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# Novel Copolymers of Vinyl Acetate and Halogen Ring-Disubstituted Methyl 2-Cyano-3-phenyl-2-propenoates

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*Equimolar alternating copolymers of vinyl acetate and electrophilic trisubstituted ethylene monomers, halogen ring-disubstituted methyl (E)-2-cyano-3-phenyl-2-propenoates,  $RC_6H_3CH=C(CN)CO_2CH_3$  (where R = 2,3-dichloro, 2,4-dichloro, 2,6-dichloro, 3,4-dichloro, 3,5-dichloro, 2,4-difluoro, 2,5-difluoro, 2,6-difluoro, and 3,4-difluoro) were prepared via copolymerization in solution with radical initiation (ABCN) at 70°C. The compositions of the copolymers were calculated from nitrogen analysis and the structures were analyzed by IR, <sup>1</sup>H- and <sup>13</sup>C-NMR. High glass transition temperatures of the copolymers in comparison with that of polyvinyl acetate indicate a decrease in chain mobility of the copolymers due to the high dipolar character of the trisubstituted ethylene monomer unit. The gravimetric analysis indicated that the decomposition of the copolymers occurs in two steps. The first step is relatively fast weight loss in 272–370°C range followed by very slow decomposition of the formed residue in 370–950°C range.*

**Keywords** trisubstituted ethylenes, radical copolymerization, alternating copolymers, vinyl acetate copolymers

## Introduction

Early studies of substituted ethylenes showed that the reactivity of the monomers in radical polymerization depends on their polarity, resonance stabilization and steric factors. 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 (1). Copolymerization of trisubstituted ethylenes (TSE,  $CHR^1=CR^2R^3$ ) having double bonds substituted with halo, cyano, and carbonyl

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groups and electron-rich monosubstituted ethylenes such as styrene (2, 3), N-vinylcarbazole (3), and vinyl acetate (4) show a tendency toward the formation of alternating copolymers.

In continuation of our studies of the monomer structure-reactivity correlation in the radical copolymerization of TSE monomers (5–7), we have prepared halogen ring-disubstituted methyl (*E*)-2-cyano-3-phenyl-2-propenoates,  $\text{RC}_6\text{H}_3\text{CH}=\text{C}(\text{CN})\text{CO}_2\text{CH}_3$  (where R is 2,3-dichloro, 2,4-dichloro, 2,6-dichloro, 3,4-dichloro, 3,5-dichloro, 2,4-difluoro, 2,5-difluoro, 2,6-difluoro, and 3,4-difluoro), and explore the feasibility of their copolymerization with vinyl acetate (VAC).

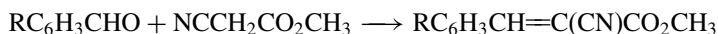
## Experimental

### 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, the glass transition temperatures ( $T_g$ ), and thermal stability of the copolymers were measured by using a TA Instruments model DSC 2010 and TGA 2090. The molecular weight of polymers was determined relative to polystyrene standards in  $\text{CHCl}_3$  solutions with sample concentrations 0.8% (wt/vol) by gel permeation chromatography using an Alltech 526 HPLC pump at an elution rate of 1.0 mL/min through Styragel HR 0.5, 1, 3, and 4 columns (Waters) at 25°C, a Model 410 refractive index and Viscotek T50A differential viscometer detectors.  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR spectra of 2–4%  $\text{CDCl}_3$  solutions of monomers and polymers were obtained on a Bruker DRX-500 spectrometer operating at 500.13 MHz for  $^1\text{H}$  and 125.76 MHz for  $^{13}\text{C}$ . Chemical shifts are reported referenced to TMS as 0 ppm. Proton spectra utilized 64 K data points with a sweep width of 31.4 kHz, a pulse delay of 10s and 5000 scans accumulated. Elemental analyses were performed by Quantitative Technologies Inc., NJ.

### Synthesis of Monomers

The TSE monomers were synthesized by Knoevenagel condensation (8) of a ring-substituted benzaldehyde with an active hydrogen compound, methyl cyanoacetate, catalyzed by a base, piperidine.



2,3-Dichloro, 2,4-dichloro, 2,6-dichloro, 3,4-dichloro, 3,5-dichloro, 2,4-difluoro, 2,5-difluoro, 2,6-difluoro, and 3,4-difluorobenzaldehydes, methyl cyanoacetate, DMF, and piperidine supplied from Aldrich Chemical Co., were used for monomer synthesis as received. The preparation procedure was essentially the same for all of the TSE monomers. In a typical synthesis, equimolar amounts of methyl cyanoacetate 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 recrystallization from 2-propanol. The preparation procedure and characterization of all the TSE monomers, except methyl (*E*)-2-cyano-3-(3,5-dichlorophenyl)-2-propenoate, was described earlier

(9, 10). The condensation reaction proceeded smoothly, yielding crystalline products, which were purified by conventional techniques.

