Synthesis and vinyl benzene copolymerization of novel trisubstituted ethylenes: 15. Halogen and methoxy ring-substituted isopropyl 2-cyano-3-phenyl-2-propenoates

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ABSTRACT
Condensation of isopropyl cyanoacetate and substituted benzoic aldehydes resulted in formation of novel isopropyl esters of 2-cyano-3-phenyl-2-propenoic acid, RPhCH = C(CN)CO₂H (where R is 2,3,4-trimethoxy, 2,4,5-trimethoxy, 2,4,6-trimethoxy, 3-bromo-4,5-dimethoxy, 5-bromo-2,3-dimethoxy, 5-bromo-2,4-dimethoxy, 6-bromo-3,4-dimethoxy, 2-bromo-3-hydroxy-4-methoxy, 4-bromo-2,6-difluoro, 2-chloro-3,4-dimethoxy, 3-chloro-4,5-dimethoxy, 5-chloro-2,3-dimethoxy, 2,3,6-trichloro, 3-chloro-2,6-difluoro, 2,3,4-trifluoro, 2,4,5-trifluoro, 2,4,6-trifluoro, 3,4,5-trifluoro, 2,3,5,6-tetrafluoro, 2,3,4,5,6-pentafluoro). Copolymerization of the esters with vinyl benzene in solution with radical initiation (ABCN) at 70°C led to formation copolymers. The products were characterized by CHN elemental analysis, IR, ¹H- and ¹³C-NMR, GPC, DSC, and TGA.

1. Introduction
Trisubstituted ethylenes, halogen and methoxy ring-substituted cyanophenyl propenoates (CPP), R²PhCH = C(N)CO₂R³ is a large group of functional compounds that found multiple applications in organic and polymer synthesis. Pharmaceutical research is reported for a number of CPP compounds [1–6]. Thus, 2,3,4,5,6-pentafluorophenyl butyl [7] and isobutyl [8] CPP was applied in palladium-catalyzed olefination and arylation of polyfluoroarenes. Electrophilic tri- and tetrasubstituted CPP are useful in demarcation of the transition from radical to ionic chemistry [9]. Most CPP compounds do not undergo homopolymerization because of steric difficulties but copolymerize readily with monosubstituted alkenes [10]. Trisubstituted alkenes substituted with carbonyl, cyano, and halo groups when copolymerized with monomers like vinyl benzene, N-vinylcarbazole, and vinyl acetate [11–13] form alternating copolymers with isolated CPP monomer units. When copolymerized with such commercial monomers, (i.e., vinyl benzene, vinyl, acetate, and vinyl ethers), CPP monomers introduce into polymer chain a variety of functional groups, like cyanoacrylate, substituted phenyl ring, etc. These reactive groups could participate in polymer modification reactions to better polymer properties and wider polymer applicability [14].

We continue to explore synthesis and copolymerization of CPP compounds; thus, we have prepared and copolymerized with vinyl benzene ring-trisubstituted methyl [15], ethyl [16], propyl [17,18], and butyl [19,20] esters of 2-cyano-3-phenyl-2-propenoic acid. Recently we have reported synthesis and vinyl benzene copolymerization of a number of novel chloro and methoxy [21] and dimethoxy [22] ring-disubstituted isopropyl esters of 2-cyano-3-phenyl-2-propenoic acid. In this study we have prepared and copolymerized novel ring-substituted isopropyl esters of 2-cyano-3-phenyl-2-propenoic acid. Condensation of isopropyl cyanoacetate and substituted benzoic aldehydes resulted in formation of novel isopropyl esters of 2-cyano-3-phenyl-2-propenoic acid, RPhCH = C(CN)CO₂H (where R is 2,3,4-trimethoxy, 2,4,5-trimethoxy, 2,4,6-trimethoxy, 3-bromo-4,5-dimethoxy, 5-bromo-2,3-dimethoxy, 5-bromo-2,4-dimethoxy, 6-bromo-3,4-dimethoxy, 2-bromo-3-hydroxy-4-methoxy, 4-bromo-2,6-difluoro, 2-chloro-3,4-dimethoxy, 3-chloro-4,5-dimethoxy, 5-chloro-2,3-dimethoxy, 2,3,6-trichloro, 3-chloro-2,6-difluoro, 2,3,4-trifluoro, 2,4,5-trifluoro, 2,4,6-trifluoro, 3,4,5-trifluoro, 2,3,5,6-tetrafluoro, 2,3,4,5,6-pentafluoro). Copolymerization of the esters with vinyl benzene in solution with radical initiation (ABCN) at 70°C led to formation copolymers. The products were characterized by CHN elemental analysis, IR, ¹H- and ¹³C-NMR, GPC, DSC, and TGA.
ethoxy, 5-chloro-2,3-dimethoxy, 2,3,6-trichloro, 3-chloro-2,6-difluoro, 2,3,4-trifluoro, 2,4,5-trifluoro, 2,4,6-trifluoro, 3,4,5-trifluoro, 2,3,5,6-tetrafluoro, 2,3,4,5,6-pentafluoro. To the best of our knowledge, there have been no studies of either synthesis of these esters (except synthesis of R = 2,4,6-trimethoxy [5]) nor their copolymerization with vinyl benzene [23].

