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Novel co-polymers of vinyl acetate and alkyl ring-substituted methyl 2-cyano-3-phenyl-2-propenoates

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Abstract—Electrophilic trisubstituted ethylene monomers, ring-substituted methyl 2-cyano-3-phenyl-2-propenoates, $RC_6H_4CH{=}C(CN)CO_2CH_3$ (where R = H, 2-CH_3, 3-CH_3, 4-CH_3, 2-C_2H_5, 4-C_2H_5, 4-iC_3H_7, 4-C_4H_9 and 2,4,6-$(CH_3)_3$), 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. Co-polymerization of the propenoates and vinyl acetate in solution with radical initiation (AIBN) at 70°C yielded equimolar alternating co-polymers. The composition of the co-polymers was calculated from nitrogen analysis and the structures were analyzed by IR, ^{1}H- and ^{13}C-NMR, GPC, DSC and TGA. The high T_g of the co-polymers in comparison with that of polyvinyl acetate indicates a substantial decrease in chain mobility of the co-polymer due to the high dipolar character of the trisubstituted ethylene monomer unit. The gravimetric analysis indicated that the co-polymers decompose in the 214–400°C range.

Keywords: Trisubstituted ethylenes; radical co-polymerization; vinyl acetate co-polymers.

1. INTRODUCTION

Previous studies showed that trisubstituted ethylenes (TSEs, $CHR^1{=}CR^2R^3$) containing substituents larger than fluorine exhibit no tendency to undergo radical polymerization, apparently because of kinetic considerations superimposed on the thermodynamic factor responsible for the difficulty with which 1,1- and 1,2-

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disubstituted ethylenes polymerize [1]. Radical co-polymerization provides the most general method of overcoming problems encountered in homo-polymerization of TSE monomers. This approach has been particularly successful in preparing co-polymers from electrophilic TSE monomers having double bonds substituted with halo, cyano and carbonyl groups, and electron-rich monosubstituted monomers like styrene [2, 3], *N*-vinyl carbazole [3] and vinyl acetate [4].

In continuation of our studies of the monomer structure–reactivity correlations in the radical co-polymerization of TSE monomers [5–7], it was of interest to prepare ring-substituted methyl 2-cyano-3-phenyl-2-propenoates, $RC_6H_4CH{=}C(CN)CO_2CH_3$, where R = H, 2-$CH_3$, 3-$CH_3$, 4-$CH_3$, 2-$C_2H_5$, 4-$C_2H_5$, 4-i$C_3H_7$, 4-$C_4H_9$ and 2,4,6-$(CH_3)_3$, and to explore the feasibility of their co-polymerization with vinyl acetate.

2. EXPERIMENTAL

2.1. General procedures

Infrared spectra of the TSE monomers and co-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 co-polymers were measured with a Thermal Analysis (New Castle, DE, USA) TA Model 2010 differential scanning calorimeter (DSC). The thermal scans were performed in the 25–250°C range at a heating and cooling rate of 10°C/min. T_g was taken as the midpoint of a straight line between the inflection of the peak's onset and endpoint. The thermal stability of the co-polymers was measured by a thermogravimetric analyzer TA Model 2090 from ambient temperature to 600°C at 20°C/min. The molecular weights of the polymers were determined relative to polystyrene standards in $CHCl_3$ solutions with sample concentrations 0.8% (w/v) by gel-permeation chromatography (GPC) using a Waters Model 510 pump at an elution rate of 1.0 ml/min; Styragel (Waters, Milford, MA, USA) columns in series: 10^6, 10^5, 10^4, 10^3 and 500 Å at 25°C, a Model 410 refractive index and T50A differential viscometer detectors (Viscotek, Houston, TX, USA).

^{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 WP270SY spectrometer (Bruker, Billerica, MA, USA) operating at 200.13 MHz for ^{1}H and 50.33 MHz for ^{13}C. Relaxation times were at least 5-times the longest T^1 value in each spectrum. The distortionless enhancement by polarization transfer (DEPT) NMR spectra were obtained with an evolution delay of 3.704 ms to produce negative methylene and positive methine and methyl ^{13}C resonance signals. ^{1}H–^{13}C correlation spectra were run using the standard XHCOR Bruker program.

Elemental analyses were performed by Quantitative Technologies (Whitehouse, NJ, USA).

