

Synthesis and styrene copolymerization of novel dihalogen ring-substituted isopropyl cyanophenylacrylates

Sebastian Flieger, Patrick M. McCaw, Stepan Mouradkhanian, Brenda Pedroza, Megan M. Peffley, Rachel L. Pride, Paolo R. Ramirez, Madeline S. Rogers, Boris Romanov, Mariam Saleh, Caleb Soler, Lee D. Warnick, Sara M Rocus, William S. Schjerven, and Gregory B. Kharas

DePaul University, Chemistry and Biochemistry Department, 1110 West Belden Avenue, Chicago, IL 60614-3214

Abstract

Novel dihalogen ring-substituted isopropyl 3-phenyl-2-cyanoacrylates, $RPhCH=C(CN)CO_2CH(CH_3)_2$ (where R is 2,5-dibromo, 3,5-dibromo, 2,3-dichloro, 2,4-dichloro, 2,5-dichloro, 2,6-dichloro, 3,4-dichloro, 3,5-dichloro, 2,4-difluoro, 2,5-difluoro, 2,6-difluoro) were prepared and copolymerized with styrene. The acrylates were synthesized by the piperidine catalyzed Knoevenagel condensation of ring-disubstituted benzaldehydes and isopropyl cyanoacetate and characterized by CHN elemental analysis, IR, 1H - and ^{13}C -

NMR. All the acrylates were copolymerized with styrene in solution with radical initiation (ABCN) at 70°C. The composition of the copolymers was calculated from nitrogen analysis, and the structures were analyzed by IR, ^1H and ^{13}C -NMR, GPC, DSC, and TGA.

Keywords: Phenylcyanoacrylates, Knoevenagel condensation, radical copolymerization, styrene copolymers

* CONTACT: Gregory B. Kharas, Chemistry and Biochemistry Department, DePaul University, Chicago, IL 60614-3214. E-mail: gkharas@depaul.edu

1. Introduction

Ring-functionalized cyanoacrylates (PCA), $\text{R}^1\text{PhCH}=\text{C}(\text{CN})\text{CO}_2\text{R}^2$ continue to attract attention as compounds with interesting properties and as comonomers for modification of commercial polymers. There are application reports exemplifying methyl 3-phenyl-2-cyanoacrylate, MPCA (1-2). Thus, dimethylamino ring-substituted MPCA was examined among other cyanovinylheteroaromatics in relation to organic nonlinear optics (1). 3,5-Dibromo ring-substituted MPCA was explored in synthesis of new phenylsuccinimide derivatives with anticonvulsant properties (2). Applications of ethyl PCA and its ring-substituted derivatives include studies of antifungal potential (3) and antileishmanial activity (4).

Recently we have reported synthesis and styrene copolymerization of a number of novel isopropyl phenyl cyanoacrylates (5-7).

With the objective to design novel structures, that could serve as a spring board for further development of novel materials with new properties and applications, we have prepared dihalogen ring-substituted isopropyl phenylcyanoacrylates, $RPhCH=C(CN)CO_2CH(CH_3)_2$ where R is 2,5-dibromo, 3,5-dibromo, 2,3-dichloro, 2,4-dichloro, 2,5-dichloro, 2,6-dichloro, 3,4-dichloro, 3,5-dichloro, 2,4-difluoro, 2,5-difluoro, 2,6-difluoro, and explore the feasibility of their copolymerization with styrene. To the best of our knowledge, there have been no reports on either synthesis of these isopropyl 2-cyano-3-phenyl-2-propenoates, nor their copolymerization with styrene.

2. Experimental

2.1. Materials

2,5-Dibromo, 3,5-dibromo, 2,3-dichloro, 2,4-dichloro, 2,5-dichloro, 2,6-dichloro, 3,4-dichloro, 3,5-dichloro, 2,4-difluoro, 2,5-difluoro, 2,6-difluorobenzaldehydes, isopropyl cyanoacetate, piperidine, styrene, 1,1'-azobiscyclohexanecarbonitrile, (ABCN), and toluene supplied from Sigma-Aldrich Co., were used as received.

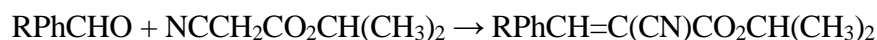
2.2. Instrumentation

Infrared spectra of the TSE monomers and polymers (NaCl plates) were determined with an ABB 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 200°C range at heating rate of 10°C/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 800°C at 20°C/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 5 μ Linear column at 25°C and Viscotek 302 detector. ^1H - 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 dihalogen isopropyl phenylcyanoacrylates

The dihalogen ring-substituted isopropyl phenylcyanoacrylates (IPCA) were synthesized by Knoevenagel condensation (8) of a ring-substituted benzaldehyde with isopropyl cyanoacetate, catalyzed by base, piperidine.



