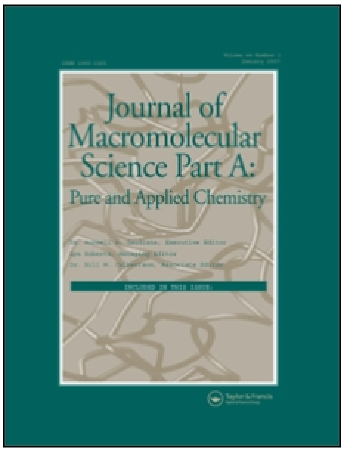

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# Novel Copolymers of Vinyl Acetate and Alkoxy Ring-Substituted Methyl 2-cyano-3-phenyl-2-propenoates

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*Electrophilic trisubstituted ethylene monomers, ring-substituted methyl 2-cyano-3-phenyl-2-propenoates, $RC_6H_4CH{=}C(CN)CO_2CH_3$, (where R is 2-$CH_3O$, 3-$CH_3O$, 4-$CH_3O$, 2-$C_2H_5O$, 3-$C_2H_5O$, 4-$C_2H_5O$, 4-$C_3H_7O$, 4-$C_4H_9O$, 4-$C_6H_{11}O$, and 4-$CH_3CO_2$), were synthesized by the piperidine catalyzed Knoevenagel condensation of ring-substituted benzaldehydes and methyl cyanoacetate, and characterized by CHN elemental analysis, IR, $^1$H- and $^{13}$C-NMR. Copolymerization of the propenoates and vinyl acetate in solution with radical initiation (AIBN) at 70°C yielded equimolar alternating copolymers. 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 200–400°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 groups and electron-rich monosubstituted ethylenes such as ST, *N*-vinylcarbazole, and vinyl acetate (2, 3) show a tendency toward the formation of alternating copolymers.

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In continuation of our studies of the monomer structure-reactivity correlation in the radical copolymerization of TSE monomers, (4–6) we have prepared ring-substituted methyl 2-cyano-3-phenyl-2-propenoates, $RC_6H_4CH{=}C(CN)CO_2CH_3$ (where R is 2-$CH_3O$, 3-$CH_3O$, 4-$CH_3O$, 2-$OC_2H_5$, 3-$OC_2H_5$, 4-$OC_2H_5$, 4-$C_3H_7O$, 4-$C_4H_9O$, 4-$C_6H_{11}O$, and 4-$CH_3CO_2$), and explore the feasibility of their copolymerization with vinyl acetate.

## 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 $CHCl_3$ 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. $^1H$ and $^{13}C$ NMR spectra of 2–4% $CDCl_3$ solutions of monomers and polymers were obtained on a Bruker DRX-500 spectrometer operating at 500.13 MHz for $^1H$ and 125.76 MHz for $^{13}C$. 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., (New Jersey).

### Synthesis of Monomers

*O*-anisaldehyde, *m*-anisaldehyde, *p*-anisaldehyde, 2-, 3-, 4-ethoxybenzaldehydes, 4-propoxybenzaldehyde, 4-butoxybenzaldehyde, 4-hexyloxybenzaldehyde, 4-acetoxybenzaldehyde, 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.

Preparation of 2-, 3-, and 4-methoxy (7), 4-ethoxy, 4-propoxy, 4-butoxy (8) ring-substituted methyl 2-cyano-3-phenyl-2-propenoates was described earlier.

*Methyl 2-cyano-3-(2-ethoxyphenyl)-2-propenoate.* Yield 84%; mp 104°C; $^1H$ NMR $\delta$ 8.8 (s, 1H, CH=), 8.3, 7.5, 7.0, 6.9(m, 4H, phenyl), 4.1 (q, 2H, $OCH_2$), 3.9 (s, 3H, $OCH_3$), 1.5 (t, 3H, $CH_3$); $^{13}C$ NMR $\delta$ 163 (C=O), 158 (HC=), 149, 139, 134, 128, 120 (phenyl), 116 (CN), 101 (C=), 64 ($OCH_2$), 52 ($OCH_3$), 14 ($CH_3$); IR (NaCl): 2984 (m, C–H), 2218 (m, CN), 1737(s, C=O), 1243 (s, C–O–$CH_3$), 796, 699 (s, C–H out of plane). Anal. Calcd. for $C_{13}H_{13}NO_3$: C, 67.52; H, 5.67; N, 6.06; Found: C, 67.28; H, 5.34; N, 5.90.