2.2. Synthesis of the monomers

Benzaldehyde, 2-, 3- and 4-methylbenzaldehydes, 2- and 4-ethylbenzaldehyde, 4-isopropylbenzaldehyde, 4-butylbenzaldehyde, 2,4,6-trimethylbenzaldehyde, methyl cyanoacetate, DMF and piperidine, supplied by Aldrich (Milwaukee, WI, USA), 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 re-crystallization from 2-propanol.

2.2.1. Methyl 2-cyano-3-phenyl-2-propenoate. Yield 53%, mp 89°C. ^{1}H-NMR δ 8.3 (s, 1H, CH=), 8.0, 7.6–7.4 (m, 5H, Ph), 3.9 (s, 3H, CH_3); ^{13}C-NMR δ 163 (CO), 155 (CH=), 133–129 (Ph), 115 (CN), 102 (=C=), 53 (CH_3); IR (cm^{-1}): 3000 (w, CH), 2230 (w, CN), 1729 (s, C=O), 1617 (m, C=C), 1205 (m, C−O−CH_3), 768 (m, Ph). Anal. calcd. for $C_{11}H_9NO_2$: C, 70.58%; H, 4.85%; N, 7.48%. Found: C, 70.43%; H, 4.5%; N, 7.38%.

2.2.2. Methyl 2-cyano-3-(2-methylphenyl)-2-propenoate. Yield 97%, mp 88°C. ^{1}H-NMR δ 8.6 (s, 1H, CH=), 8.1, 7.4–7.3 (m, 4H, Ph), 3.9 (s, 3H, OCH_3), 2.4 (s, CH_3); ^{13}C-NMR δ 163 (CO), 154 (CH=), 140–127 (Ph), 116 (CN), 104 (=C=), 54 (OCH_3), 20 (CH_3); IR (cm^{-1}): 3045 (w, CH), 2214 (w, CN), 1729 (m, C=O), 1658 (w, C=C), 1208 (w, C−O−CH_3), 969 (m, Ph). Anal. calcd. for $C_{12}H_{11}NO_2$: C, 71.63%; H, 5.51%; N, 6.96%. Found: C, 71.47%; H, 5.46%; N, 6.88%.

2.2.3. Methyl 2-cyano-3-(3-methylphenyl)-2-propenoate. Yield 46%, mp 96°C. ^{1}H-NMR δ 8.2 (s, 1H, CH=), 7.8, 7.7, 7.4 (m, 4H, Ph), 3.9 (s, 3H, OCH_3), 2.4 (s, 3H, CH_3); ^{13}C-NMR δ 162 (CO), 155 (CH=), 139–128 (Ph), 115 (CN), 102 (=C=), 53 (OCH_3), 21 (CH_3); IR (cm^{-1}): 3045, 2950 (w, CH), 2214 (w, CN), 1724 (m, C=O), 1658 (w, C=C), 1234 (w, C−O−CH_3), 954 (m, Ph). Anal. calcd. for $C_{12}H_{11}NO_2$: C, 71.63%; H, 5.51%; N, 6.96%. Found: C, 71.54%; H, 5.47%; N, 6.78%.

2.2.4. Methyl 2-cyano-3-(4-methylphenyl)-2-propenoate. Yield 49%, mp 109°C. ^{1}H-NMR δ 8.2 (s, 1H, CH=), 7.9, 7.3 (m, 4H, Ph), 3.9 (s, 3H, CH_3), 2.4 (s, 3H, CH_3); ^{13}C-NMR δ 163 (CO), 155 (CH=), 144, 131, 130, 129 (Ph), 116 (CN), 101 (=C=), 53 (CH_3), 22 (CH_3); IR (cm^{-1}): 2957 (w, CH), 2228 (w, CN), 1732 (m, C=O), 1611 (w, C=C), 1206 (w, C−O−CH_3), 767 (m, Ph). Anal. calcd. for $C_{12}H_{11}NO_2$: C, 71.63%; H, 5.51%; N, 6.96%. Found: C, 71.47%; H, 5.43%; N, 6.89%.