### *Methyl (E)-2-cyano-3-(3,5-dichlorophenyl)-2-propenoate*

Yield 64%; mp 150°C;  $^1\text{H NMR}$   $\delta$  8.1 (s, 1H, CH=), 7.8, 7.5 (d, 3H, phenyl), 3.9 (s, 3H, OCH<sub>3</sub>);  $^{13}\text{C NMR}$   $\delta$  163 (C=O), 152 (HC=), 136, 134, 133, 129 (phenyl), 114 (CN), 106 (C=), 54 (OCH<sub>3</sub>); IR (NaCl): 3076 (m, C–H), 2220 (m, CN), 1725 (s, C=O), 1611, 1580 (C=C), 1271 (s, C–O–CH<sub>3</sub>), 807, 761 (s, C–H out of plane). Anal. Calcd. for C<sub>11</sub>H<sub>7</sub>Cl<sub>2</sub>NO<sub>2</sub>: C, 51.59; H, 2.76; N, 5.47; Found: C, 51.54; H, 2.44; N, 5.34.

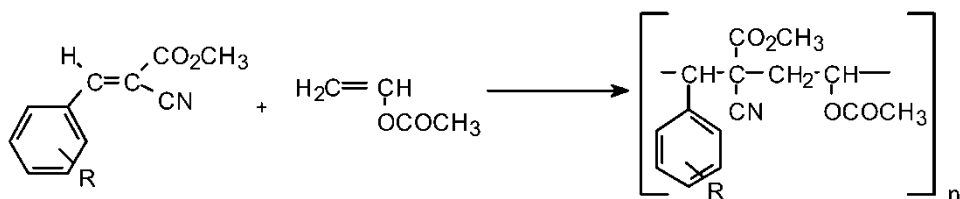
### *Copolymerization*

Vinyl acetate (Aldrich) was distilled at 72°C before use. Ethyl acetate (Aldrich) was 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 TSE monomers and VAC were prepared in 25-ml Pyrex screw cap ampoules at VAC/TSE = 2/1 molar ratio of the monomer feed using 0.12 mol/l of ABCN at an overall monomer concentration 2.4 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 dropwise 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.

## 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 petroleum ether. The inability of the monomers to polymerize is associated with steric difficulties encountered in the homopolymerization of 1,1- and 1,2-disubstituted ethylenes (1). This type of steric hindrance would increase the activation energy required for addition and slow down the rate of propagation to such an extent as to favor the occurrence of a chain transfer or termination instead. The homopolymerization of VAC under conditions identical to those in the copolymerization experiments yielded 26.8% of polyvinyl acetate, when polymerized for 30 min.



**Scheme 1.** VAC-TSE copolymer synthesis. R = 2,3-dichloro, 2,4-dichloro, 2,6-dichloro, 3,4-dichloro, 3,5-dichloro, 2,4-difluoro, 2,5-difluoro, 2,6-difluoro, and 3,4-difluoro.

**Table 1**Copolymerization of vinyl acetate ( $M_1$ ) and halogen ring-disubstituted methyl 2-cyano-3-phenyl-2-propenoates,  $RC_6H_3CH=C(CN)CO_2CH_3$  ( $M_2$ )

R	Yield <sup>a</sup> (wt%)	Nitrogen (wt%)	$m_2$ in copolymer (mol%)	$M_w \times 10^{-3}$ (Da)	$T_g^b$ (°C)	TGA			
						Onset of decomp. (°C)	10% wt loss	50% wt loss	% Residue
2,3-dichloro	32.0	4.08	49.73	15.0	123	286	273	369	21.0
2,4-dichloro	43.9	4.06	49.25	16.7	134	294	289	367	20.7
2,6-dichloro	26.7	4.05	49.01	9.6	126	292	282	351	21.9
3,4-dichloro	32.8	3.98	47.37	9.6	124	290	273	364	19.9
3,5-dichloro	37.7	3.99	47.60	6.4	125	303	290	357	18.6
2,4-difluoro	32.4	4.01	48.06	14.9	139	305	286	355	16.3
2,5-difluoro	22.9	4.06	49.25	23.8	133	300	280	355	18.0
2,6-difluoro	34.0	4.03	48.53	31.7	127	272	240	343	20.7
3,4-difluoro	26.8	4.09	49.97	21.1	122	299	268	353	18.4

<sup>a</sup>Polymerization time was 8 h.<sup>b</sup> $T_g$  transition was observed by DSC.

### Copolymerization

Copolymerization (Scheme 1) of VAC and the halogen ring-disubstituted methyl (*E*)-2-cyano-3-phenyl-2-propenoates resulted in the formation of copolymers (Table 1) with weight-average molecular masses of  $6.4 \times 10^3$  to  $31.7 \times 10^3$  Da.

