

Novel copolymers of vinyl acetate. 4. Halogen ring-substituted ethyl 2-cyano-3-phenyl-2-propenoates

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Novel copolymers of vinyl acetate and halogen ring-substituted ethyl 2-cyano-3-phenyl-2-propenoates, $\text{RPhCH}=\text{C}(\text{CN})\text{CO}_2\text{C}_2\text{H}_5$ (where R is 2-Br, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 2-F, 3-F, 4-F, 2,3-dichloro, 2,4-dichloro, 2,6-dichloro, 3,4-dichloro, 2,4-difluoro, 2-bromo-3,4-dimethoxy) were prepared in solution with radical initiation at 70°C. The propenoates were synthesized by the piperidine catalyzed Knoevenagel condensation of halogen ring-substituted benzaldehydes and ethyl cyanoacetate, and characterized by CHN analysis, IR, ^1H and ^{13}C -NMR. 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 (T_g) and TGA. Decomposition of the copolymers in

nitrogen occurred in two steps, first in the 159-500°C range with residue (8.8-15.2 wt%), which then decomposed in the 500-650°C range.

1. Introduction

Functionalization of commercial polymers via copolymerization leads to a variety of polymers with interesting properties. Halogen ring-substituted ethyl 2-cyano-3-phenyl-2-propenoates (HECP) offer a convenient way to introduce a variety of functional groups in polyvinyl acetate backbone. 2-Bromo HECP is reported in preparation of highly loaded MWCNT-polyamine hybrids and their application in catalysis [1], as well as in synthesis of thiazacridine derivatives as anticancer agents against breast and hematopoietic neoplastic cells [2]. 3-Bromo HECP is involved in synthesis of novel selenophenes from activated acetylenes, ethyl 2-cyano-3-arylacrylate and potassium selenocyanate [3], also in straightforward preparation of highly loaded MWCNT-polyamine hybrids and their application in catalysis [4]. The report on design, synthesis, anti-proliferative evaluation and cell cycle analysis of hybrid 2-quinolones cites 2-chloro HECP [5]. Novel synthesis of 3-cyano-2-pyridones derivatives catalyzed by Au-Co/TiO₂ involves 3-chloro HECP [6]. This HECP also was involved in the study of selenotungstates incorporating organophosphonate ligands and metal ions describing synthesis, characterization, magnetism and catalytic efficiency in the Knoevenagel condensation reaction [7]. 4-Chloro HECP was reported in the study new hybrid organic-inorganic multifunctional materials based on polydopamine-like chemistry [8]. 2-Fluoro HECP was mentioned in study of optimized monofluoromethylsulfonium reagents for fluoromethylene-transfer chemistry [9].

Discovery, stereospecific characterization and peripheral modification of 1-(pyrrolidin-1-ylmethyl)-2-[(6-chloro-3-oxo-indan)-formyl]-1,2,3,4-tetrahydroisoquinolines as novel selective κ opioid receptor agonists involves 3-fluoro HECP [10]. 4-Fluoro HECP was mentioned in study of aerobic oxidative cleavage of C=C bond to carbonyl compound [11]. 2,3-Dichloro HECP was reported in synthesis of thiazacridine derivatives as anticancer agents against breast and hematopoietic neoplastic cells [12], whereas 2,4-dichloro HECP was in synthesis of some new dihydropyrimidine derivatives by cyclization of polarized unsaturated systems [13]. Synthesis of multifunctional polymer containing Ni-Pd NPs via thiol-ene reaction for one-pot cascade reactions mentioned 2,6-dichloro HECP [14]. 3,4-dichloro HECP was reported in a highly efficient protocol for the regio- and stereo-selective synthesis of spiro pyrrolidine and pyrrolizidine derivatives by multicomponent reaction [15]. 2,4-Difluoro HECP was involved in preparation of indolyl acrylates and related compounds alone and in compositions and methods for modulating hair growth [16].

