Novel functional copolymers of vinyl acetate: 1. Alkyl ring-substituted ethyl 2-cyano-3-phenyl-2-propenoates

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Alkyl ring-substituted ethyl 2-cyano-3-phenyl-2-propenoates, $RPhCH{=}C(CN)CO_2C_2H_5$ (where R is 2-methyl, 3-methyl, 4-methyl, 4-ethyl, 4-isopropyl, 4-*t*-butyl, 4-trifluoromethyl, 2-trifluoromethyl) were prepared and copolymerized with vinyl acetate in solution with radical initiation. The compositions of the copolymers were calculated from nitrogen analysis and the structures were analyzed by IR, ^1H and ^{13}C-NMR. Thermal behavior of the copolymers was studied by DSC and TGA. Decomposition of the copolymers in nitrogen occurred in two steps, first in the 200-500ºC range with residue (13-16 wt%), which then decomposed in the 500-800ºC range.

1. Introduction

Synthetic manipulation of polymer substrates via copolymerization is one of the oldest and most reliable methods to increase the functional diversity of soft materials [1]. Ring-substituted ethyl 2-cyano-3-phenyl-2-propenoates (ECPP), $RPhCH=C(CN)CO_2C_2H_5$ continue to attract attention as comonomers for modification of commercial polymers. Ring unsubstituted ECPP has been copolymerized with acrylonitrile [2], styrene [3], vinyl acetate [4, 5], acrylic esters [6], and 1,2-ethanediyl ester of 2-methylpropenoic acid [7]. Terpolymerization of ECPP was reported with acrylonitrile and styrene [8], and ethyl acrylate and styrene [9]. Also reported are curable adhesive and coating compositions containing trifunctional olefinic monomers, including ECPP [10].

In continuation of our exploration of synthesis and radical copolymerization of esters 2-cyano-3-phenyl-2-propenoic acid, we have prepared alkyl ring-substituted ethyl 2-cyano-3-phenyl-2-propenoates, $RPhCH=C(CN)CO_2C_2H_5$ (ECPP), where R is 2-methyl, 3-methyl, 4-methyl, 4-ethyl, 4-isopropyl, 4-*t*-butyl, 1,1,1-trifluoro-4-methyl, 1,1,1-trifluoro-2-methyl, and explore the feasibility of their copolymerization with vinyl acetate. There are reports of syntheses of 2-methyl, 3-methyl, 4-methyl [11], 4-ethyl, 4-isopropyl, 4-*t*-butyl [12], 4-trifluoromethyl [13], and 2-trifluoromethyl [14] ring-substituted ECPP. To the best of our knowledge, there have been no reports on copolymerization of these ethyl 2-cyano-3-phenyl-2-propenoates with vinyl acetate [15].

2 Experimental

2.1 Materials

2-Methyl, 3-methyl, 4-methyl, 4-ethyl, 4-isopropyl, 4-*t*-butyl, 4-trifluoromethyl, 2-trifluoromethyl - substituted benzaldehydes, propyl cyanoacetate, piperidine, vinyl acetate, 1,1'-azobiscyclohexanecarbonitrile, (ABCN), and toluene supplied from Sigma-Aldrich Co., were used as received.

2.2 Instrumentation

Infrared spectra of the ECPP monomers and copolymers (NaCl plates) were determined with an ABB FTLA 2000 FT-IR spectrometer. The melting points of the monomers, the glass transition temperatures (T_g), of the copolymers were measured with TA (Thermal Analysis, Inc.) Model Q10 differential scanning calorimeter (DSC). The thermal scans were performed in a 25 to 200ºC range at heating rate of 10ºC/min. T_g 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 thermogravimetric analyzer (TGA) TA Model Q50 from ambient temperature to 800ºC at 20ºC/min. The molecular weights of the polymers was determined relative to polystyrene standards in THF solutions with sample concentrations 0.8% (w/v) by gel permeation chromatography (GPC) using a Altech 426 HPLC pump at an elution rate of 1.0 mL/min; Phenogel 5µ Linear column at 25ºC and Viscotek 302 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 Avance 300 MHz spectrometer. Elemental analyses were performed by Midwest Microlab, LLC (IN).