In an attempt to qualitatively correlate the observed monomer reactivities, we considered copolymer composition data obtained at VAC/TSE = 2 monomer feed. The relative reactivity of VAC in copolymerization with these monomers can be estimated by assuming applicability of the copolymer composition ((Equation (1) of the terminal copolymerization model (1)):

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

$m_1$  and  $m_2$  are the mole fractions of VAC and TSE monomer units in the copolymer, respectively;  $(M_1)$  and  $(M_2)$  are the concentrations of VAC and a TSE in the monomer feed, respectively;  $r_1 = k_{11}/k_{12}$ , and  $r_2 = k_{22}/k_{21}$ . In the absence of the self-propagation of TSE monomers ( $k_{22} = 0$ ,  $r_2 = 0$ ), and at monomer feed,  $(M_1)/(M_2) = 2$ , (Equation 1) yields:

$$r_1 = 0.5 (m_1/m_2 - 1) \quad (2)$$

Consideration of the copolymerization constants according to Equation (2) also involves the assumption of minimal copolymer compositional drift at this monomer feed and given conversion. This nonrigorous kinetic treatment nevertheless allows estimation of the reactivity of a vinyl acetate-ended polymer radical in reaction with electrophilic monomer. Very low values of  $r_1$ , 2,3-dichloro (0.01), 2,4-dichloro (0.02), 2,6-dichloro (0.02), 3,4-dichloro (0.06), 3,5-dichloro (0.05), 2,4-difluoro (0.04), 2,5-difluoro (0.02), 2,6-difluoro (0.03), and 3,4-difluoro (0.00) suggest that VAC and TSE enter into the copolymer in equimolar amounts in a nonrandom, alternating arrangement along the copolymer chain.

### Structure and Thermal Properties

The structures of the copolymers were characterized by IR and NMR spectroscopy. 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 3300–2600  $\text{cm}^{-1}$  region corresponding to C–H vibrations. The absorptions of the VAC units appear at 1748–1751  $\text{cm}^{-1}$  (carbonyl group), 1366–1374  $\text{cm}^{-1}$  (wagging  $\text{CH}_3$ ), 1221–1236  $\text{cm}^{-1}$  (stretching COO), and 1010–1016 and 1095–1110  $\text{cm}^{-1}$  (stretching C–C–C). The bands for the TSE monomer unit are 2237–2245  $\text{cm}^{-1}$  (w, CN), 1748–1751  $\text{cm}^{-1}$  (s, C=O), and 1221–1238  $\text{cm}^{-1}$  (m, C–O).

All NMR spectra show broad resonance signals. Broadening of the NMR signals in the spectra of the copolymers is apparently associated with head-to-tail and head-to-head structures, which formed through the attack of a VAC-ended radical on both sides of the TSE monomer unit. It was demonstrated that both head-to-tail and head-to-head structures TSE-styrene dyads exist in the copolymers of styrene and 2-phenyl-1,1-dicyanoethene (11). All  $^1\text{H}$ -NMR spectra show a broad peak in the 6.5–8.0 ppm region corresponding to the phenyl ring protons of the TSE. A broad signal in the 4.7–5.7 ppm region is assigned to the VAC methine protons. The peaks in the range 3.5–4.2 ppm and 3.2–3.5 ppm are assigned to the methoxy and the methine protons of

the TSE monomer unit. A signal in 1.7–2.7 ppm range corresponds to VAC methyl group. Broad, overlapping resonances in the 0.9–2.5 ppm region are assigned to the methylene proton of VAC monomer unit. The  $^{13}\text{C}$ -NMR and DEPT spectra of the copolymers also support the suggested skeletal structure of the copolymers. Thus, the assignment of the peaks as follows: 167–175 ppm (C=O), 120–140 ppm (phenyl carbons), 115–120 ppm (CN), 52–57 ppm (OCH<sub>3</sub> and methine), 46–52 ppm (quaternary carbon) of TSE unit. The peaks corresponding to the carbons of VAC monomer unit are at 170 ppm (C=O), 65–72 ppm (methine), 35–47 ppm (CH<sub>2</sub>), and 20–30 ppm (CH<sub>3</sub>). The 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<sub>3</sub> and insoluble hexane, cyclohexane, and in ethyl and petroleum ether. They are amorphous and show no crystalline DSC endotherm. High  $T_g$  of the copolymers (Table 1), in comparison with that of polyvinyl acetate ( $T_g = 28\text{--}31^\circ\text{C}$ ) indicates a decrease in the chain mobility of the copolymer due to the high dipolar character of the TSE structural unit. 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 occurs in two steps, presumably acetic acid elimination in the 272–370°C range followed by very slow decomposition of the formed residue (22–16%) at about 400°C. Such two step degradation, acetic acid elimination followed by polyacetylene degradation is known for polyvinyl acetate (12). The continued heating up to 950°C brings down the weight of the residue to about 10%. The decomposition products were not analyzed in this study and the mechanism has yet to be investigated.

## Conclusion

The copolymerization of vinyl acetate and trisubstituted ethylenes, halogen ring-disubstituted methyl 2-cyano-3-phenyl-2-propenoates results in equimolar alternating copolymers. The compositions of the copolymers were calculated from nitrogen analysis and the structures were analyzed by IR,  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR. High glass transition temperatures of the copolymers, in comparison with that of polyvinyl acetate, indicate a substantial decrease in the chain mobility of the copolymers due to the high dipolar character of the trisubstituted ethylene monomer unit. The gravimetric analysis indicated that the decomposition of the copolymers occurs in two steps. The first step is relatively fast weight loss in 272–370°C range, followed by very slow decomposition of the formed residue in 370–950°C range.

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