In continuation of our studies of radical copolymerization of vinyl acetate and aryl-substituted esters 2-cyano-3-phenyl-2-propenoic acid, we have prepared halogen ring-substituted ethyl 2-cyano-3-phenyl-2-propenoates, $RPhCH=C(CN)CO_2C_2H_5$ (where R is 2-Br, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 2-F, 3-F, 4-F, 2,3-dichloro, 2,4-dichloro, 2,6-dichloro, 3,4-dichloro, 2,4-difluoro, 2-bromo-3,4-dimethoxy) and copolymerized them with vinyl acetate. We reported syntheses of 2-Cl, 3-Cl, 4-Cl, 2-Br, 3-Br, 4-Br, 2-F, 3-F, 4-F, 2-Cl-4-F, 2-Cl-6-F, 3-Cl-4-F ring-substituted HECP and copolymerization with styrene [17].

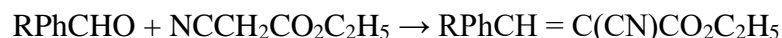
There are no reports on synthesis of 2-bromo-3,4-dimethoxy HECP. To the best of our knowledge, there have been no reports on copolymerization of these ethyl 2-cyano-3-phenyl-2-propenoates with vinyl acetate [18].

2 Experimental

2-Br, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 2-F, 3-F, 4-F, 2,3-dichloro, 2,4-dichloro, 2,6-dichloro, 3,4-dichloro, 2,4-difluoro, 2-bromo-3,4-dimethoxy-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 [19].

3 Synthesis of Monomers

The halogen ring-substituted ethyl 2-cyano-3-phenyl-2-propenoates (HECP) were synthesized by Knoevenagel condensation [20] of a ring-substituted benzaldehyde with ethyl cyanoacetate, catalyzed by base, piperidine. The preparation procedure was essentially the same for all the monomers [19].



where R is 2-Br, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 2-F, 3-F, 4-F, 2,3-dichloro, 2,4-dichloro, 2,6-dichloro, 3,4-dichloro, 2,4-difluoro, 2-bromo-3,4-dimethoxy.

3.1 Ethyl 2-cyano-3-(2-bromophenyl)-2-propenoate

Yield 84%; mp 73.3°C, $^1\text{H-NMR}$ δ 8.1 (s, 4H, CH=), 7.6-7.4 (m, 4H, Ph), 4.3 (t, 2H, OCH₂), 1.3 (t, 3H, OCH₂CH₃); $^{13}\text{C-NMR}$ δ 163 (C=O), 152 (HC=), 138, 133, 131, 130, 128 (Ph), 116 (CN), 106 (C=), 61 (OCH₂), 14 (OCH₂CH₃); IR (cm⁻¹): 3011-2830 (m, C-

H), 2223 (m, CN), 1745 (s, C=O), 1595 (C=C), 1253 (s, C-O-CH₃), 790-729 (s, C-H out of plane). Anal. Calcd. for C₁₂H₁₀BrNO₂: C, 51.45; H, 3.60; N, 5.00; Found: C, 51.41; H, 3.54; N, 4.90.

3.2 Ethyl 2-cyano-3-(3-bromophenyl)-2-propenoate

Yield 72%; mp 100.5°C, ¹H-NMR δ 8.2 (s, 1H, CH=), 7.8-7.3 (m, 4H, Ph), 4.3 (t, 2H, OCH₂), 1.3 (t, 3H, OCH₂CH₃); ¹³C-NMR δ 163 (C=O), 154 (HC=), 136, 130, 133, 122 (Ph), 116 (CN), 103 (C=), 61 (OCH₂), 14 (OCH₂CH₃); IR (cm⁻¹): 3045-2869 (m, C-H), 2223 (m, CN), 1734 (s, C=O), 1599 (C=C), 1244 (s, C-O-CH₃), 854 (s, C-H out of plane). Anal. Calcd. for C₁₃H₁₀BrNO₂: C, 52.45; H, 3.60; N, 5.00; Found: C, 51.42; H, 3.53; N, 5.01.

3.3 Ethyl 2-cyano-3-(4-bromophenyl)-2-propenoate

Yield 82%; mp 98.1°C, ¹H-NMR δ 8.2 (s, 1H, CH=), 7.6, 7.5 (d, 4H, Ph), 4.3 (t, 2H, OCH₂), (t, 3H, OCH₂CH₃); ¹³C-NMR δ 163 (C=O), 154 (HC=), 133, 132, 131 (Ph), 116 (CN), 133 (C=), 61 (OCH₂), 14 (OCH₂CH₃); IR (cm⁻¹): 3061-2934 (m, C-H), 2222 (m, CN), 1737 (s, C=O), 1243 (s, C-O-C), 844, 759 (s, C-H out of plane). Anal. Calcd. for C₁₂H₁₀BrNO₂: C, 51.45; H, 3.60; N, 5.00; Found: C, 51.42; H, 3.35; N, 4.89.