*Methyl 2-cyano-3-(3-ethoxyphenyl)-2-propenoate.* Yield 87%; mp 72°C; $^1H$ NMR $\delta$ 8.1 (s, 1H, CH=), 7.5, 7.4, 7.3, 7.1(m, 4H, phenyl), 4.1 (q, 2H, $OCH_2$), 3.9 (s, 3H, $OCH_3$), 1.4

(t, 3H, $CH_3$); $^{13}C$ NMR $\delta$ 163 (C═O), 159 (HC═), 155, 132, 130, 123, 120 (phenyl), 115 (CN), 102 (C═), 63 ($OCH_2$), 53 ($OCH_3$), 14 ($CH_3$); IR (NaCl): 2996 (m, C–H), 2222 (m, CN), 1743(s, C═O), 1240 (s, C–O–$CH_3$), 790, 700 (s, C–H out of plane). Anal. Calcd. for $C_{13}H_{13}NO_3$: C, 67.52; H, 5.67; N, 6.06; Found: C, 67.49; H, 5.58; N, 6.00.

*Ethyl 2-cyano-3-(4-hexyloxyphenyl)-2-propenoate.* Yield 89%; mp 73°C; $^1H$ NMR $\delta$ 8.2 (s, 1H, CH═), 8.0, 6.9 (d, 4H, phenyl), 4.0 (q, 2H, $OCH_2$), 3.9 (s, 3H, $OCH_3$), 1.8 (q, 2H, $CH_2$), 1.5 (q, 2H, $CH_2$), 1.4 (q, 4H, $(CH_2)_2$), 0.9 (t, 3H, $CH_3$); $^{13}C$ NMR $\delta$ 163 (C═O), 154 (HC═), 133, 124, 116 (phenyl), 115 (CN), 98 (C═), 68 ($OCH_2$), 52 ($OCH_3$), 31 ($CH_2$), 29 ($CH_2$), 25 ($CH_2$), 22 ($CH_2$), 14 ($CH_3$); IR (NaCl): 2982 (m, C–H), 2218 (m, CN), 1737(s, C═O), 1243 (s, C–O–$CH_3$), 796, 699 (s, C–H out of plane). Anal. Calcd. for $C_{17}H_{23}NO_2$: C, 71.06; H, 7.37; N, 4.87; Found: C, 71.00; H, 7.39; N, 4.75.

*Methyl 2-cyano-3-(4-acetoxyphenyl)-2-propenoate.* Yield 65%; mp 143°C; $^1H$ NMR $\delta$ 8.2 (s, 1H, CH═), 8.0, 7.3 (d, 4H, phenyl), 3.9 (q, 3H, $OCH_3$), 2.3 (s, 3H, $CH_3C$═O); $^{13}C$ NMR $\delta$ 168 (aceto C═O), 163 (C═O), 154 (═CH), 132, 129, 122 (phenyl), 115 (CN), 102 (C═), 53 ($OCH_3$), 20 ($CH_3$); IR (NaCl) 2991 (m, C–H), 2217 (m, CN), 1728 (C═O), 1272 (s, C–O–$CH_3$), 818, 760 (s, C–H out of plane). Anal. Calcd. for $C_{13}H_{11}NO_4$: C, 63.67; H, 4.52; N, 5.71. Found: C, 63.75; H, 4.38; N, 5.63.

### Copolymerization

Vinyl acetate (VAC) (Aldrich) was dried over $CaCl_2$ and distilled at 72°C before use. Ethyl acetate (Aldrich) was used as received. 2,2′-Azobisisobutyronitrile (AIBN) (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 TSE/VAC = 0.5 ratio of the monomer feed using 0.0045 mol/l of AIBN at an overall monomer concentration 2 mol/l in 20 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 methanol. The crude copolymers were repeatedly precipitated by petroleum ether-methanol mixtures (50/50) from chloroform solutions. Then the copolymers were dried under reduced pressure at 60°C until constant weight. The composition of the copolymers was determined based on the nitrogen content.