2. Experimental

2.1. Materials

2,3,4-trimethoxy, 2,4,5-trimethoxy, 2,4,6-trimethoxy, 3-bromo-4,5-dimethoxy, 5-bromo-2,3-dimethoxy, 5-bromo-2,4-dimethoxy, 6-bromo-3,4-dimethoxy, 2-bromo-3-hydroxy-4-methoxy, 4-bromo-2,6-difluoro, 2-chloro-3,4-dimethoxy, 3-chloro-4,5-dimethoxy, 5-chloro-2,3-dimethoxy, 2,3,6-trichloro, 3-chloro-2,6-difluoro, 2,3,4-trifluoro, 2,4,5-trifluoro, 2,4,6-trifluoro, 3,4,5-trifluoro, 2,3,5,6-tetrafluoro, 2,3,4,5,6-pentafluorobenzoic aldehydes, isopropyl cyanoacetate, piperidine, vinyl benzene, 1,1′-azobiscyclohexanecarbonitrile, (ABCN), and toluene supplied from Sigma-Aldrich Co., were used as received.

2.2. Instrumentation

Infrared spectra of the TSE monomers and polymers (NaCl plates) were determined with an ABB FTIR 2000 FT-IR spectrometer. The melting points of the monomers, the glass transition temperatures (Tg), 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 200°C range at heating rate of 10°C/min. The thermal stability of the copolymers was measured by thermogravimetric analyzer (TGA) TA Model Q50 from ambient temperature to 800°C at 20°C/min. The molecular weights of the polymers were determined relative to polystyrene standards in THF solutions with sample concentrations 0.8% (w/v) by gel permeation chromatography (GPC) using an Altech 426 HPLC pump at an elution rate of 1.0 mL/min; Phenogel 5μ Linear column at 25°C and Viscotek 302 detector. 1H- and 13C-NMR spectra were obtained on 10–25% (w/v) monomer or polymer solutions in CDCl3 at ambient temperature using Avance 300 MHz spectrometer. Elemental analyses, CHN (wt%) for ICPP compounds, and nitrogen (wt%) for the copolymers were determined accurately to 0.3% for analysis by Midwest Microlab, LLC (IN).

3 Results and discussion

3.1 Synthesis of ring-substituted isopropyl esters of 2-cyano-3-phenyl-2-propenoic acid

The isopropyl esters of 2-cyano-3-phenyl-2-propenoic acid (ICPA) were synthesized by piperidine catalyzed Knoevenagel condensation [24] of an appropriate benzoic aldehyde with isopropyl cyanoacetate.

\[ R\text{PhCHO} + \text{NCCH}_2\text{CO}_2\text{CH(CH}_3)_2 \rightarrow R\text{PhCH} = C(\text{CN})\ \text{CO}_2\text{CH(CH}_3)_2 \]

where R is 2,3,4-trimethoxy, 2,4,5-trimethoxy, 2,4,6-trimethoxy, 3-bromo-4,5-dimethoxy, 5-bromo-2,3-dimethoxy, 5-bromo-2,4-dimethoxy, 6-bromo-3,4-dimethoxy, 2-bromo-3-hydroxy-4-methoxy, 4-bromo-2,6-difluoro, 2-chloro-3,4-dimethoxy, 3-chloro-4,5-dimethoxy, 5-chloro-2,3-dimethoxy, 2,3,6-trichloro, 3-chloro-2,6-difluoro, 2,3,4-trifluoro, 2,4,5-trifluoro, 2,4,6-trifluoro, 3,4,5-trifluoro, 2,3,5,6-tetrafluoro, 2,3,4,5,6-pentafluorobenzoic aldehydes, isopropyl cyanoacetate, piperidine, vinyl benzene, 1,1′-azobiscyclohexanecarbonitrile, (ABCN), and toluene supplied from Sigma-Aldrich Co., were used as received.