3.4 Ethyl 2-cyano-3-(2-chlorophenyl)-2-propenoate

Yield 72%; mp 59.2°C, ¹H-NMR δ 8.7 (s, 1H, CH=), 8.1-7.0 (m, 4H, Ph), 4.3 (t, 2H, OCH₂), 1.3 (t, 3H, OCH₂CH₃); ¹³C-NMR δ 163 (C=O), 152 (HC=), 137, 132, 131, 130, 128 (Ph), 116 (CN), 106 (C=), 61 (OCH₂), 14 (OCH₂CH₃); IR (cm⁻¹): 3068-2822 (m, C-H), 2222 (m, CN), 1732 (s, C=O), 1606 (C=C), 1247 (s, C-O-C), 942 (s, C-H out of

plane). Anal. Calcd. for $C_{12}H_{10}ClNO_2$: C, 61.16; H, 4.28; N, 5.94; Found: C, 61.12; H, 4.25; N, 5.94.

3.5 Ethyl 2-cyano-3-(3-chlorophenyl)-2-propenoate

Yield 74%; mp 108.2°C; 1H -NMR δ 8.2 (s, 1H, CH=), 8.0-7.0 (m, 4H, Ph), 4.3 (t, 2H, OCH₂), 1.3 (t, 3H, OCH₂CH₃); ^{13}C -NMR δ 163 (C=O), 154 (HC=), 135, 133, 130, 128 (Ph), 116 (CN), 103 (C=), 61 (OCH₂), 14 (OCH₂CH₃); IR (cm⁻¹): 3017-2819 (m, C-H), 2224 (m, CN), 1741 (s, C=O), 1568 (C=C), 1225 (s, C-O-C), 874 (s, C-H out of plane).
Anal. Calcd. for $C_{12}H_{10}ClNO_2$: C, 61.16; H, 4.28; N, 5.94; Found: C, 60.89; H, 4.24; N, 5.80.

3.6 Ethyl 2-cyano-3-(4-chlorophenyl)-2-propenoate

Yield 78%; mp 99.9°C; 1H -NMR δ 8.2 (s, 1H, CH=), 7.9-7.0 (m, 4H, Ph), 4.3 (t, 2H, OCH₂), 1.3 (t, 3H, OCH₂CH₃); ^{13}C -NMR δ 163 (C=O), 153 (HC=), 138, 132, 129 (Ph), 116 (CN), 114 (C=), 61 (OCH₂), 14 (OCH₂CH₃); IR (cm⁻¹): 3020-2861 (m, C-H), 2223 (m, CN), 1741 (s, C=O), 1584 (C=C), 1220 (s, C-O-C), 811, 757 (s, C-H out of plane).
Anal. Calcd. for $C_{12}H_{10}ClNO_2$: C, 61.16; H, 4.28; N, 5.94; Found: C, 61.09; H, 4.24; N, 5.90.

3.7 Ethyl 2-cyano-3-(2-fluorophenyl)-2-propenoate

Yield 90%; mp 55.7°C; 1H -NMR δ 8.2 (s, 1H, CH=), 7.9-7.0 (m, 4H, Ph), 4.3 (t, 2H, OCH₂), 1.3 (t, 3H, OCH₂CH₃); ^{13}C -NMR δ 163 (C=O), 152 (HC=), 141, 131, 130, 125, 119 (Ph), 116 (CN), 105 (C=), 61 (OCH₂), 14 (OCH₂CH₃); IR (cm⁻¹): 3051-2841 (m, C-H), 2223 (m, CN), 1741 (s, C=O), 1592 (C=C), 1227 (s, C-O-C), 865 (s, C-H out of

plane). Anal. Calcd. for $C_{12}H_{10}FNO_2$: C, 65.75; H, 4.60; N, 6.39; Found: C, 65.64; H, 4.22; N, 6.36.

