Novel copolymers of vinyl acetate. 3 Ring-substituted ethyl 2-cyano-3-phenyl-2-propenoates

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Abstract

Novel copolymers of vinyl acetate and ring-substituted ethyl 2-cyano-3-phenyl-2-propenoates, RPhCH=C(CN)$CO_2C_2H_5$ (where R is 4-acetoxy, 4-acetamido, 2-cyano, 3-cyano, 4-cyano, 4-dimethylamino, 4-diethylamino, 2,4,6-trimethyl, 2,3-dimethyl-4-methoxy, 2,4-dimethoxy-3-methyl were prepared in solution with radical initiation at 70°C. The propenoates were synthesized by the piperidine catalyzed Knoevenagel condensation of ring-substituted benzaldehydes and ethyl cyanoacetate, and characterized by CHN analysis, IR, ^{1}H and ^{13}C-NMR. The compositions of the copolymers were calculated from nitrogen analysis and the structures were analyzed by IR, ^{1}H and ^{13}C-NMR. Thermal behavior of the copolymers was studied by DSC (*T*g) and TGA. Decomposition of the copolymers in

nitrogen occurred in two steps, first in the 160-350ºC range with residue (1.5-15.1 wt%), which then decomposed in the 500-650ºC range.

1. Introduction

Electrophilic aryl–functionalized trisubstituted ethylenes, ethyl 2-cyano-3-phenyl-2-propenoates, RPhCH=C(CN)$CO_2C_2H_5$ (ECPP) continue to attract attention as organic intermediates and compounds with useful properties. Thus, acetoxy ring-substituted ECPP was used as intermediate in microwave-promoted sequential three-component synthesis of tetrahydrobenzo[b]pyran in water catalyzed by heterogeneous amine grafted on silica [1], in Knoevenagel reactions catalyzed by nano-silica PAMAM dendrimer [2] and by amine supported on silica gel [3].

4-Acetamido ECPP was involved in studies of enaminones in heterocyclic syntheses as a new one-step synthetic route to pyrrolo[3,4-b]pyridine and convenient syntheses of 1,4-dihydropyridines and 1,1'-(1,4-phenylene)bis(1,4-dihydropyridine) [4]. It was also used as nonlinear optical material based on cyano(acetylamino)cinnamate ester [5]. 2-Cyano ECPP was used in studies of structure-activity relationships and brain uptake of a novel series of benzopyran inhibitors of insulin-regulated aminopeptidase [6]. 3-Cyano ECPP was involved in AgNO3-catalysed intramolecular cyclization leading to functionalized cyclopentanones and spiro-cyclopentanones [7]. It also was reported in studies of adenine-based coordination polymers [8]. 4-Cyano ECPP is reported in synthesis of 1,7-bis (N-substituted-aminomethyl)-2,8-dihydroxy-troger's bases and their application in Aldol-Ullmann reaction [9] and also in studies on synthesis, antitumor activity and molecular docking of seven novel thiazacridine derivatives [10]. 4-Dimethylamino ECPP

was reported in synthesis of 1-[(aryl)(3-amino-5-oxopyrazolidin-4-ylidene) methyl]-2-oxo-1,2-dihydroquinoline-3-carboxylic acid derivatives and studies of their breast anticancer activity [11]. 4-Diethylamino ECPP was mentioned in the report on design, synthesis and vasorelaxant evaluation of novel coumarin-pyrimidine hybrids [12]. 2,4,6-trimethyl ECPP is reported in catalyst study of the Knoevenagel condensation [13].