3.1.1 Isopropyl 2-cyano-3-(2,3,4-trimethoxyphenoxy)-2-propenoate

Yield 87%; mp 77.3°C, 1H-NMR δ 8.6 (s, 1 H, CH = ), 8.2–6.7 (m, 2 H, Ph), 5.2 (m, 1 H, OCH), 4.2–3.7 (m, 9 H, OCH3), 1.4–1.1 (d, 6 H, CH3); 13C-NMR δ 163 (C = O), 155 (HC = ), 158, 149, 142, 125, 119, 107 (Ph), 116 (CN), 101 (C = ), 70 (OCH), 62, 61, 56 (CH3O), 22 (CH3); IR (cm⁻¹): 3049–2732 (m, C-H), 2212 (m, CN), 1722 (s, C = O), 1585 (s, C = C), 1288 (s, C-O-C), 1009, 953 (s, C-H out of plane). Anal. Calcd. for C16H19NO2: C, 62.94; H, 6.27; N, 4.59; Found: C, 62.52; H, 6.47; N, 3.71.

3.1.2 Isopropyl 2-cyano-3-(2,4,5-trimethoxyphenoxy)-2-propenoate

Yield 76%; mp 109.7°C, 1H-NMR δ 8.7 (s, 1 H, CH = ), 8.1–6.3 (m, 2 H, Ph), 5.2 (m, 1 H, OCH), 4.1–3.8 (m, 9 H, OCH3), 1.4 (d, 6 H, CH3); 13C-NMR δ 163 (C = O), 155 (HC = ), 158, 156, 148, 143, 112, 100 (Ph), 117 (CN), 198 (C = ), 70 (OCH), 56 (CH3O), 22 (CH3); IR (cm⁻¹): 3023–2782 (m, C-H), 2212 (m, CN), 1695 (s, C = O), 1584 (s, C = C), 1278 (s, C-O-C), 1010, 953, 824 (s, C-H out of plane). Anal. Calcd. for C16H19NO3: C, 62.94; H, 6.27; N, 4.59; Found: C, 61.98; H, 6.43; N, 3.41.

3.1.3 Isopropyl 2-cyano-3-(2,4,6-trimethoxyphenoxy)-2-propenoate

Yield 91%; mp 94.2°C, 1H-NMR δ 8.6 (s, 1 H, CH = ), 8.2–6.6 (m, 2 H, Ph), 5.1 (m, 1 H, OCH), 3.8 (m, 9 H, OCH3), 2.2, 3, 4, 5-trimethoxy, 2,4,6-trimethoxy, 3,4,5-trimethoxy, 2,4,6-trimethoxy, 3-bromo-4,5-dimethoxy, 5-bromo-2,3-dimethoxy, 5-bromo-2,4-dimethoxy, 6-bromo-3,4-dimethoxy, 2-bromo-3-hydroxy-4-methoxy, 4-bromo-2,6-difluoro, 2-chloro-3,4-dimethoxy, 3-chloro-4,5-dimethoxy, 5-chloro-2,3-dimethoxy, 2,3,6-trichloro, 3-chloro-2,6-difluoro, 2,3,4-trifluoro, 2,4,5-trifluoro, 2,4,6-trifluoro, 3,4,5-trifluoro, 2,3,5,6-tetrafluoro, 2,3,4,5,6-pentafluorobenzoic aldehydes, isopropyl cyanoacetate, piperidine, vinyl benzene, 1,1′-azobiscyclohexanecarbonitrile, (ABCN), and toluene supplied from Sigma-Aldrich Co., were used as received.
3.1.7. Isopropyl 2-cyano-3-(6-bromo-5-bromo-3-bromo-2,4-dimethoxyphenyl)-2-propenoate

Yield 80%; mp 134.8°C, 1 H-NMR δ 8.1 (s, 1 H, CH = ), 7.1, 7.0 (m, 2 H, Ph), 5.1 (m, 1 H, OCH), 3.8 (d, 6 H, OCH3), 1.3 (d, 6 H, CH3); 13 C-NMR δ 162 (C = O), 153 (HC = ), 157, 149, 143, 126, 119, 108 (Ph), 116 (CN), 140 (C = ), 68 (OCH), 55 (CH3O), 22 (CH3); IR (cm⁻¹): 3402–2817 (m, C-H), 2224 (m, CH3); δ 3424–2819 (m, C-H), 2218 (m, CN), 1712 (s, C = O), 1584 (s, C = C), 1249 (s, C-O-C), 955, 833 (s, C-H out of plane). Anal. Calcd. for C16H16NO5: C, 60.08; H, 4.55; N, 3.95; Found: C, 60.01; H, 4.46; N, 3.98.