2.3 Synthesis of Monomers

The ring-substituted ethyl 2-cyano-3-phenyl-2-propenoates (ECPP) were synthesized by Knoevenagel condensation [16] of a ring-substituted benzaldehydes with ethyl cyanoacetate, catalyzed by base, piperidine.

$$\mathrm{RPhCHO + NCCH_2CO_2C_2H_5 \rightarrow RPhCH = C(CN)CO_2C_2H_5}$$

where R is 2-methyl, 3-methyl, 4-methyl, 4-ethyl, 4-isopropyl, 4-*t*-butyl, 4-trifluoromethyl, 2-trifluoromethyl.

The preparation procedure was essentially the same for all the monomers. In a typical synthesis, equimolar amounts of ethyl cyanoacetate and an appropriate ring-substituted benzaldehyde were mixed in equimolar ratio in a 20 mL vial. A few drops of piperidine were added with stirring. The product of the reaction was isolated by filtration and purified by crystallization from 2-propanol. The condensation reaction proceeded smoothly, yielding products, which were purified by conventional techniques.

2.3.1 *Ethyl 2-cyano-3-(2-methylphenyl)-2-propenoate*

Yield 74%; mp 63°C, ^{1}H-NMR δ 8.6 (s, 1H, CH=), 8.2-7.1 (m, 4H, Ph), 4.3 (q, 2H, OCH_2), 2.5 (s, 3H, $PhCH_3$), 1.4 (t, 3H, $OCH_2C\underline{H}_3$); ^{13}C-NMR δ 162 (C=O), 153 (HC=), 140, 133, 131, 129, 128, 127 (Ph), 115 (CN), 105 (C=), 63 (OCH_2), 20 ($PhCH_3$), 14 ($OCH_2\underline{C}H_3$); IR (cm^{-1}): 3011-2830 (m, C-H), 2223 (m, CN), 1741 (s, C=O), 1594 (C=C), 1254 (s, $C\text{-}O\text{-}CH_3$), 799 (s, C-H out of plane). Anal. Calcd. for $C_{13}H_{13}NO_2$: C, 72.54; H, 6.09; N, 6.51; Found: C, 71.79; H, 6.09; N, 6.53.

2.3.2 ***Ethyl 2-cyano-3-(3-methylphenyl)-2-propenoate***

Yield 72%; mp 91.6°C, ^{1}H-NMR δ 8.2 (s, 1H, CH=), 7.1-6.3 (m, 4H, Ph), 4.3 (q, 2H, OCH_2), 2.3 (s, 3H, $PhCH_3$), 1.3 (t, 3H, $OCH_2C\underline{H}_3$); ^{13}C-NMR δ 163 (C=O), 153 (HC=), 138, 137, 133, 131, 129, 126 (Ph), 116 (CN), 104 (C=), 61 (OCH_2), 21 ($PhCH_3$), 14 ($OCH_2\underline{C}H_3$); IR (cm^{-1}): 3041-2834 (m, C-H), 2224 (m, CN), 1727 (s, C=O), 1582 (C=C), 1240 (s, C-O-CH_3), 864 (s, C-H out of plane). Anal. Calcd. for $C_{13}H_{13}NO_2$: C, 72.54; H, 6.09; N, 6.51; Found: C, 72.23; H, 6.08; N, 6.50.

2.3.3 ***Ethyl 2-cyano-3-(4-methylphenyl)-2-propenoate***

Yield 83%; mp 99.9°C, ^{1}H-NMR δ 8.4 (s, 1H, CH=), 7.8, 7.0 (d, 4H, Ph), 4.3 (q, 2H, OCH_2), 2.3 (t, 3H, $PhCH_3$), 1.3 (t, 3H, $OCH_2C\underline{H}_3$); ^{13}C-NMR δ 163 (C=O), 155 (HC=), 145, 131, 130, 129 (Ph), 116 (CN), 102 (C=), 62 (OCH_2), 22 ($PhCH_3$), 14 ($OCH_2\underline{C}H_3$); IR (cm^{-1}): 3031-2924 (m, C-H), 2225 (m, CN), 1742 (s, C=O), 1234 (s, C-O-C), 847, 759 (s, C-H out of plane). Anal. Calcd. for $C_{13}H_{13}NO_2$: C, 72.54; H, 6.09; N, 6.51; Found: C, 72.19; H, 6.12; N, 6.34.