In continuation of our research on radical copolymerization of vinyl acetate and aryl-substituted esters 2-cyano-3-phenyl-2-propenoic acid, we have prepared ring-substituted ethyl 2-cyano-3-phenyl-2-propenoates, RPhCH=C(CN)$CO_2C_2H_5$ (where R is 4-acetoxy, 4-acetamido, 2-cyano, 3-cyano, 4-cyano, 4-dimethylamino, 4-diethylamino, 2,4,6-trimethyl, 2,3-dimethyl-4-methoxy, 2,4-dimethoxy-3-methyl) and copolymerized them with vinyl acetate. There are reports of syntheses of 4-acetoxy, 4-acetamido, 2-cyano, 3-cyano, 4-cyano, 4-dimethylamino, 4-diethylamino ECPP and copolymerization with styrene [14]. There are no reports on synthesis of 2,3-dimethyl-4-methoxy and 2,4-dimethoxy-3-methyl 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

4-Acetoxy, 4-acetamido, 2-cyano, 3-cyano, 4-cyano, 4-dimethylamino, 4-diethylamino, 2,4,6-trimethyl, 2,3-dimethyl-4-methoxy, 2,4-dimethoxy-3-methyl-substituted benzaldehydes, ethyl cyanoacetate, piperidine, vinyl acetate, 1,1'-azobiscyclohexanecarbonitrile, (ABCN), and toluene supplied from Sigma-Aldrich Co., were used as received. Instrumentation is described in [16].

3 Synthesis of Monomers

The ring-substituted ethyl 2-cyano-3-phenyl-2-propenoates (ECPP) were synthesized by Knoevenagel condensation [17] of a ring-substituted benzaldehyde with ethyl cyanoacetate, catalyzed by base, piperidine. The preparation procedure was essentially the same for all the monomers [16].

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

where R is 4-acetoxy, 4-acetamido, 2-cyano, 3-cyano, 4-cyano, 4-dimethylamino, 4-diethylamino, 2,4,6-trimethyl, 2,3-dimethyl-4-methoxy, 2,4-dimethoxy-3-methyl.

3.1 *Ethyl 2-cyano-3-(4-acetoxyphenyl)-2-propenoate*

Yield 87%; mp 95.3°C, ^{1}H-NMR δ8.2 (s, 1H, CH=), 7.5, 6.9 (m, 4H, Ph), 4.3 (q, 2H, OCH_2), 2.2 (s, 3H, $PhCO_2CH_3$), 1.3 (t, 3H, $OCH_2C\underline{H}_3$); ^{13}C-NMR δ163, 162 (C=O), 152 (HC=), 148, 131, 124, 121 (Ph), 116 (CN), 111 (C=), 61 (OCH_2), 21 (PhO_2CH_3), 14 ($OCH_2\underline{C}H_3$); IR (cm^{-1}): 3023-2832 (m, C-H), 2224 (m, CN), 1742 (s, C=O), 1573 (C=C), 1232 (s, C-O-CH_3), 811 (s, C-H out of plane). Anal. Calcd. for $C_{14}H_{13}NO_4$: C, 64.86; H, 5.05; N, 5.40; Found: C, 64.82; H, 5.10; N, 5.36.

3.2 *Ethyl 2-cyano-3-(4-acetamidophenyl)-2-propenoate*

Yield 84%; mp 195.8°C, ^{1}H-NMR δ8.2 (s, 1H, CH=), 8.0, 7.6 (m, 4H, Ph), 5.2 (s, 1H, NH), 4.3 (q, 2H, OCH_2), 2.1 (s, 3H, $PhNHCOCH_3$), 1.3 (t, 3H, $OCH_2C\underline{H}_3$); ^{13}C-NMR δ 168, 163 (C=O), 154 (HC=), 151, 134, 120, 119 (Ph), 116 (CN), 96 (C=), 61 (OCH_2), 23 ($PhCOCH_3$), 14 ($OCH_2\underline{C}H_3$); IR (cm^{-1}): 3038-2833 (m, C-H), 2223 (m, CN), 1722 (s,

C=O), 1582 (C=C), 1221 (s, C-O-CH_3), 841 (s, C-H out of plane). Anal. Calcd. for $C_{14}H_{14}N_2O_3$: C, 65.11; H, 5.46; N, 10.85; Found: C, 65.67; H, 5.46; N, 10.84.