3.1.8. Isopropyl 2-cyano-3-(2-bromo-3-hydroxy-4-methoxyphenyl)-2-propenoate

Yield 79%; mp 126.7°C, 1 H-NMR δ 10.3 (s, 1 H, OH), 8.2 (s, 1 H, CH = ), 7.5, 6.9 (m, 2 H, Ph), 5.1 (m, 1 H, OCH), 3.8 (s, 3 H, OCH3), 1.3 (d, 6 H, CH3); 13 C-NMR δ 166 (C = O), 152 (HC = ), 153, 128, 127, 114 (Ph), 116 (CN), 129 (C = ), 68 (OCH), 56 (CH3O), 22 (CH3); IR (cm⁻¹): 3434–2821 (m, C-H), 2221 (m, CN), 1719 (s, C = O), 1586 (s, C = C), 1254 (s, C-O-C), 958, 842 (s, C-H out of plane). Anal. Calcd. for C16H16BrNO5: C, 49.43; H, 4.15; N, 4.12; Found: C, 48.91; H, 4.31; N, 4.20.

3.1.9. Isopropyl 2-cyano-3-(4-bromo-2,6-difluorophenyl)-2-propenoate

Yield 95%; mp 67.8°C, 1 H-NMR δ 8.1 (s, 1 H, CH = ), 7.2, 7.1 (m, 2 H, Ph), 5.1 (m, 1 H, OCH), 1.3 (d, 6 H, CH3); 13 C-NMR δ 166 (C = O), 152 (HC = ), 151, 115 (Ph), 116 (CN), 103 (C = ), 68 (OCH), 22 (CH3); IR (cm⁻¹): 3436–2823 (m, C-H), 2218 (m, CN), 1718 (s, C = O), 1589 (s, C = C), 1231 (s, C-O-C), 956, 821 (s, C-H out of plane). Anal. Calcd. for C16H16BrF2NO5: C, 47.30; H, 3.05; N, 4.24; Found: C, 47.88; H, 3.33; N, 4.65.

3.1.10. Isopropyl 2-cyano-3-(2-chloro-3,4-dimethoxyphenyl)-2-propenoate

Yield 79%; mp 126.7°C, 1 H-NMR δ 8.1 (s, 1 H, CH = ), 7.7, 7.5 (m, 2 H, Ph), 5.2 (m, 1 H, OCH), 4.0 (d, 6 H, OCH3), 1.4 (d, 6 H, CH3); 13 C-NMR δ 162 (C = O), 154 (HC = ), 149, 129, 128, 127, 111 (Ph), 116 (CN), 103 (C = ), 71 (OCH), 61, 56 (CH3O), 22 (CH3); IR (cm⁻¹): 3424–2819 (m, C-H), 2218 (m, CN), 1709 (s, C = O), 1580 (s, C = C), 1246 (s, C-O-C), 951, 835 (s, C-H out of plane). Anal. Calcd. for C16H16ClNO5: C, 58.16; H, 5.21; N, 4.52; Found: C, 57.91; H, 5.31; N, 4.40.

3.1.11. Isopropyl 2-cyano-3-(3-chloro-4,5-dimethoxyphenyl)-2-propenoate

Yield 82%; mp 94.5°C, 1 H-NMR δ 8.6 (s, 1 H, CH = ), 8.2–6.7 (m, 2 H, Ph), 5.2 (m, 1 H, OCH), 4.0, 3.9 (s, 6 H, OCH3), 1.4 (d, 6 H, CH3); 13 C-NMR δ 162 (C = O), 157 (HC = ), 145, 132, 126, 123, 110 (Ph), 116 (CN), 103 (C = ), 71 (OCH), 61, 56 (CH3O), 22 (CH3); IR (cm⁻¹): 3150–2802 (m, C-H), 2220 (m, CN), 1717 (s, C = O), 1607 (s, C = C), 1263 (s, C-O-C), 932, 843 (s, C-H out of plane). Anal. Calcd. for C16H16ClO5: C, 58.16; H, 5.21; N, 4.52; Found: C, 58.00; H, 5.10; N, 4.56.

3.1.12. Isopropyl 2-cyano-3-(5-chloro-2,3-dimethoxyphenyl)-2-propenoate

Yield 77%; mp 103.7°C, 1 H-NMR δ 8.2 (s, 1 H, CH = ), 7.8–7.5 (m, 2 H, Ph), 5.1 (m, 1 H, OCH), 3.8 (d, 6 H, OCH3), 1.3 (d, 6 H, CH3); 13 C-NMR δ 166 (C = O), 152 (HC = ), 152, 130, 121 (Ph), 116 (CN), 103 (C = ), 68 (OCH), 60, 56.
3.1.13. Isopropyl 2-cyano-3-(2,3,6-trichlorophenyl)-2-propenoate

Yield 78%; mp 64.0°C, 1H-NMR δ 8.4 (1 H, CH = ), 8.2, 7.2 (2 H, Ph), 5.2 (m, 1 H, OCH), 1.3 (d, 6 H, CH₃); 13C-NMR δ 160 (C = O), 150 (HC = ), 133, 132, 120, 128 (Ph), 116 (CN), 126 (C = ), 71 (OCH), 21 (CH₃); IR (cm⁻¹): 3423–2829 (m, C-H), 2227 (m, CN), 1722 (s, C = O), 1593 (s, C = C), 1256 (s, C-O-C), 974, 844 (s, C-H out of plane). Anal. Calcd. for C₁₃H₁₂Cl₅NO₂: C, 58.16; H, 5.21; N, 4.52; Found: C, 57.21; H, 5.34; N, 4.48.