2.2.5. Methyl 2-cyano-3-(2-ethylphenyl)-2-propenoate. Yield 68%, mp 48°C. ^{1}H-NMR δ 8.6 (s, 1H, CH=), 8.1, 7.5, 7.3 (m, 4H, Ph), 3.9 (s, 3H, OCH_3),

2.8 (q, 2H, CH_2), 1.2 (t, 3H, CH_3); ^{13}C-NMR δ 163 (CO), 153 (CH=), 146, 133, 126 (Ph), 115 (CN), 104 (=C=), 53 (OCH_3), 26 (CH_2), 16 (CH_3); IR (cm^{-1}): 2957 (w, CH), 2225 (w, CN), 1736 (m, C=O), 1609 (w, C=C), 1206 (w, C−O−CH_3), 740 (m, Ph). Anal. calcd. for $C_{13}H_{13}NO_2$: C, 72.54%; H, 6.09%; N, 6.51%. Found: C, 72.46%; H, 6.13%; N, 6.40%.

2.2.6. Methyl 2-cyano-3-(4-ethylphenyl)-2-propenoate. Yield 45%, mp 62°C. ^{1}H-NMR δ 8.3 (s, 1H, CH=), 7.9, 7.3 (m, 4H, Ph), 3.9 (s, 3H, OCH_3), 2.7 (q, 2H, CH_2), 1.3 (t, 3H, CH_3); ^{13}C-NMR δ 163 (CO), 155 (CH=), 150–129 (Ph), 116 (CN), 101 (=C=), 53 (OCH_3), 29 (CH_2), 15 (CH_3); IR (cm^{-1}): 2957 (w, CH), 2225 (w, CN), 1736 (m, C=O), 1609 (w, C=C), 1206 (w, C−O−CH_3), 740 (m, Ph). Anal. calcd. for $C_{13}H_{13}NO_2$: C, 72.54%; H, 6.09%; N, 6.51%. Found: C, 72.46%; H, 6.13%; N, 6.40%.

2.2.7. Methyl 2-cyano-3-(4-isopropylphenyl)-2-propenoate. Yield 49%, mp 48°C. ^{1}H-NMR δ 8.2 (s, 1H, CH=), 7.9, 7.3 (m, 4H, Ph), 3.1 (s, 3H, CH_3), 2.9 (m, 1H, CH), 1.3 (s, 6H, CH_3); ^{13}C-NMR δ 163 (CO), 155 (CH=), 150, 131–127 (Ph), 116 (CN), 101 (=C=), 53 (OCH_3), 34 (CH), 23 (CH_3); IR (cm^{-1}): 2950 (w, CH), 2221 (w, CN), 1741 (m, C=O), 1613 (w, C=C), 1206 (w, C−O−CH_3), 763 (m, Ph). Anal. calcd. for $C_{14}H_{15}NO_2$: C, 73.34%; H, 6.59%; N, 6.11%. Found: C, 73.00%; H, 6.34%; N, 6.15%.

2.2.8. Methyl 2-cyano-3-(4-butylphenyl)-2-propenoate. Yield 87%, mp 109°C. ^{1}H-NMR δ 8.2 (s, 1H, CH=), 7.9, 7.3 (m, 4H, Ph), 3.9 (s, 3H, OCH_3), 2.6 (t, 2H, CH_2), 1.6 (quintet, 2H, CH_2), 1.4 (sextet, 2H, CH_2), 1.0 (t, 3H, CH_3); ^{13}C-NMR δ 163 (CO), 155 (CH=), 149, 131, 129, 128.7 (Ph), 116 (CN), 101 (=C=), 53 (CH_3), 36 (CH_2), 33 (CH_2), 22 (CH_2), 14 (CH_3); IR (cm^{-1}): 3027 (w, CH), 2228 (w, CN), 1724 (m, C=O), 1614 (w, C=C), 1255 (w, C−O−CH_3), 781 (m, Ph). Anal. calcd. for $C_{15}H_{17}NO_2$: C, 74.05%; H, 7.04%; N, 5.76%. Found: C, 73.75%; H, 6.75%; N, 5.93%.