3.3 ***Ethyl 2-cyano-3-(2-cyanophenyl)-2-propenoate***

Yield 89%; mp 223.4°C, ^{1}H-NMR δ 8.2 (s, 1H, CH=), 7.9-7.0 (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), 152 (HC=), 147, 136, 133, 131, 130 (Ph), 117, 116 (CN), 100 (C=), 61 (OCH_2), 14 ($OCH_2\underline{C}H_3$); IR (cm^{-1}): 3021-2922 (m, C-H), 2223 (m, CN), 1742 (s, C=O), 1232 (s, C-O-C), 843 (s, C-H out of plane). Anal. Calcd. for $C_{13}H_{10}N_2O_2$: C, 69.02; H, 4.46; N, 12.38; Found: C, 63.85; H, 4.45; N, 12.40.

3.4 ***Ethyl 2-cyano-3-(3-cyanophenyl)-2-propenoate***

Yield 76%; mp 128.8°C, ^{1}H-NMR δ 8.2 (s, 1H, CH=), 7.7-7.0 (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), 154 (HC=), 136, 129, 113 (Ph), 119, 116 (CN), 103 (C=), 61 (OCH_2), 14 ($OCH_2\underline{C}H_3$); IR (cm^{-1}): 3124-2825 (m, C-H), 2222 (m, CN), 1724 (s, C=O), 1618 (C=C), 1242 (s, C-O-C), 849 (s, C-H out of plane). Anal. Calcd. for $C_{13}H_{10}N_2O_2$: C, 69.02; H, 4.46; N, 12.38; Found: C, 69.05; H, 4.27; N, 12.37.

3.5 ***Ethyl 2-cyano-3-(4-cyanophenyl)-2-propenoate***

Yield 82%; ^{1}H-NMR δ 8.2 (s, 1H, CH=), 7.9, 7.8 (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), 154 (HC=), 136, 133, 131, 118 (Ph), 116 (CN), 113 (C=), 61 (OCH_2), 14 ($OCH_2\underline{C}H_3$); IR (cm^{-1}): 3031-2857 (m, C-H), 2223 (m, CN),

1736 (s, C=O), 1611 (C=C), 1243 (s, C-O-C), 842 (s, C-H out of plane). Anal. Calcd. for $C_{13}H_{10}N_2O_2$: C, 69.02; H, 4.46; N, 12.38; Found: C, 69.01; H, 4.17; N, 12.27.

3.6 ***Ethyl 2-cyano-3-(4-dimethylaminophenyl)-2-propenoate***

Yield 72%; mp 130.2°C; ^{1}H-NMR δ 8.2 (s, 1H, CH=), 7.6, 7.0 (m, 4H, Ph), 4.3 (q, 2H, OCH_2), 3.0 (s, 6H, $N(CH_3)_2$, 1.3 (m, 3H, CH_3); ^{13}C-NMR δ 163 (C=O), 154 (HC=), 152, 134, 121, 111 (Ph), 61 (OCH_2), 40 ($PhNCH_3$), 14 ($OCH_2\underline{C}H_3$); IR (cm^{-1}): 3005-2885 (m, C-H), 2223 (m, CN), 1723 (s, C=O), 1581 (C=C), 1221 (s, C-O-C), 843 (s, C-H out of plane). Anal. Calcd. for $C_{14}H_{16}N_2O_2$: C, 68.83; H, 6.60; N, 11.47; Found: C, 69.02; H, 6.60; N, 11.40.

3.7 ***Ethyl 2-cyano-3-(4-diethylaminophenyl)-2-propenoate***

Yield 85%; mp 99.6°C; ^{1}H-NMR δ 8.2 (s, 1H, CH=), 7.6, 7.0 (m, 4H, Ph), 4.3 (q, 2H, OCH_2), 3.4 (s, 4H, NCH_2, 1.3 (t, 3H, $OCH_2C\underline{H}_3$), 1.2 (t, 6H, $NCH_2C\underline{H}_3$); ^{13}C-NMR δ 163 (C=O), 154 (HC=), 151, 134, 120, 111 (Ph), 116 (CN), 96 (C=), 61 (OCH_2), 44 (NCH_2), 14 ($OCH_2\underline{C}H_3$), 13 ($NCH_2\underline{C}H_3$); IR (cm^{-1}): 3024-2821 (m, C-H), 2222 (m, CN), 1742 (s, C=O), 1576 (C=C), 1221 (s, C-O-C), 845 (s, C-H out of plane). Anal. Calcd. for $C_{16}H_{20}N_2O_2$: C, 70.56; H, 7.40; N, 10.29; Found: C, 70.73; H, 7.32; N, 10.22.