2.3.4 ***Ethyl 2-cyano-3-(4-ethylphenyl)-2-propenoate***

Yield 79%; ^{1}H-NMR δ 8.3 (s, 1H, CH=), 7.9, 7.3 (d, 4H, Ph), 4.4 (q, 2H, OCH_2), 2.7 (q, 2H, $PhC\underline{H}_2$), 1.4 (t, 3H, $OCH_2C\underline{H}_3$), 1.2 (t, 3H, $PhCH_2C\underline{H}_3$); ^{13}C-NMR δ 163 (C=O), 151 (HC=), 154, 131, 130, 129, 128 (Ph), 116 (CN), 102 (C=), 63 (OCH_2), 29 ($PhCH_2$), 16 ($PhCH_2\underline{C}H_3$), 14 ($OCH_2\underline{C}H_3$); IR (cm^{-1}): 3100-2825 (m, C-H), 2220 (m, CN), 1720 (s, C=O), 1609 (C=C), 1248 (s, C-O-C), 840 (s, C-H out of plane). Anal. Calcd. for $C_{14}H_{15}NO_2$: C, 73.34; H, 6.59; N, 6.11; Found: C, 72.89; H, 6.39; N, 5.89.

2.3.5 *Ethyl 2-cyano-3-(4-isopropylphenyl)-2-propenoate*

Yield 74%; ^{1}H-NMR δ 8.2 (s, 1H, CH=), 7.9, 7.3 (m, 4H, Ph), 4.4 (q, 2H, OCH_2), 2.9 (m, 1H, PhCH), 1.3 (t, 3H, $OCH_2C\underline{H}_3$), 1.2 (d, 6H, $CH(CH_3)_2$; ^{13}C-NMR δ 163 (C=O), 153 (HC=), 132, 130, 129, 127 (Ph), 116 (CN), 103 (C=), 63 (OCH_2), 34 (PhCH), 24 ($PhCH(\underline{C}H_3)_2$, 14 ($OCH_2\underline{C}H_3$); IR (cm^{-1}): 3028-2814 (m, C-H), 2223 (m, CN), 1725 (s, C=O), 1597 (C=C), 1268 (s, C-O-C), 828 (s, C-H out of plane). Anal. Calcd. for $C_{15}H_{17}NO_2$: C, 74.05; H, 7.04; N, 5.76; Found: C, 73.61; H, 7.06; N, 5.97.

2.3.6 *Ethyl 2-cyano-3-(4-t-butylphenyl)-2-propenoate*

Yield 83%; mp 62.2C°; ^{1}H-NMR δ 8.2 (s, 1H, CH=), 7.8, 7.4 (m, 4H, Ph), 4.3 (q, 2H, OCH_2), 1.3 (m, 12H, CH_3); ^{13}C-NMR δ 162 (C=O), 153 (HC=), 132, 131, 129, 126 (Ph), 116 (CN), 117 (C=), 61 (OCH_2), 34 ($\underline{C}CH_3$), 31 ($C\underline{C}H_3$), 14 ($CH_2\underline{C}H_3$); IR (cm^{-1}): 3022-2867 (m, C-H), 2221 (m, CN), 1720 (s, C=O), 1589 (C=C), 1220 (s, C-O-C), 811, 753 (s, C-H out of plane). Anal. Calcd. for $C_{16}H_{19}NO_2$: C, 74.68; H, 7.44; N, 5.44; Found: C, 75.01; H, 7.33; N, 5.83.

2.3.7 *Ethyl 2-cyano-3-[4-(trifluoromethyl)phenyl]-2-propenoate*

Yield 87%; mp 116.5°C; ^{1}H-NMR δ 8.2 (s, 1H, CH=), 7.9-7.7 (m, 4H, Ph), 4.3 (q, 2H, OCH_2), 1.3 (t, 3H, $OCH_2C\underline{H}_3$); ^{13}C-NMR δ 163 (C=O), 153 (HC=), 132, 131, 129, 126 (Ph), 116 (CN), 124 (CF_3), 117 (C=), 61 (OCH_2), 14 ($OCH_2\underline{C}H_3$); IR (cm^{-1}): 3056-2842 (m, C-H), 2224 (m, CN), 1741 (s, C=O), 1598 (C=C), 1223 (s, C-O-C), 865 (s, C-H out of plane). Anal. Calcd. for $C_{13}H_{10}F_3NO_2$: C, 58.00; H, 3.74; N, 5.20; Found: C, 58.02; H, 3.68; N, 5.11.