## Results and Discussion

### Monomer Synthesis

The TSE monomers were synthesized by Knoevenagel condensation (9) of a ring-substituted benzaldehyde with an active hydrogen compound, methyl cyanoacetate, catalyzed by a base, piperidine:

$$RC_6H_4CHO + NCCH_2CO_2CH_3 \longrightarrow RC_6H_4CH{=}C(CN)CO_2CH_3$$

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

### Homopolymerization

An attempted homopolymerization of the TSE monomers in the presence of AIBN did not produce any polymer as indicated by the lack of a precipitate in methanol. The inability of the monomers to polymerize is associated with steric difficulties encountered in the homopolymerization of 1,1- and 1,2-disubstituted ethylenes. 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. Homopolymerization of VAC under conditions identical to those in the copolymerization experiments yielded 28.7% of polyvinyl acetate, when polymerized for 30 min.

### Copolymerization

Copolymerization of the ring-substituted methyl 2-cyano-3-phenyl-2-propenoates with VAC resulted in formation of copolymers (Table 1) with weight-average molecular weights of $5.3 \times 10^3$ to $13.4 \times 10^3$ daltons. According to elemental analysis, the copolymerization of the propenoates with VAC results in equimolar copolymers, which is indicative of high reactivity of the monomers in cross-propagation reactions.

### 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 $cm^{-1}$ region corresponding to C–H vibrations. The absorptions of the VAC units appear at 1770–1650 $cm^{-1}$ (carbonyl group), 1380–1360 $cm^{-1}$ (wagging $CH_3$), 1250–1210 $cm^{-1}$ (stretching COO), and 1030–1010 and 1130–1110 $cm^{-1}$ (stretching C–C–C). The bands for the TSE monomer unit are 2235–2245 $cm^{-1}$ (w, CN), 1740–1748 $cm^{-1}$ (s, C=O), and 1232–1238 $cm^{-1}$ (m, C–O). All NMR spectra show broad resonance

**Table 1**
Copolymerization of vinyl acetate ($M_1$) and methyl 2-cyano-3-phenyl-2-propenoates $RC_6H_4CH{=}C(CN)CO_2CH_3$ ($M_2$)

| R | Yield[a], wt% | Nitrogen (wt%) | $m_2$ in pol., mol%. | $M_W \times 10^{-3}$, D | $T_g$, °C | Onset of decmp. (TGA), °C |
|---|---|---|---|---|---|---|
| 2-$OCH_3$ | 58 | 4.54 | 48.6 | 13.1 | 96.4 | 253 |
| 3-$OCH_3$ | 63 | 4.55 | 48.8 | 8.3 | 94.4 | 203 |
| 4-$OCH_3$ | 59 | 4.59 | 49.5 | 11.4 | 108.7 | 232 |
| 2-$OC_2H_5$ | 27 | 4.42 | 50.0 | 13.4 | 76.1 | 270 |
| 3-$OC_2H_5$ | 57 | 4.41 | 49.9 | 5.3 | 87.8 | 299 |
| 4-$OC_2H_5$ | 85 | 4.42 | 50.0 | 12.2 | 107.1 | 276 |
| 4-$OC_3H_7$ | 46 | 4.23 | 50.1 | 11.6 | 87.9 | 240 |
| 4-$OC_4H_9$ | 49 | 4.01 | 48.9 | 8.4 | 102.6 | 295 |
| 4-$OC_6H_{11}$ | 81 | 3.72 | 49.2 | 7.4 | 88.2 | 303 |
| 4-$CO_2CH_3$ | 67 | 4.21 | 49.7 | 8.6 | 93.5 | 203 |

[a] Polymerization time was 8 h.

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 (10). All 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 3.5–4.5 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 $^{13}$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 ($OCH_3$ 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 ($CH_2$), and 20–30 ppm ($CH_3$). 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 $CHCl_3$ and insoluble cyclohexane, and in ethyl and petroleum ethers. They are amorphous and show no crystalline DSC endotherm. High $T_g$ of the copolymers (Table 1), in comparison with that of polyvinyl acetate ($T_g = 28$–$31°C$) 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 decomposition products were not analyzed in this study, and the mechanism has yet to be investigated. The decomposition of all copolymers in nitrogen occurs rapidly in one stage in 200–400°C range.

## Conclusion

Trisubstituted ethylenes, ring-substituted methyl 2-cyano-3-phenyl-2-propenoates, were prepared via a base-catalyzed condensation of appropriate substituted benzaldehyde and methyl cyanoacetate. The copolymerization of the propenoates with vinyl acetate results in equimolar alternating copolymers. The compositions of the copolymers were calculated from nitrogen analysis and the structures were analyzed by IR, $^1$H- and $^{13}$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 copolymers decompose in the range 200–400°C.

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