3.8 ***Ethyl 2-cyano-3-(2,4,6-trimethylphenyl)-2-propenoate***

Yield 79%; ^{1}H-NMR δ 8.1 (s, 1H, CH=), 6.9 (s, 2H, Ph), 4.3 (q, 2H, OCH_2), 2.3 (m, 9H, $PhCH_3$), 1.3 (t, 3H, $OCH_2C\underline{H}_3$); ^{13}C-NMR δ 163 (C=O), 152 (HC=), 131, 129, 125 (Ph), 116 (CN), 104 (C=), 61 (OCH_2), 20, 21 ($PhCH_3$), 14 ($OCH_2\underline{C}H_3$); IR (cm^{-1}): 3021-2845 (m, C-H), 2223 (m, CN), 1724 (s, C=O), 1583 (C=C), 1233 (s, C-O-CH_3), 840 (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, 73.82; H, 7.06; N, 5.71.

3.9 ***Ethyl 2-cyano-3-(2,3-dimethyl-4-methoxyphenyl)-2-propenoate***

Yield 84%; mp 129.8°C, ^{1}H-NMR δ 8.1 (s, 1H, CH=), 7.5, 7.1 (m, 2H, Ph), 4.3 (q, 2H, OCH_2), 3.8 (s, 3H, $PhOCH_3$), 2.2, 2.3 (m, 6H, $PhCH_3$), 1.3 (t, 3H, $OCH_2C\underline{H}_3$); ^{13}C-NMR δ 163 (C=O), 152 (HC=), 151, 131, 126, 114 (Ph), 116 (CN), 100 (C=), 61 (OCH_2), 56 ($PhOCH_3$), 14 ($OCH_2\underline{C}H_3$), 17, 11 ($PhCH_3$); IR (cm^{-1}): 3022-2842 (m, C-H), 2224 (m, CN), 1731 (s, C=O), 1565 (C=C), 1235 (s, C-O-CH_3), 841 (s, C-H out of plane). Anal. Calcd. for $C_{15}H_{17}NO_3$: C, 69.48; H, 6.61; N, 5.40; Found: C, 69.44; H, 6.53; N, 5.20.

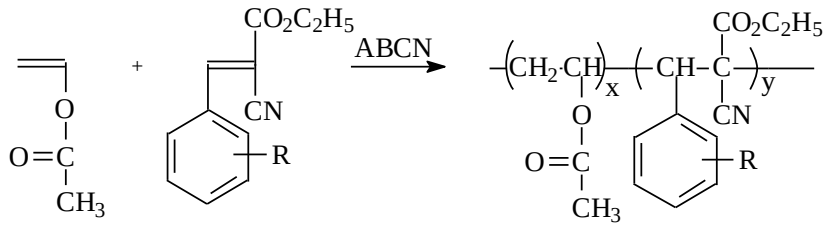
3.10 ***Ethyl 2-cyano-3-(2,4-dimethoxy-3-methylphenyl)-2-propenoate***

Yield 86%; mp 110.7°C, ^{1}H-NMR δ 8.2 (s, 1H, CH=), 7.5, 7.1 (m, 2H, Ph), 4.3 (q, 2H, OCH_2), 3.8 (s, 6H, $PhOCH_3$), 2.3 (m, 3H, $PhCH_3$), 1.3 (t, 3H, $OCH_2C\underline{H}_3$); ^{13}C-NMR δ 163 (C=O), 152 (HC=), 143, 131, 114, 113, 108 (Ph), 116 (CN), 97 (C=), 61 (OCH_2), 56 ($PhOCH_3$), 14 ($OCH_2\underline{C}H_3$), 8 ($PhCH_3$); IR (cm^{-1}): 3001-2832 (m, C-H), 2222 (m, CN), 1727 (s, C=O), 1576 (C=C), 1232 (s, C-O-CH_3), 847 (s, C-H out of plane). Anal. Calcd. for $C_{15}H_{17}NO_4$: C, 65.44; H, 6.22; N, 5.09; Found: C, 65.76; H, 6.27; N, 5.09.