2.3.8 *Ethyl 2-cyano-3-[2-(trifluoromethyl)phenyl]-2-propenoate*

Yield 72%; mp 114.2°C; ^{1}H-NMR δ 8.6 (s, 1H, CH=), 7.9-7.1 (m, 4H, Ph), 4.3 (q, 2H, OCH_2), 1.3 (t, 3H, $OCH_2C\underline{H}_3$); ^{13}C-NMR δ 163 (C=O), 153 (HC=), 140, 133, 129, 127, 126 (Ph), 116 (CN), 123 (CF_3), 105 (C=), 61 (OCH_2), 14 ($OCH_2\underline{C}H_3$); IR (cm^{-1}): 3061-2854 (m, C-H), 2222 (m, CN), 1732 (s, C=O), 1567 (C=C), 1212 (s, C-O-C), 843 (s, C-H out of plane). Anal. Calcd. for $C_{13}H_{10}F_3NO_2$: C, 58.00; H, 3.74; N, 5.20; Found: C, 57.88; H, 3.76; N, 5.13.

2.4 Copolymerization

Copolymers of the VAC and the ECPP monomers were prepared in 25-mL glass screw cap vials at VAC/ECPP = 3 (mol) the monomer feed using 0.12 mol/L of ABCN at an overall monomer concentration 2.44 mol/L in 10 mL of toluene. The copolymerization was conducted at 70ºC. After a predetermined time, the mixture was cooled to room temperature, and precipitated dropwise in methanol. The composition of the copolymers was determined based on the nitrogen content.

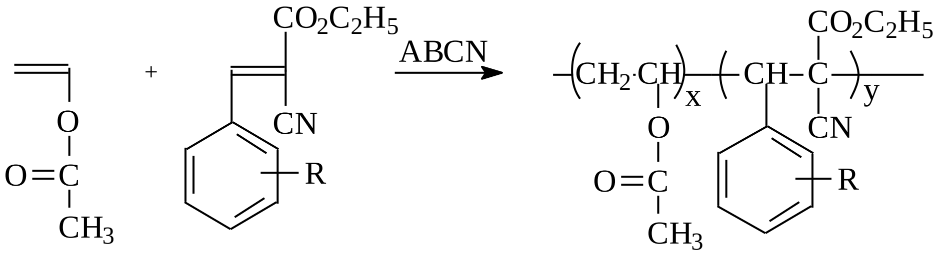
3 Results and Discussion

3.1 Homopolymerization

An attempted homopolymerization of the ECPP compounds in the presence of ABCN did not produce any polymer as indicated by the lack of a precipitate in methanol. The inability of the compounds to polymerize is associated with steric difficulties encountered in homopolymerization of 1,1- and 1,2-disubstituted ethylenes [17]. Homopolymerization of VAC under conditions identical to those in copolymerization experiments yielded 24.8% of polyvinyl acetate, when polymerized for 60 min.

3.2 Copolymerization

Copolymerization (Sch. 1) of VAC and the ring-substituted ECPP resulted in formation of copolymers (Table 1) with weight-average molecular masses 20 to 70 kD.



Sch. 1. Copolymerization of vinyl acetate and the ring-substituted propyl 2-cyano-3-phenyl-2-propenoates, RPhCH = C(CN)$CO_2C_2H_5$. R is 2-methyl, 3-methyl, 4-methyl, 4-ethyl, 4-isopropyl, 4-*t*-butyl, 4-trifluoromethyl, 2-trifluoromethyl.

According to the nitrogen elemental analysis, between 46.9 and 49.9 mol% of TSE monomer is present in the copolymers prepared at VAC/ECPP = 3 (mol), which is indicative of relatively high reactivity of the monomers towards VAC.

Table 1. Copolymerization of vinyl acetate and ring-substituted ethyl 2-cyano-3-phenyl-2-propenoates, RPhCH=C(CN)$CO_2C_2H_5$.

						TGA			
R	Yield [a] wt%	N wt%	ECPP in copol., mol%	M_W kD	T_g ºC	Onset of decomp., ºC	10% wt loss, ºC	50% wt loss, ºC	Residue at 500ºC, wt%
2-Methyl	13.1	4.36	49.5	43.2	87	201	278	344	13
3-Methyl	14.8	4.32	48.8	48.3	93	200	284	342	13
4-Methyl	13.7	4.33	49.0	55.5	91	177	264	340	16
4-Ethyl	15.6	4.2	49.9	42.9	101	178	269	342	14
4-Isopropyl	12.2	3.98	48.9	49.0	111	199	277	338	15
4-tert-Butyl	19.2	3.86	49.6	47.4	96	201	283	341	14
4-Trifluoromethyl	14.2	3.62	46.9	42.1	98	198	287	337	13
2-Trifluoromethyl	13.6	3.64	47.4	54.5	96	188	276	333	14

[a] Polymerization time was 5 h

3.3 Structure and Thermal Properties

The structure of VAC-ECPP copolymers was characterized by IR and NMR spectroscopy. A comparison of the spectra of the monomers, copolymers and polyvinyl acetate shows, that the reaction between the ECPP monomers and VAC is a copolymerization.