3.8 Ethyl 2-cyano-3-(3-fluorophenyl)-2-propenoate

Yield 73%; mp 103.2°C; 1H -NMR δ 8.2 (s, 1H, CH=), 7.8-7.0 (m, 4H, Ph), 4.3 (t, 2H, OCH₂), 1.3 (t, 3H, OCH₂CH₃); ^{13}C -NMR δ 164 (C=O), 154 (HC=), 162, 135, 130, 127, 120 (Ph), 116 (CN), 103 (C=), 68 (OCH₂), 14 (OCH₂CH₃); IR (cm⁻¹): 3062-2842 (m, C-H), 2221 (m, CN), 1730 (s, C=O), 1580 (C=C), 1262 (s, C-O-C), 931, 853 (s, C-H out of plane). Anal. Calcd. for $C_{12}H_{10}FNO_2$: C, 65.75; H, 4.60; N, 6.39; Found: C, 65.61; H, 4.59; N, 6.29.

3.9 Propyl 2-cyano-3-(4-fluorophenyl)-2-propenoate

Yield 87%; mp 105.3°C; 1H -NMR δ 8.2 (s, 1H, CH=), 8.1-7.1 (m, 4H, Ph), 4.3 (t, 2H, OCH₂), 1.3 (t, 3H, OCH₂CH₃); ^{13}C -NMR δ 163 (C=O), 154 (HC=), 132, 129, 116 (Ph), 116 (CN), 109 (C=), 61 (OCH₂), 10 (OCH₂CH₃); IR (cm⁻¹): 3042-2812 (m, C-H), 2221 (m, CN), 1728 (s, C=O), 1608 (C=C), 1214 (s, C-O-C), 810 (m, C-H out of plane). Anal. Calcd. for $C_{12}H_{10}FNO_2$: C, 65.75; H, 4.60; N, 6.39; Found: C, 65.88; H, 4.46; N, 6.34.

3.10 Ethyl 2-cyano-3-(2,3-dichlorophenyl)-2-propenoate

Yield 82%; mp 82.0°C; 1H -NMR δ 8.1 (s, 1H, CH=), 8.0-7.0 (m, 3H, Ph), 4.3 (t, 2H, OCH₂), 1.3 (t, 3H, OCH₂CH₃); ^{13}C -NMR δ 163 (C=O), 153 (HC=), 134, 133, 130, 128 (Ph), 116 (CN), 108 (C=), 61 (OCH₂), 14 (OCH₂CH₃); IR (cm⁻¹): 3012-2811 (m, C-H), 2222 (m, CN), 1740 (s, C=O), 1562 (C=C), 1221 (s, C-O-C), 870 (s, C-H out of plane).

Anal. Calcd. for $C_{12}H_9Cl_2NO_2$: C, 53.36; H, 3.36; N, 5.19; Found: C, 53.33; H, 3.13; N, 5.09.

3.11 Ethyl 2-cyano-3-(2,4-dichlorophenyl)-2-propenoate

Yield 89%; mp $84.73^\circ C$; 1H -NMR δ 8.2 (s, 1H, CH=), 7.9-7.0 (m, 3H, Ph), 4.3 (t, 2H, OCH₂), 1.3 (t, 3H, OCH₂CH₃); ^{13}C -NMR δ 163 (C=O), 152 (HC=), 138, 131, 129 (Ph), 116 (CN), 104 (C=), 61 (OCH₂), 14 (OCH₂CH₃); IR (cm⁻¹): 3020-2861 (m, C-H), 2222 (m, CN), 1740 (s, C=O), 1582 (C=C), 1221 (s, C-O-C), 810, 754 (s, C-H out of plane).

Anal. Calcd. for $C_{12}H_9Cl_2NO_2$: C, 53.36; H, 3.36; N, 5.19; Found: C, 53.42; H, 3.36; N, 5.07.