4 Copolymerization

An attempted radical homopolymerization of the ECPP compounds did not produced polymeric products similarly to other ring-substituted ECPP [18]. Homopolymerization of vinyl acetate yielded 28.7 of poly(vinyl acetate) under these conditions [18].

Copolymerization (Sch. 1) of VAC and the ring-substituted ECPP resulted in formation of copolymers (Table 1) with weight-average molecular masses 8.8 to 12.6 kD.



Scheme 1. Copolymerization of vinyl acetate and the ring-substituted ethyl 2-cyano-3-phenyl-2-propenoates, RPhCH = $C(CN)CO_2C_2H_5$, where R is 4-acetoxy, 4-acetamido, 2-cyano, 3-cyano, 4-cyano, 4-dimethylamino, 4-diethylamino, 2,4,6-trimethyl, 2,3-dimethyl-4-methoxy, 2,4-dimethoxy-3-methyl.

According to the nitrogen elemental analysis, between 42.1 and 49.5 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.

						TGA			
R	Yield[a] wt%	N wt%	ECCP in pol., mol%	M_W kD	T_g ºC	Onset of decomp. ºC	10% wt loss, ºC	50% wt loss, ºC	Residue at 500ºC, wt%
4-Acetoxy	62.1	4.01	48.8	12.6	102	216	277	340	12.3
p-Acetamido	45.9	8.10	49.5	8.8	96	206	255	334	12.6
2-Cyano	57.2	8.13	42.1	9.2	98	159	249	341	14.1
3-Cyano	51.2	8.26	43.2	10.4	96	150	201	245	9.6
4-Cyano	49.3	8.23	43.0	11.1	89	153	208	254	9.5
4-Dimethylamino	54.2	8.17	46.6	9.1	88	190	256	301	9.2.4
4-Diethylamino	68.4	7.61	47.3	10.4	94	193	257	301	1.5
2,4,6-trimethyl	76.3	3.92	43.0	9.8	101	147	201	323	11.9
2,3-Dimethyl-4-methoxy	45.4	3.91	46.5	11.4	98	186	246	279	7.2
2,4-Dimethoxy-3-methyl	54.2	3.67	44.7	12.5	102	177	223	327	15.1

[a]Polymerization time was 5 h

5 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 with the spectra of ring-unsubstituted ethyl 2-cyano-3-phenyl-2-propenoate – VAC [19] shows, that the reaction between the ECPP monomers and VAC is a copolymerization.

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 (88-102 ºC) in comparison with that of polyvinyl acetate, T_g = 28-31ºC [20] 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, apparently due to acetic acid elimination [21] in 150-340ºC range followed by more slow decomposition of formed residue (15.1-1.5 wt%), which then decomposed in the 500-650ºC range.

6 Conclusions

Ring-substituted ethyl 2-cyano-3-phenyl-2-propenoates, $RPhCH = C(CN)CO_2C_2H_5$ (R is 4-acetoxy, 4-acetamido, 2-cyano, 3-cyano, 4-cyano, 4-dimethylamino, 4-diethylamino, 2,4,6-trimethyl, 2,3-dimethyl-4-methoxy, 2,4-dimethoxy-3-methyl) were prepared and copolymerized with vinyl acetate. The compositions of the copolymers were calculated from nitrogen analysis and the structures were analyzed by IR, H^1 and ^{13}C-NMR. 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 500-650ºC range.

Acknowledgments

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