2.2.9. Methyl 2-cyano-3-(2,4,6-trimethylphenyl)-2-propenoate. Yield 86%, mp 103°C. ^{1}H-NMR δ 8.5 (s, 1H, CH=), 6.9 (s, 5H, Ph), 3.9 (s, 3H, OCH_3), 2.3 (m, 9H, CH_3); ^{13}C-NMR δ 162 (CO), 158 (CH=), 140, 136, 129, 128 (Ph), 114 (CN), 110 (=C=), 53 (CH_3), 21, 20 (CH_3); IR (cm^{-1}): 3055 (w, CH), 2221 (w, CN), 1724 (m, C=O), 1601 (w, C=C), 1249 (w, C−O−CH_3), 762 (m, Ph). Anal. calc. for $C_{14}H_{15}NO_2$: C, 73.34%; H, 6.59%; N, 6.11%. Found: C, 73.36%; H, 6.63%; N, 6.06%.

2.3. Co-polymerization

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 re-crystallized twice from ethyl alcohol and then dried under reduced pressure at room temperature. Co-polymers of the TSE monomers and VAC were prepared in 25-ml Pyrex screw cap ampoules at a TSE/VAC ratio of 0.5 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 co-polymerization was conducted at 70°C. After a predetermined time, the mixture was cooled to room temperature, and precipitated dropwise in methanol. The crude co-polymers were repeatedly precipitated by petroleum ether-methanol mixtures (50:50) from solutions of chloroform. Then the co-polymers were dried under reduced pressure at 60°C until constant weight. The composition of the co-polymers was determined based on the nitrogen content.

3. RESULTS AND DISCUSSION

3.1. Monomer synthesis

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:

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

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

3.2. Homo-polymerization

An attempted homo-polymerization 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 homo-polymerization 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. The homo-polymerization of VAC under conditions identical to those in the co-polymerization experiments yielded 28.7% of polyvinyl acetate, when polymerized for 30 min.

3.3. Co-polymerization

Co-polymerization of the ring-substituted methyl 2-cyano-3-phenyl-2-propenoates with VAC resulted in formation of co-polymers (Table 1) with weight-average molecular weights of 3.2×10^3 to 1.6×10^4. According to elemental analysis, the co-polymerization of the propenoates with VAC results in equimolar co-polymers, which is indicative of high reactivity of the monomers in cross-propagation reactions.

Table 1.
Co-polymerization 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 (wt%)	Nitrogen (wt%)	M_2 in polymer (mol%)	$M_w \times 10^{-3}$	T_g (°C)	Onset of decomposition (TGA) (°C)
H	35	5.08	49.3	10.9	120	214
2-CH_3	52	4.95	51.3	7.0	117	231
3-CH_3	61	4.03	49.6	11.7	105	234
4-CH_3	49	4.59	48.4	13.7	125	234
2-C_2H_5	56	4.56	49.2	3.2	112	235
4-C_2H_5	37	4.52	49.8	8.2	128	259
4-iC_3H_7	22	4.81	50.0	15.6	125	294
4-C_4H_9	49	4.86	49.8	4.4	127	281
2,4,6-Trimethyl	61	4.77	49.7	5.4	71	266

Polymerization time was 8 h, T_g transition was observed by DSC.

3.4. Co-polymer structure

The structures of the co-polymers were characterized by IR and NMR spectroscopy. A comparison of the spectra of the co-polymers and polyvinyl acetate shows that the reaction between the TSE monomers and VAC is a co-polymerization. All the IR spectra of the co-polymers show overlapping bands in 3300–2600 cm^{-1} region, corresponding to C−H vibrations. The absorptions of the VAC units appear at 1760 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 2235–2245 cm^{-1} (w, CN), 1740–1748 cm^{-1} (s, C=O) and 1232–1238 cm^{-1} (m, C−O).

A typical ^{1}H-NMR spectrum of the methyl 2-cyano-3-phenyl-2-propenoate–VAC co-polymer in $CDCl_3$ is shown in Fig. 1. The assignment of proton resonances for the TSE–VAC co-polymers was carried out based on the spectra of model compounds, monomers, polymers, as well as the results of the peaks' areas integration. The integration data support the equimolar composition of the co-polymers. 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 the VAC methyl group. Broad, overlapping resonances in the 0.9–2.5 ppm region are assigned to the methylene proton of VAC monomer unit. Broadening of the NMR signals in the spectra of the co-polymers 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 co-polymers of styrene and 2-phenyl-1,1-dicyanoethene [9].