3.12 Ethyl 2-cyano-3-(2,6-dichlorophenyl)-2-propenoate

Yield 76%; mp $73.7^\circ C$; 1H -NMR δ 8.1 (s, 1H, CH=), 7.4, 7.2 (m, 3H, Ph), 4.3 (t, 2H, OCH₂), 1.3 (t, 3H, OCH₂CH₃); ^{13}C -NMR δ 163 (C=O), 151 (HC=), 135, 132, 130, 129 (Ph), 116 (CN), 102 (C=), 61 (OCH₂), 14 (OCH₂CH₃); IR (cm⁻¹): 3018-2868 (m, C-H), 2224 (m, CN), 1742 (s, C=O), 1567 (C=C), 1227 (s, C-O-C), 813 (s, C-H out of plane).

Anal. Calcd. for $C_{12}H_9Cl_2NO_2$: C, 53.36; H, 3.36; N, 5.19; Found: C, 53.47; H, 3.32; N, 5.01.

3.13 Ethyl 2-cyano-3-(3,4-dichlorophenyl)-2-propenoate

Yield 67%; 1H -NMR δ 8.2 (s, 1H, CH=), 8.0-7.4 (m, 3H, Ph), 4.3 (t, 2H, OCH₂), 1.3 (t, 3H, OCH₂CH₃); ^{13}C -NMR δ 163 (C=O), 154 (HC=), 134, 132, 131, 128 (Ph), 116 (CN), 102 (C=), 61 (OCH₂), 14 (OCH₂CH₃); IR (cm⁻¹): 3024-2869 (m, C-H), 2224 (m, CN),

1742 (s, C=O), 1576 (C=C), 1212 (s, C-O-C), 819 (s, C-H out of plane). Anal. Calcd. for $C_{12}H_9Cl_2NO_2$: C, 53.36; H, 3.36; N, 5.19; Found: C, 53.27; H, 3.14; N, 5.12.

3.14 Ethyl 2-cyano-3-(2,4-difluorophenyl)-2-propenoate

Yield 79%; mp 58.9°C; 1H -NMR δ 8.3 (s, 1H, CH=), 8.1-7.0 (m, 3H, Ph), 4.3 (t, 2H, OCH₂), 1.3 (t, 3H, OCH₂CH₃); ^{13}C -NMR δ 163 (C=O), 152 (HC=), 135, 131, 130, 119, 112, 105 (Ph), 116 (CN), 102 (C=), 61 (OCH₂), 14 (OCH₂CH₃); IR (cm⁻¹): 3028-2834 (m, C-H), 2222 (m, CN), 1747 (s, C=O), 1543 (C=C), 1223 (s, C-O-C), 813 (s, C-H out of plane). Anal. Calcd. for $C_{12}H_9F_2NO_2$: C, 60.76; H, 3.82; N, 5.90; Found: C, 60.69; H, 3.61; N, 5.87.

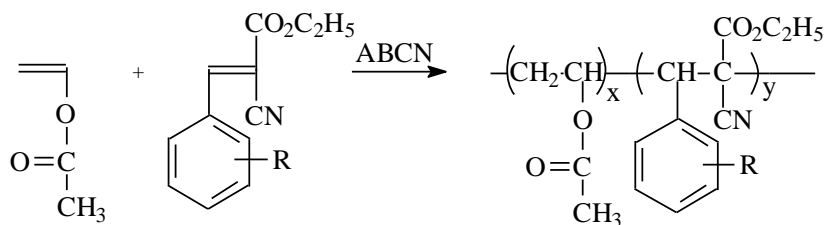
3.15 Ethyl 2-cyano-3-(2-bromo-3,4-dimethoxyphenyl)-2-propenoate

Yield 87%; 1H -NMR δ 8.1 (s, 1H, CH=), 7.5, 6.9, (m, 2H, Ph), 4.3 (t, 2H, OCH₂), 3.8 (s, 6H, PhOCH₃), 1.3 (t, 3H, OCH₂CH₃); ^{13}C -NMR δ 163 (C=O), 152 (HC=), 151, 128, 127, 113 (Ph), 116 (CN), 107 (C=), 61 (OCH₂), 55 (PhOCH₃), 14 (OCH₂CH₃); IR (cm⁻¹): 3008-2854 (m, C-H), 2223 (m, CN), 1747 (s, C=O), 1569 (C=C), 1227 (s, C-O-C), 818 (s, C-H out of plane). Anal. Calcd. for $C_{14}H_{14}BrNO_4$: C, 49.43; H, 4.15; N, 4.12; Found: C, 49.21; H, 3.85; N, 3.93.