IR spectra of the copolymers show overlapping bands in 3280-2700 cm^{-1} region corresponding to C-H stretch vibrations. The bands for the ECPP monomer unit are 2232-2220 (w, CN), 1750-1710 (s, C=O), and 1240-1220 cm^{-1} (m, C-O). Benzene ring of ECPP monomers show ring stretching bands at 1520-1480 and 1510-1460 cm^{-1} as well as a doublet 800-900, 820-700 cm^{-1}, associated with C-H out of plane deformations. The absorptions of the VAC units appear at 1760-1740 cm^{-1} (carbonyl group), 1370-1360 cm^{-1} (wagging CH_3), 1280-1220 cm^{-1} (stretching COO), 1010 and1110 cm^{-1} (stretching C-C-C, These bands can be readily identified in VAC copolymers with TSE monomers containing cyano and carbonyl electron withdrawing groups.

The ^{1}H-NMR spectra of the VAC-ECPP copolymers show a broad peak in a 7.2-6.8 ppm region corresponding to phenyl ring protons. The peak at 5.3 ppm is assigned to the methine proton resonance of the VAC unit since the same signal is also observed in the spectra of polyvinyl acetate (PVAC) and various random and alternating copolymers of VAC [18]. A broad resonance at 4.2 ppm is assigned to methylene protons of ECPP ethyl group. The two peaks in the region of 2.4-3.4 ppm are assigned to the methine proton of ECPP [5]. The resonance signal at 2.0 ppm corresponds to absorbance of VAC methyl protons. The peak at 1.3 ppm is assigned to the methyl protons of the ECPP unit. The protons of alkyl ring-substituted ECPP-VAC copolymers are observed as broad overlapping peaks at 2.3 ppm for metha, orto, and para-substituted methyls, 2.6 and 1.2 ppm for CH_2 and CH_3 of ethyl, 2.8 ppm (CH) and 1.2 ppm (CH_3) of isopropyl, and 1.3 ppm for CH_3 of 4-tert-butyl.

The ^{13}C-NMR spectra also support the suggested skeletal structure of the copolymers. Thus, the assignment of the peaks is as follows: 164-160 ppm (C=O), 158-134 ppm (quaternary carbons of phenyls), 145-120 ppm (phenyl carbons), 120-110 ppm (CN), 60-50 ppm (alkoxy ECPP carbons), 72-66 ppm and 42-38 ppm (methylene and methine of VAC), 43-10 ppm - alkyl carbons of ECPP. 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 though the attack of a styrene-ended radical on both sides of TSE monomer (22). The IR and NMR data showed that these are true copolymers, composed of both TSE and ST monomer units.

The copolymers prepared in the present work are all soluble in ethyl acetate, THF, DMF and $CHCl_3$ and insoluble in methanol, ethyl ether, and petroleum ether. They are amorphous and show no crystalline DSC endotherm. Results of thermal analysis of VAC-ECPP copolymers are presented in Table 1. Relatively high T_g of the copolymers in comparison with that of polyvinyl acetate (T_g = 28-31ºC) indicates decrease of chain mobility of the copolymer due to the high dipolar character of the ECPP structural units. Information on the degradation of the copolymers was obtained from thermogravimetric analysis. Decomposition of the copolymers in nitrogen occurred in two steps, presumably acetic acid elimination in 190-350ºC range followed by a more slow decomposition of formed residue (13-16 wt%), which then decomposed in the 500-800ºC range. The decomposition products were not analyzed in this study, and the mechanism has yet to be investigated.

4 Conclusions

Alkyl ring-substituted ethyl 2-cyano-3-phenyl-2-propenoates were prepared and copolymerized with styrene. The compositions of the copolymers were calculated from nitrogen analysis and the structures were analyzed by IR, H^1 and ^{13}C-NMR. The thermal gravimetric analysis indicated that the copolymers decompose in in two steps, first in the 200-500°C range with residue (13-16 wt%), which then decomposed in the 500-800ºC range.

Acknowledgments

The authors are grateful to acknowledge that the project was partly supported by the Chicago Society of Coating Technology.

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