3.1.14. Isopropyl 2-cyano-3-(3-chloro-2,6-difluorophenyl)-2-propenoate

Yield 97%; mp 59.4°C, 1H-NMR δ 8.1 (1 H, CH = ), 7.3, 7.0 (m, 2 H, Ph), 5.1 (m, 1 H, OCH), 1.3 (d, 6 H, CH₃); 13C-NMR δ 166 (C = O), 152 (HC = ), 149, 133, 113, 112 (Ph), 116 (CN), 101 (C = ), 68 (OCH), 22 (CH₃); IR (cm⁻¹): 3419–2823 (m, C-H), 2221 (m, CN), 1716 (s, C = O), 1576 (s, C = C), 1249 (s, C-O-C), 936, 843 (s, C-H out of plane). Anal. Calcd. for C₁₃H₁₀Cl₂F₂NO₂: C, 54.66; H, 3.53; N, 4.90; Found: C, 54.13; H, 3.83; N, 5.05.

3.1.15. Isopropyl 2-cyano-3-(2,3,4-trifluorophenyl)-2-propenoate

Yield 92%; mp 55.2°C, 1H-NMR δ 8.3 (1 H, CH = ), 8.2, 7.1 (2 H, Ph), 5.2 (m, 1 H, OCH), 1.3 (d, 6 H, CH₃); 13C-NMR δ 160 (C = O), 152 (HC = ), 144, 142, 132, 118, 112 (Ph), 116 (CN), 123 (C = ), 70 (OCH), 21 (CH₃); IR (cm⁻¹): 3427–2807 (m, C-H), 2231 (m, CN), 1718 (s, C = O), 1598 (s, C = C), 1259 (s, C-O-C), 965, 843 (s, C-H out of plane). Anal. Calcd. for C₁₃H₁₀F₃NO₂: C, 58.00; H, 3.74; N, 5.20; Found: C, 59.19; H, 4.02; N, 5.46.

3.1.16. Isopropyl 2-cyano-3-(2,4,5-trifluorophenyl)-2-propenoate

Yield 96%; mp 60.3°C, 1H-NMR δ 8.3 (1 H, CH = ), 8.2, 7.0 (2 H, Ph), 5.2 (m, 1 H, OCH), 1.3 (d, 6 H, CH₃); 13C-NMR δ 160 (C = O), 152 (HC = ), 158, 156, 155, 146, 144, 143 (Ph), 116 (CN), 108 (C = ), 70 (OCH), 21 (CH₃); IR (cm⁻¹): 3234–2824 (m, C-H), 2226 (m, CN), 1724 (s, C = O), 1578 (s, C = C), 1245 (s, C-O-C), 954, 849 (s, C-H out of plane). Anal. Calcd. for C₁₃H₁₀F₃NO₂: C, 58.00; H, 3.74; N, 5.20; Found: C, 58.75; H, 3.77; N, 5.27.

3.1.17. Isopropyl 2-cyano-3-(2,4,6-trifluorophenyl)-2-propenoate

Yield 78%; mp 64.0°C, 1H-NMR δ 8.1 (1 H, CH = ), 6.9 (m, 2 H, Ph), 5.2 (m, 1 H, OCH), 1.3 (d, 6 H, CH₃); 13C-NMR δ 163 (C = O), 159 (HC = ), 160, 141, 112 (Ph), 116 (CN), 103 (C = ), 70 (OCH), 21 (CH₃); IR (cm⁻¹): 3412–2813 (m, C-H), 2236 (m, CN), 1721 (s, C = O), 1576 (s, C = C), 1267 (s, C-O-C), 972, 849 (s, C-H out of plane). Anal. Calcd. for C₁₃H₁₀F₃NO₂: C, 58.00; H, 3.74; N, 5.20; Found: C, 57.88; H, 3.89; N, 5.29.

3.1.18. Isopropyl 2-cyano-3-(3,4,5-trifluorophenyl)-2-propenoate

Yield 82%; mp 96.7°C, 1H-NMR δ 8.1 (1 H, CH = ), 8.7 (m, 2 H, Ph), 5.2 (m, 1 H, OCH), 1.3 (d, 6 H, CH₃); 13C-NMR δ 161 (C = O), 153 (HC = ), 151, 150, 144, 141, 128, 118, (Ph), 115 (CN), 106 (C = ), 71 (OCH), 22 (CH₃); IR (cm⁻¹): 3446–2907 (m, C-H), 2234 (m, CN), 1721 (s, C = O), 1576 (s, C = C), 1243 (s, C-O-C), 971, 841 (s, C-H out of plane). Anal. Calcd. for C₁₃H₁₀F₃NO₂: C, 58.00; H, 3.74; N, 5.20; Found: C, 58.42; H, 3.84; N, 5.19.