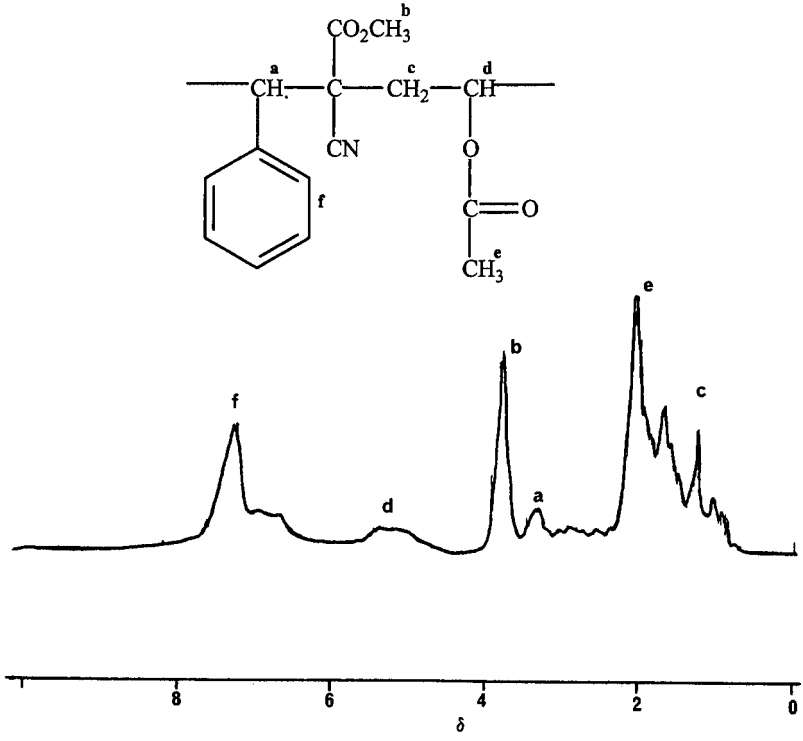

Figure 1. ^{1}H-NMR spectrum of methyl 2-cyano-3-phenyl-2-propenoate–VAC co-polymer in $CDCl_3$.

The ^{13}C-NMR and DEPT spectra of the co-polymers also support the suggested skeletal structure of the co-polymers. Thus, in the typical spectrum of the VAC–TSE co-polymer in $CDCl_3$ (Fig. 2) the assignment of peaks is as follows: 167–175 ppm (C=O), 120–140 ppm (phenyl carbons), 115–120 ppm (CN), 52–57 ppm (OCH_3 and methine) and 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 broad carbon resonances are most likely due to the presence of both H−T and H−H dyads. The IR and NMR data showed that these are true co-polymers, composed of both TSE and VAC monomer units.

3.5. Physical properties

The co-polymers prepared in the present work are all soluble in methyl ethyl ketone, acetone, benzene, THF, DMF and $CHCl_3$ and insoluble in cyclohexane, and in ethyl and petroleum ether. They are amorphous and show no crystalline DSC endotherm. Figure 3 shows a typical DSC and TG analysis of the methyl 2-cyano-3-(4-methylphenyl)-2-propenoate–VAC co-polymer heated in nitrogen. The high T_g of the co-polymers (Table 1 and Fig. 3), in comparison with that of polyvinyl acetate (T_g = 28–31°C) indicates a decrease in the chain mobility of the co-polymer

