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

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Abstract—Equimolar alternating co-polymers of vinyl acetate and electrophilic trisubstituted ethylene monomers, halogen ring-substituted methyl (E)-2-cyano-3-phenyl-2-propenoates, RC₆H₄CH=C(CN)CO₂CH₃ (where R = 2-Br, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 2-F, 3-F, 4-F), were prepared via co-polymerization in solution with radical initiation (ABCN) at 70°C. The compositions of the co-polymers were calculated from nitrogen analysis and the structures were analyzed by IR, ¹H- and ¹³C-NMR. High glass transition temperatures of the co-polymers in comparison with that of polyvinyl acetate indicate a decrease in chain mobility of the co-polymers due to the high dipolar character of the tri-substituted ethylene monomer unit. The gravimetric analysis indicated that the decomposition of the co-polymers occurs in two steps. The first step is relatively fast weight loss in 227–370°C range, followed by very slow decomposition of the formed residue in 370–950°C range.

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

1. INTRODUCTION

An interesting and useful aspect of radical co-polymerization is that monomers that show little or no tendency to homo-polymerize can readily participate in co-polymerization reactions. Previous studies showed that tri-substituted ethylenes (TSE, CHR₁=CR₂R₃) containing substituents larger than fluorine exhibit no tendency to undergo radical polymerization, apparently because of kinetic consid-
erations superimposed on the thermodynamic factor responsible for the difficulty with which 1,1- and 1,2-di-substituted 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 mono-substituted 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 explore the feasibility of co-polymerization of halogen ring-substituted methyl \((E)\)-2-cyano-3-phenyl-2-propenoates, \(\text{RC}_6\text{H}_4\text{CH} = \text{C(CN)CO}_2\text{CH}_3\), where \(R = 2\)-Br, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 2-F, 3-F, 4-F, with vinyl acetate (VAC).

### 2. MATERIALS AND METHODS

#### 2.1. General procedures

Infrared spectra of the VAC-TSE co-polymers (KBr pellets) were determined with a Nicolet Avatar 360 FT-IR spectrometer. The glass transition temperatures \((T_g)\) of the polymers were measured with a TA (Thermal Analysis) Model 2010 differential scanning calorimeter (DSC). The thermal scans were performed from ambient to 200\(^\circ\)C range at a heating rate of 10\(^\circ\)C/min. \(T_g\) was taken as a midpoint of a straight line between the inflection of the peak’s onset and end-point. The thermal stability of the co-polymers was measured by a thermogravimetric analyzer TA Model 2090 from ambient temperature to 600\(^\circ\)C at 20\(^\circ\)C/min. The molecular weights of the polymers were determined relative to polystyrene standards in CHCl\(_3\) solutions with sample concentrations of 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) columns in series: 10\(^6\), 10\(^5\), 10\(^4\), 10\(^3\) and 500 Å at 25\(^\circ\)C, a Model 410 refractive index and Viscotek T50A differential viscometer detectors.

\(^1\)H- and \(^{13}\)C-NMR spectra were obtained on 10% polymer solutions in CDCl\(_3\) at ambient temperature using a Bruker WP270SY spectrometer operating at 200.13 MHz for \(^1\)H-NMR and 50.33 MHz for \(^{13}\)C-NMR. 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 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.
2.2. Synthesis of the TSE monomers

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:

$$RC_6H_4CHO + NCCH_2CO_2CH_3 \rightarrow RC_6H_4CH=\text{C}(\text{CN})CO_2CH_3$$ (1)

2-Bromobenzaldehyde, 3-bromobenzaldehyde, 4-bromobenzaldehyde, 2-chlorobenzaldehyde, 3-chlorobenzaldehyde, 4-chlorobenzaldehyde, 2-fluorobenzaldehyde, 3-fluorobenzaldehyde, 4-fluorobenzaldehyde, methyl cyanoacetate, DMF and piperidine, supplied by Aldrich, were used for monomer synthesis as received. The preparation procedure and characterization of the TSE monomers was described earlier [9, 10]. The condensation reaction proceeded smoothly, yielding crystalline products, which were purified by conventional techniques.

2.3. Co-polymerization

Vinyl acetate (VAC, 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. Co-polymers of the TSE monomers and vinyl acetate 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 2.44 mol/l in 10 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 drop-wise in petroleum ether. The crude co-polymers were purified by re-precipitation from chloroform solution into an excess of petroleum ether. The composition of the co-polymers was determined based on the nitrogen content.

3. RESULTS AND DISCUSSION

3.1. Homo-polymerization

An attempted homo-polymerization 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 homo-polymerization of 1,1- and 1,2-di-substituted ethylenes [11]. 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 26.8% of polyvinyl acetate, when polymerized for 30 min.
3.2. Co-polymerization

Co-polymerization (Scheme 1) of V AC and the halogen ring-substituted methyl (E)-2-cyano-3-phenyl-2-propenoates resulted in the formation of co-polymers (Table 1) with weight-average molecular masses of 12.3 to 20.2 kDa.