3.1.19. Isopropyl 2-cyano-3-(2,3,5,6-tetrafluorophenyl)-2-propenoate

Yield 93%; mp 63.2°C, 1H-NMR δ 8.1 (1 H, CH = ), 6.9 (m, 2 H, Ph), 5.2 (m, 1 H, OCH), 1.3 (d, 6 H, CH₃); 13C-NMR δ 161 (C = O), 153 (HC = ), 145, 141, 128, 115 (Ph), 115 (CN), 106 (C = ), 71 (OCH), 22 (CH₃); IR (cm⁻¹): 3422–2834 (m, C-H), 2238 (m, CN), 1722 (s, C = O), 1556 (s, C = C), 1273 (s, C-O-C), 976, 841 (s, C-H out of plane). Anal. Calcd. for C₁₃H₁₀F₄NO₂: C, 58.00; H, 3.74; N, 5.20; Found: C, 54.55; H, 3.45; N, 4.96.

3.1.20. Isopropyl 2-cyano-3-(2,3,4,5,6-pentafluorophenyl)-2-propenoate

Yield 78%; mp 63.2°C, 1H-NMR δ 8.0 (1 H, CH = ), 5.2 (m, 1 H, OCH), 1.2 (d, 6 H, CH₃); 13C-NMR δ 163 (C = O), 152 (HC = ), 140, 113 (Ph), 116 (CN), 104 (C = ), 71 (OCH), 21 (CH₃); IR (cm⁻¹): 3392–2808 (m, C-H), 2232 (m, CN), 1712 (s, C = O), 1566 (s, C = C), 1282 (s, C-O-C), 967, 832 (s, C-H out of plane). Anal. Calcd. for C₁₃H₁₀F₅NO₂: C, 51.16; H, 2.64; N, 4.59; Found: C, 50.71; H, 3.09; N, 4.97.

3.2. Homopolymerization

The IPCA compounds did not homopolymerize on ABCN initiation at 70°C for 48 h with no polymer precipitated in methanol. Vinyl benzene (VB) polymerization (30 min) resulted in 18.3% yield of polyethylenebenzene.

3.3. Copolymerization

Copolymers of the vinyl benzene (VB) and the ICPA monomers were prepared at VB/ICPA = 3 (mol) the monomer feed with 0.12 mol/L of ABCN at total monomer concentration 2.44 mol/L in 10 mL of toluene at 70°C. Polymerization time was 8 h. To stop reaction the
mixture was cooled and precipitated in methanol. Nitrogen elemental analysis was used to determine composition of the copolymers. The yield of copolymers was kept low to decrease copolymer compositional drift.

Copolymerization (Sch. 1) of VB and the ring-substituted ICPA resulted in the formation of copolymers (Table 1) with weight-average molecular masses 52 to 61 kD. Copolymer composition was calculated based on nitrogen analysis in the following way: ICPA (mole) = N (wt %)/14; ICPA (wt%) = ICPA (mole) x Mol. Weight of ICPA; VB (wt%) = 100 – ICPA (wt%); VB (mol) = VB (wt %)/104; VB (mol %) = VB (mol)/[(ICPA (mol) + VB (mol)) • 100%; ICPA (mol %) = 100 – VB mol %.

According to elemental analysis, between 9.4 and 35.2 mol% of ICPA monomer is present in the copolymers prepared at VB/ICPA = 3 (mol), which is indicative of relatively high reactivity of the monomers towards ST.

The copolymers were all soluble in ethyl acetate, THF, DMF and CHCl₃ and insoluble in methanol, ethyl ether, and petroleum ether.

### 3.4 Monomer relative reactivity

Relative reactivities of VB and the ICPA monomers in the copolymerization can be estimated by application of the copolymerization equation for the terminal copolymerization model [10].

\[
m_1/m_2 = [M_1] (r_1 [M_1] + [M_2])/[M_2] ([M_1] + r_2 [M_2])
\]

where \(m_1\) and \(m_2\) are mole fractions of VB and ICPA monomer units in the copolymer, \([M_1]\) and \([M_2]\) are concentrations of VB and an ICPA in the monomer feed, and \(r_1\) and \(r_2\) are monomer reactivity ratios, \(r_1 = k_{-VB-VB}/k_{VB-ICPA}\) and \(r_2 = k_{ICPA-ICPA}/k_{ICPA-VB}\). In the absence of self-propagation of ICPA monomers, none of them