Where R is 2,5-dibromo, 3,5-dibromo, 2,3-dichloro, 2,4-dichloro, 2,5-dichloro, 2,6-dichloro, 3,4-dichloro, 3,5-dichloro, 2,4-difluoro, 2,5-difluoro, 2,6-difluoro. The preparation procedure was essentially the same for all the monomers. In a typical synthesis, equimolar amounts of isopropyl cyanoacetate and an appropriate dihalogen 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. Isopropyl 3-(2,5-dibromophenyl)-2-cyanoacrylate

Yield 73; mp 93.9°C, $^1\text{H-NMR}$ δ 8.5 (s, 1H, CH=), 8.3-7.3 (m, 3H, Ph), 5.3 (m, 1H, OCH), 1.3 (d, 6H, CH₃); $^{13}\text{C-NMR}$ δ 166 (C=O), 152 (HC=), 137, 135, 122 (Ph), 116 (CN), 138 (C=), 68 (OCH), 22 (CH₃); IR (cm⁻¹): 3102-2834 (m, C-H), 2236 (m, CN), 1725 (s, C=O), 1585 (s, C=C), 1278 (s, C-O-C), 892, 775 (s, C-H out of plane). Anal. Calcd. for C₁₃H₁₁Br₂NO₂: C, 41.86; H, 2.97; N, 3.75; Found: C, 39.64; H, 2.87; N, 3.27.

2.3.2. Isopropyl 3-(3,5-dibromophenyl)-2-cyanoacrylate

Yield 87; mp 134.6°C, $^1\text{H-NMR}$ δ 8.5 (s, 1H, CH=), 8.4-7.0 (m, 3H, Ph), 5.2 (m, 1H, OCH), 1.4 (d, 6H, CH₃); $^{13}\text{C-NMR}$ δ 166 (C=O), 151 (HC=), 138, 135, 121 (Ph), 116 (CN), 137 (C=), 71 (OCH), 22 (CH₃); IR (cm⁻¹): 3126-2811 (m, C-H), 2226 (m, CN), 1744 (s, C=O), 1597 (s, C=C), 1256 (s, C-O-C), 892, 771 (s, C-H out of plane). Anal. Calcd. for C₁₃H₁₁Br₂NO₂: C, 41.86; H, 2.97; N, 3.75; Found: C, 41.54; H, 2.99; N, 3.63.

2.3.3. Isopropyl 3-(2,3-dichlorophenyl)-2-cyanoacrylate

Yield 79; mp 69.3°C, $^1\text{H-NMR}$ δ 8.6 (s, 1H, CH=), 8.2-7.3 (m, 3H, Ph), 5.2 (m, 1H, OCH), 1.4 (d, 6H, CH₃); $^{13}\text{C-NMR}$ δ 163 (C=O), 150 (HC=), 137, 136, 129, 128 (Ph), 116 (CN), 104 (C=), 68 (OCH), 22 (CH₃); IR (cm⁻¹): 3126-2812 (m, C-H), 2229 (m, CN),

1725 (s, C=O), 1592 (s, C=C), 1267 (s, C-O-C), 892, 778 (s, C-H out of plane). Anal.

Calcd. for C₁₃H₁₁Cl₂NO₂: C, 54.95; H, 3.90; N, 4.93; Found: C, 54.54; H, 4.14; N, 5.20.

2.3.4. Isopropyl 3-(2,4-dichlorophenyl)-2-cyanoacrylate

Yield 84; mp 100.8°C, ¹H-NMR δ 8.6 (s, 1H, CH=), 8.3-7.3 (m, 3H, Ph), 5.2 (m, 1H,

OCH), 1.4 (d, 6H, CH₃); ¹³C-NMR δ 166 (C=O), 150 (HC=), 133, 131, 129, 128 (Ph),

116 (CN), 103 (C=), 67 (OCH), 22 (CH₃); IR (cm⁻¹): 3128-2811 (m, C-H), 2237 (m, CN),

1725 (s, C=O), 1598 (s, C=C), 1268 (s, C-O-C), 898, 771 (s, C-H out of plane). Anal.

Calcd. for C₁₃H₁₁Cl₂NO₂: C, 54.95; H, 3.90; N, 4.93; Found: C, 54.58; H, 3.95; N, 4.79.