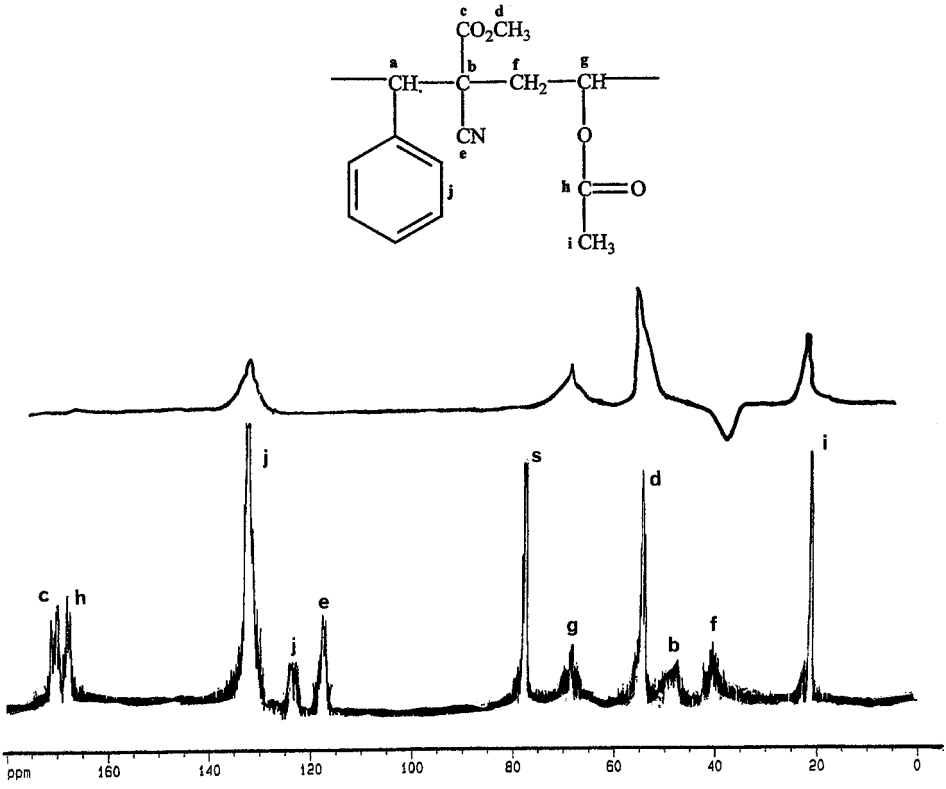

Figure 2. ^{13}C-NMR and DEPT spectrum of methyl 2-cyano-3-phenyl-2-propenoate–VAC co-polymer in $CDCl_3$.

due to the high dipolar character of the TSE structural unit. Information on the degradation of the co-polymers 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 co-polymers in nitrogen occurs in the range 214–400°C.

4. 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 co-polymerization of the propenoates with vinyl acetate results in equimolar alternating co-polymers. The compositions of the co-polymers were calculated from nitrogen analysis and the structures were analyzed by IR, ^{1}H- and ^{13}C-NMR. High glass transition temperatures of the co-polymers, in comparison with that of polyvinyl acetate, indicate a substantial decrease in the chain mobility of the co-polymers due to the high dipolar character

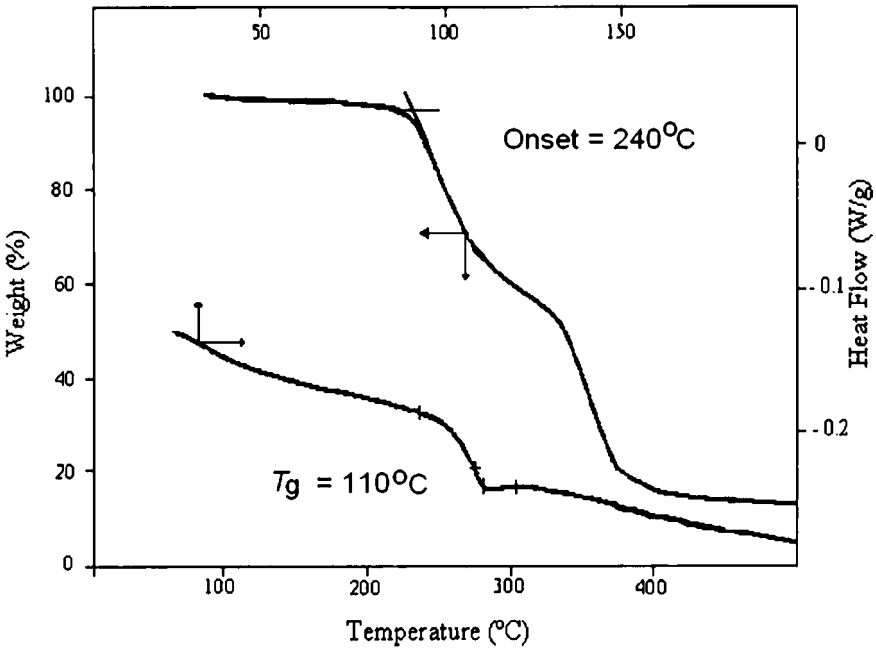

Figure 3. DSC and TGA traces of methyl 2-cyano-3-phenyl-2-propenoate–VAC co-polymer.

of the trisubstituted ethylene monomer unit. The gravimetric analysis indicated that the co-polymers decompose in the range 214–400°C.

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