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**Scheme 1.** VB-ICPA copolymerization, \(R = 2,3,4\)-trimethoxy, 2,4,5-trimethoxy, 2,4,6-trimethoxy, 3-bromo-4,5-dimethoxy, 5-bromo-2,3-dimethoxy, 5-bromo-2,4-dimethoxy, 6-bromo-3,4-dimethoxy, 2-bromo-3-hydroxy-4-methoxy, 4-bromo-2,6-difluoro, 2-chloro-3,4-dimethoxy, 3-chloro-4,5-dimethoxy, 5-chloro-2,3-dimethoxy, 2,3,6-trichloro, 3-chloro-2,6-difluoro, 2,3,4-trifluoro, 2,4,5-trifluoro, 2,4,6-trifluoro, 3,4,5-trifluoro, 2,3,5,6-tetrafluoro, 2,3,4,5,6-pentafluoro.

**Table 1.** Copolymerization of VB with ICPA.

| R                    | N (wt%) | VB in copol (mol%) | ICPA in copol (mol%) | 1/r₁ | \(M_w\) (kD) |
|----------------------|---------|--------------------|----------------------|------|-------------|
| 2,3,4-Trimethoxy     | 2.03    | 78.7               | 21.3                 | 1.11 | 56          |
| 2,4,5-Trimethoxy     | 1.39    | 87.1               | 12.9                 | 0.52 | 56          |
| 2,4,6-Trimethoxy     | 1.67    | 83.7               | 16.3                 | 0.73 | 52          |
| 3-Bromo-4,5-dimethoxy| 2.45    | 67.6               | 32.4                 | 2.75 | 53          |
| 5-Bromo-2,3-dimethoxy| 2.46    | 67.4               | 32.6                 | 2.81 | 56          |
| 5-Bromo-2,4-dimethoxy| 2.44    | 67.9               | 32.1                 | 2.69 | 54          |
| 6-Bromo-3,4-dimethoxy| 2.14    | 65.2               | 34.8                 | 3.43 | 57          |
| 2-bromo-3-hydroxy-4-methoxy | 2.45 | 75.1               | 24.9                 | 1.48 | 54          |
| 4-Bromo-2,6-difluoro | 2.6     | 66.7               | 33.3                 | 2.99 | 58          |
| 3-Chloro-2,6-difluoro| 2.7     | 69.1               | 30.9                 | 2.43 | 57          |
| 2-Chloro-3,4-dimethoxy| 1.07   | 90.6               | 9.4                  | 0.35 | 54          |
| 3-Chloro-4,5-dimethoxy| 2.39   | 72.6               | 27.4                 | 1.82 | 59          |
| 5-Chloro-2,3-dimethoxy| 2.79   | 64.8               | 35.2                 | 3.55 | 56          |
| 2,3,6-Trichloro      | 2.06    | 77.6               | 22.4                 | 1.21 | 55          |
| 2,3,4-Trifluoro      | 2.21    | 77.8               | 22.2                 | 1.20 | 61          |
| 2,4,5-Trifluoro      | 2.03    | 81.2               | 18.8                 | 0.99 | 59          |
| 2,4,6-Trifluoro      | 1.85    | 82.4               | 17.6                 | 0.81 | 58          |
| 3,4,5-Trifluoro      | 2.19    | 78.1               | 21.9                 | 1.17 | 60          |
| 2,3,5,6-tetrafluoro  | 2.06    | 79.1               | 20.9                 | 1.08 | 58          |
| 2,3,4,5,6-Pentafluoro| 2.21    | 76.0               | 24.0                 | 1.39 | 59          |

*Polymerization time was 8 h.
formed homopolymers, \( k_{ICPA-ICPA} = 0, r_2 = 0 \) \[10\], Eq. (1) yields
\[
m_1/m_2 = r_1 ([M_1]/[M_2]) + 1 \tag{2}
\]

**Equation 2** assumes a minimal copolymer compositional drift during a copolymerization reaction, i.e., a low conversion. The fact that ICPA monomers do not self-propagate allows the use of Eq. (2) for a single-point estimation of the relative reactivity of ICPA monomers with respect to VB; it is represented by the 1/\( r_1 \) = \( k_{VB-ICPA} \)/\( k_{VB-VB} \) ratio (the rate constant ratio of attaching an ICPA monomer unit to or higher than polystyrene (104ºC) \[ 25 \]). Introduction of trimethoxy and bromo-dimethoxy phenyl substitution does not change significantly \( T_g \) which is related to segmental mobility \[ 26 \], whereas chloro-dimethoxy, trifluoro, tetrafluoro, and pentafluoro phenyl substitution in VB-ICPA copolymer lead to decrease of segmental mobility in the polymer chain. More precise correlation of the segmental mobility to the size and position of the ICPA ring substitution is difficult apparently due to non-uniform composition, monomer unit distribution, and/or molecular weight and MWV of the copolymers.

