1}H-NMR spectrum of the unsubstituted TSE-VAC copolymer shows a broad peak in the 6.2–7.5 ppm region corresponding to the phenyl ring protons of TSE. A broad signal in the 5.7 ppm region is assigned to the VAC methine protons. The resonance signal at 2.8 ppm is assigned to the methine proton of TSE unit. The band at 1.6 ppm is assigned to methyl protons whereas the two shoulders at 1.2 and 0.9 are assigned to the methylene of VAC unit. The ^{13}C-NMR spectra of the copolymers also support the suggested skeletal structure of the copolymers. Thus, in the typical spectrum of the VAC-TSE copolymer the assignment of peaks as follows 170–162 ppm (C=O), 115–133 ppm (phenyl carbons), 160 ppm (phenyl carbons bonded to halogen), 121 ppm (CN) of TSE unit. The absorbance at 170 and 21 ppm may be assigned to the carbonyl and methyl of VAC. The absorptions at 45 and 74 ppm are assigned to the methylene and the methine signals carbon resonances respectively, of the VAC unit. IR and NMR data showed that these are true copolymers, composed of both TSE and VAC 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 polyvinyl acetate ($T_g = 28–31°C$) 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 decomposition of the copolymers occurred in two steps, presumably acetic acid elimination in the 190–350°C range followed by a more slow decomposition of the formed residue at 350–800°C. Such two step degradation, acetic acid elimination followed by polyacetylene degradation is known for polyvinyl acetate (22). The decomposition products were not analyzed in this study, and the mechanism has yet to be investigated.

4 Conclusions

Novel trisubstituted ethylenes, 3-Br, 4-CH_3O; 5-Br, 2-CH_3O; 4-Cl, 3-NO_2; 5-Cl, 2-NO_2; 2-CN, 3-CN, 4-CN, and 4-$(CH_3)_2N$ ring-substituted 2-phenyl-1,1-dicyanoethylenes were prepared via a base catalyzed condensation of appropriate substituted benzaldehyde and malononitrile. The copolymerization of the monomers with vinyl acetate results in equimolar alternating copolymers. The composition of the copolymers was calculated from nitrogen analysis and the structure was analyzed by IR, ^{1}H and ^{13}C-NMR. High glass transition temperature of the copolymers in comparison with that of polyvinyl acetate indicates a substantial decrease in chain mobility of the copolymer due to the high dipolar character of the trisubstituted monomer unit. The decomposition of the copolymers occurred in two steps, acetic acid elimination in 190–350°C range followed by a more slow decomposition of the formed residue at 350–800°C.

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