4 Copolymerization

An attempted radical homopolymerization of the HECp compounds did not produce polymeric products similarly to other ring-substituted HECp [19]. Homopolymerization of vinyl acetate yielded 28.7 of poly(vinyl acetate) under these conditions [21].

Copolymerization (Sch. 1) of VAC and the halogen ring-substituted HECP resulted in formation of copolymers (Table 1) with weight-average molecular masses 5.2 to 9.2 kD.



Scheme 1. Copolymerization of vinyl acetate and the ring-substituted ethyl 2-cyano-3-phenyl-2-propenoates, RPhCH = C(CN)CO₂C₂H₅, where R is 2-Br, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 2-F, 3-F, 4-F, 2,3-dichloro, 2,4-dichloro, 2,6-dichloro, 3,4-dichloro, 2,4-difluoro, 2-bromo-3,4-dimethoxy.

According to the nitrogen elemental analysis, between 45.2 and 49.4 mol% of TSE monomer is present in the copolymers prepared at VAC/HECP = 3 (mol), which is indicative of relatively high reactivity of the monomers towards VAC.

5 Structure and Thermal Properties

The structure of VAC-HECP 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 [22] shows, that the reaction between the HECP monomers and VAC is a copolymerization.

Table 1. Copolymerization of vinyl acetate and halogen ring-substituted ethyl 2-cyano-3-phenyl-2-propenoates.

						<i>TGA</i>			
R	Yield ^a wt%	N wt%	HECP in pol., mol%	M _w kD	T _g °C	Onset of decomp. °C	10% wt loss, °C	50% wt loss, °C	Residue at 500°C, wt%
2-Bromo	65.5	3.75	48.0	7.6	101	203	282	332	11.4
3-Bromo	56.8	3.68	46.1	6.2	105	211	276	312	10.2
4-Bromo	54.1	3.76	48.2	9.2	105	223	281	321	13.2
2-Chloro	52.1	4.14	45.7	5.9	115	219	286	338	15.2
3-Chloro	48.3	4.32	49.4	7.3	103	198	272	320	13.4
4-Chloro	53.2	4.17	46.3	9.1	102	201	271	334	11.5
2-Fluoro	67.2	4.44	47.2	7.4	95	209	271	339	13.1
3-Fluoro	71.1	4.51	48.5	8.8	98	205	274	332	12.2
4-Fluoro	34.4	4.34	45.4	6.4	114	208	258	331	12.3
2,3-Dichloro	56.2	3.67	43.6	7.5	107	206	265	326	14.7
2,4-Dichloro	67.2	3.76	45.7	5.2	101	159	227	331	13.0
2,6-Dichloro	56.2	3.81	46.9	5.7	115	187	268	301	14.3
3,4-Dichloro	45.7	3.74	45.2	7.2	112	191	269	321	10.8
2,4-Difluoro	67.2	4.12	45.5	8.2	110	227	278	335	8.8
2-Bromo-3,4-dimethoxy	56.3	3.21	47.2	7.2	112	201	276	323	11.4

^aPolymerization time was 5 h

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-HECP copolymers are presented in Table 1. Relatively high T_g of the copolymers (95-115 °C) in comparison with that of polyvinyl acetate, $T_g = 28\text{-}31^\circ\text{C}$ [23] indicates decrease of chain mobility of the copolymer due to the high dipolar character of the HECP 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 [24] in 160-340°C range followed by more slow decomposition of formed residue (15.1-1.5 wt%), which then decomposed in the 500-650°C range.

6 Conclusions

Ring-substituted ethyl 2-cyano-3-phenyl-2-propenoates, $\text{RPhCH}=\text{C}(\text{CN})\text{CO}_2\text{C}_2\text{H}_5$ (R is 2-Br, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 2-F, 3-F, 4-F, 2,3-dichloro, 2,4-dichloro, 2,6-dichloro, 3,4-dichloro, 2,4-difluoro, 2-bromo-3,4-dimethoxy) 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 two steps, first in the 159-500°C range with residue (8.8-15.2 wt%), which then decomposed in the 500-650°C range.

Acknowledgments

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