**3.5. Thermal behavior**

Thermal transitions of the VB-ICPA copolymers were analyzed by differential scanning calorimetry (DSC). The second heating results were obtained in all cases so that the samples become more dry and without ‘thermal memory’. DSC analysis confirmed amorphous morphology of the EB-ICPA copolymers showing glass transition temperatures \( T_g \) and absence of crystalline endotherm on repeated heating and cooling cycles (Table 2). A single \( T_g \) value was observed for all the copolymers with values close to or higher than polystyrene (104ºC) \[ 25 \]. Introduction of trimethoxy and bromo-dimethoxy phenyl substitution does not change significantly \( T_g \) which is related to segmental mobility \[ 26 \], whereas chloro-dimethoxy, trifluoro, tetrafluoro, and pentafluoro phenyl substitution in VB-ICPA copolymer lead to decrease of segmental mobility in the polymer chain. More precise correlation of the segmental mobility to the size and position of the ICPA ring substitution is difficult apparently due to non-uniform composition, monomer unit distribution, and/or molecular weight and MWV of the copolymers.

Thermogravimetric analysis (TGA) provided information on thermal stability of the copolymers (Table 2). Thermal stability of the P(VC-co-ICPA) copolymers is lower than that of poly(vinylbenzene, PVB) \[ 27 \], the onset of decomposition at 219ºC (PVB 350ºC), 10% weight loss at 301ºC (PVB 425ºC), 50% weight loss at 343ºC (PVB 428ºC). Lower thermal stability of the VB-ICPA copolymers apparently associated with presence of ICPA quaternary carbon in the chain similarly to poly-alpha-methylstyrene \[ 28 \]. TGA showed that the copolymers decomposed in nitrogen in two steps, first

| Table 2. Thermal Behavior of VB – ICPA copolymers. |
|---------------------|---------------------|---------------------|---------------------|---------------------|
| R                    | \( T_g \) (ºC) | Onset of decomp. (ºC) | 10 wt% loss (ºC) | 50 wt% loss (ºC) |
|---------------------|---------------------|---------------------|---------------------|---------------------|
| 2,3,4-Trimethoxy     | 103                 | 225                 | 302                 | 340                 |
| 2,4,5-Trimethoxy     | 119                 | 258                 | 306                 | 361                 |
| 2,4,6-Trimethoxy     | 94                  | 222                 | 296                 | 350                 |
| 3-Bromo-4,5-dimethoxy| 103                 | 265                 | 302                 | 356                 |
| 5-Bromo-2,3-dimethoxy| 107                 | 278                 | 321                 | 374                 |
| 5-Bromo-2,4-dimethoxy| 112                 | 265                 | 319                 | 387                 |
| 6-Bromo-3,4-dimethoxy| 107                 | 268                 | 316                 | 379                 |
| 2-Bromo-3-hydroxy-4-methoxy | 108       | 271                 | 317                 | 345                 |
| 4-Bromo-2,6-difluoro | 111                 | 272                 | 314                 | 387                 |
| 3-Chloro-2,6-difluoro| 107                 | 267                 | 312                 | 367                 |
| 2-Chloro-3,4-dimethoxy| 115                | 201                 | 310                 | 346                 |
| 3-Chloro-4,5-dimethoxy| 157                 | 232                 | 295                 | 345                 |
| 5-Chloro-2,3-dimethoxy| 103                 | 262                 | 302                 | 340                 |
| 2,3,6-Trichloro      | 78                  | 252                 | 270                 | 342                 |
| 2,3,4-Trifluoro      | 125                 | 263                 | 298                 | 364                 |
| 2,4,5-Trifluoro      | 141                 | 237                 | 284                 | 335                 |
| 2,4,6-Trifluoro      | 125                 | 251                 | 296                 | 348                 |
| 3,4,5-Trifluoro      | 147                 | 222                 | 285                 | 345                 |
| 2,3,5,6-tetrafluoro  | 151                 | 234                 | 289                 | 355                 |
| 2,3,4,5,6-Pentafluoro| 143                 | 174                 | 283                 | 356                 |
| Residue wt%          |                      |                     |                     |                     |
|---------------------|---------------------|---------------------|---------------------|---------------------|
in the 200–500°C range with residue (1–7% wt.), and second in the 500–800°C range.

4. Conclusions

Novel isopropyl esters of ring-substituted 2-cyano-3-phenyl-2-propenoic acid were prepared and copolymerized with vinyl benzene. The compositions of novel 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 two steps, first in the 200–500°C range with a residue, which then decomposed in the 500–800°C range.

Disclosure statement

No potential conflict of interest was reported by the authors.

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