In an attempt to qualitatively correlate the observed monomer reactivities, we considered co-polymer composition data obtained at V AC/TSE = 2 monomer feed. The relative reactivity of V AC in co-polymerization with these monomers can be estimated by assuming applicability of the co-polymer composition (equation (2)) of the terminal co-polymerization model [11]:

\[
m_1/m_2 = [M_1](r_1[M_1] + [M_2])/[M_2]([M_1] + r_2[M_2]) \tag{2}
\]

\(m_1\) and \(m_2\) are the mol fractions of V AC and TSE monomer units in the co-polymer, respectively; \([M_1]\) and \([M_2]\) are the concentrations of V AC 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 (2) yields:

\[
r_1 = 0.5(m_1/(m_2 - 1)) \tag{3}
\]

![Scheme 1. VAC-TSE co-polymer synthesis. R = 2-, 3- and 4-Br, Cl and F.](image)

**Table 1.** VAC-TSE co-polymer synthesis. R = 2-, 3- and 4-Br, Cl and F.

<table>
<thead>
<tr>
<th>R (M2)</th>
<th>Yield(^a) (wt%)</th>
<th>Nitrogen (^b) (wt%)</th>
<th>(m_2) in co-polymer (mol%)</th>
<th>Molecular mass (kDa)</th>
<th>T(_g) (^b) (°C)</th>
<th>TGA (°C)</th>
<th>Residue (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-Br</td>
<td>35.0</td>
<td>4.04</td>
<td>49.2</td>
<td>13.3</td>
<td>110</td>
<td>240</td>
<td>251</td>
</tr>
<tr>
<td>3-Br</td>
<td>51.9</td>
<td>4.03</td>
<td>49.8</td>
<td>13.1</td>
<td>117</td>
<td>227</td>
<td>238</td>
</tr>
<tr>
<td>4-Br</td>
<td>60.7</td>
<td>4.03</td>
<td>49.6</td>
<td>14.6</td>
<td>133</td>
<td>232</td>
<td>283</td>
</tr>
<tr>
<td>2-Cl</td>
<td>48.8</td>
<td>4.59</td>
<td>48.4</td>
<td>20.2</td>
<td>121</td>
<td>235</td>
<td>269</td>
</tr>
<tr>
<td>3-Cl</td>
<td>55.7</td>
<td>4.56</td>
<td>49.2</td>
<td>12.7</td>
<td>126</td>
<td>233</td>
<td>279</td>
</tr>
<tr>
<td>4-Cl</td>
<td>37.4</td>
<td>4.52</td>
<td>49.8</td>
<td>12.3</td>
<td>131</td>
<td>225</td>
<td>254</td>
</tr>
<tr>
<td>2-F</td>
<td>21.9</td>
<td>4.81</td>
<td>50.0</td>
<td>16.7</td>
<td>101</td>
<td>227</td>
<td>252</td>
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<tr>
<td>3-F</td>
<td>49.0</td>
<td>4.61</td>
<td>46.8</td>
<td>19.9</td>
<td>102</td>
<td>228</td>
<td>257</td>
</tr>
<tr>
<td>4-F</td>
<td>60.8</td>
<td>4.77</td>
<td>49.7</td>
<td>14.3</td>
<td>110</td>
<td>232</td>
<td>261</td>
</tr>
</tbody>
</table>

\(^a\) Polymerization time was 8 h.
\(^b\) T\(_g\) transition was observed by DSC.
Consideration of the co-polymerization constants according to equation (3) also involves the assumption of minimal co-polymer compositional drift at this monomer feed and given conversion. This non-rigorous kinetic treatment nevertheless allows estimation of the reactivity of a vinyl acetate-ended polymer radical in reaction with electrophilic monomer. Very low values of $r_1$ for 2-Br (0.02), 3-Br (0.00), 4-Br (0.01), 2-Cl (0.03), 3-Cl (0.02), 4-Cl (0.00), 2-F (0.00), 3-F (0.07) and 4-F (0.01) suggest that VAC and TSE enter into the co-polymer in equimolar amounts in a non-random, alternating arrangement along the co-polymer chain.

3.3. Characterization

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

3.3.2. NMR spectra. A typical $^1$H-NMR spectrum of a halogen substituted VAC-TSE co-polymer in CDCl$_3$ is shown in Fig. 1. The assignment of proton resonances for the co-polymers was carried out based on the spectra of model compounds, monomers and polymers, DEPT, $^1$H–$^{13}$C correlation spectra, 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 3.5–4.2 ppm and 3.2–3.5 ppm are assigned to the methoxy and the methine protons of the TSE monomer unit, respectively. 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. 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 [12].

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),
Figure 1. $^1$H-NMR spectrum of VAC-methyl 2-cyano-3-(4-bromophenyl)-2-propenoate co-polymer in CDCl$_3$.

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 NMR data showed that these are true co-polymers, composed of both VAC and TSE monomer units.

3.4. 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 hexane, 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 VAC-methyl 2-cyano-3-(2-chlorophenyl)-2-propenoate co-polymer heated in nitrogen. High $T_g$ of the co-polymers (Table 1 and Fig. 3), in comparison with that of polyvinyl acetate ($T_g = 28–31^\circ$C) indicates a decrease in the chain mobility of the co-polymer 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 TGA in nitrogen and air produce similar traces. The decomposition of the co-polymers occurs in two steps, presumably acetic acid elimination in the 227–370$^\circ$C range followed by very slow decomposition of the formed at about 400$^\circ$C residue.
Figure 2. $^{13}$C-NMR and DEPT spectrum of VAC-methyl 2-cyano-3-(4-bromophenyl)-2-propenoate co-polymer in CDCl$_3$.

(20–15%). Such a two-step degradation, acetic acid elimination followed by polyacetylene degradation, is known for polyvinyl acetate [13]. 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.

4. CONCLUSIONS

The co-polymerization of vinyl acetate and tri-substituted ethylenes, halogen ring-substituted methyl 2-cyano-3-phenyl-2-propenoates, 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 of the tri-substituted ethylene monomer unit. The gravi-
metric analysis indicated that the decomposition of the co-polymers occurs in two steps. The first step is relatively fast weight loss in the 227–370°C range, followed by very slow decomposition of the formed residue in the 370–950°C range.

Acknowledgements

We are grateful to acknowledge that the project was partly the Coatings Industry Education Fund (CIEF), the Chicago Society of Coating Technology, and the Office of Sponsored Programs and Research of DePaul University. J.G. was supported by a CIEF graduate fellowship.

REFERENCES