2.3.5. Isopropyl 3-(2,5-dichlorophenyl)-2-cyanoacrylate

Yield 72; mp 71.4°C, ¹H-NMR δ 8.6 (s, 1H, CH=), 8.2-7.4 (m, 3H, Ph), 5.2 (m, 1H,

OCH), 1.3 (d, 6H, CH₃); ¹³C-NMR δ 161 (C=O), 150 (HC=), 134, 132, 129, 127 (Ph),

116 (CN), 108 (C=), 71 (OCH), 22 (CH₃); IR (cm⁻¹): 3225-2811 (m, C-H), 2226 (m, CN),

1726 (s, C=O), 1587 (s, C=C), 1281 (s, C-O-C), 932, 812 (s, C-H out of plane). Anal.

Calcd. for C₁₃H₁₁Cl₂NO₂: C, 54.95; H, 3.90; N, 4.93; Found: C, 53.04; H, 4.17; N, 5.27.

2.3.6. Isopropyl 3-(2,6-dichlorophenyl)-2-cyanoacrylate

Yield 91; mp 70.9°C, ¹H-NMR δ 8.7 (s, 1H, CH=), 7.9-6.9 (m, 3H, Ph), 5.1 (m, 1H,

OCH), 1.3 (d, 6H, CH₃); ¹³C-NMR δ 166 (C=O), 150 (HC=), 133, 132, 129, 128 (Ph),

116 (CN), 107 (C=), 68 (OCH), 22 (CH₃); IR (cm⁻¹): 3124-2818 (m, C-H), 2231 (m, CN),

1705 (s, C=O), 1596 (s, C=C), 1268 (s, C-O-C), 894, 779 (s, C-H out of plane). Anal.

Calcd. for C₁₃H₁₁Cl₂NO₂: C, 54.95; H, 3.90; N, 4.93; Found: C, 51.63; H, 3.75; N, 4.43.

2.3.7. Isopropyl 3-(3,4-dichlorophenyl)-2-cyanoacrylate

Yield 76; mp 120.3°C, $^1\text{H-NMR}$ δ 8.1(s, 1H, CH=), 8.0-7.5 (m, 3H, Ph), 5.2 (m, 1H, OCH), 1.4 (d, 6H, CH₃); $^{13}\text{C-NMR}$ δ 206 (C=O), 152 (HC=), 134, 131, 129, 127 (Ph), 116 (CN), 103 (C=), 71 (OCH), 22 (CH₃); IR (cm⁻¹): 3104-2813 (m, C-H), 2237 (m, CN), 1725 (s, C=O), 1587 (s, C=C), 1267 (s, C-O-C), 891, 771 (s, C-H out of plane). Anal. Calcd. for C₁₃H₁₁Cl₂NO₂: C, 54.95; H, 3.90; N, 4.93; Found: C, 53.15; H, 3.91; N, 4.57.

2.3.8. Isopropyl 3-(3,5-dichlorophenyl)-2-cyanoacrylate

Yield 89; mp 128.5°C, $^1\text{H-NMR}$ δ 8.1 (s, 1H, CH=), 7.9-7.4 (m, 3H, Ph), 5.2 (m, 1H, OCH), 1.4 (d, 6H, CH₃); $^{13}\text{C-NMR}$ δ 162 (C=O), 152 (HC=), 137, 135, 133, 129 (Ph), 116 (CN), 107 (C=), 72 (OCH), 22 (CH₃); IR (cm⁻¹): 3124-2818 (m, C-H), 2231 (m, CN), 1705 (s, C=O), 1596 (s, C=C), 1268 (s, C-O-C), 894, 779 (s, C-H out of plane). Anal. Calcd. for C₁₃H₁₁Cl₂NO₂: C, 54.95; H, 3.90; N, 4.93; Found: C, 53.14; H, 3.84; N, 4.76.

2.3.9. Isopropyl 3-(2,4-difluorophenyl)-2-cyanoacrylate

Yield 82; mp 73.1°C, $^1\text{H-NMR}$ δ 8.4 (s, 1H, CH=), 7.1-6.7 (m, 3H, Ph), 5.2 (m, 1H, OCH), 1.4 (d, 6H, CH₃); $^{13}\text{C-NMR}$ δ 165 (C=O), 156 (HC=), 145, 131, 129, 127 (Ph), 117 (CN), 104 (C=), 72 (OCH), 22 (CH₃); IR (cm⁻¹): 3122-2816 (m, C-H), 2237 (m, CN), 1727 (s, C=O), 1612 (s, C=C), 1286 (s, C-O-C), 874, 727 (s, C-H out of plane). Anal. Calcd. for C₁₃H₁₁F₂NO₂: C, 62.15; H, 4.41; N, 5.58; Found: C, 60.17; H, 4.72; N, 5.67.

2.3.10. Isopropyl 3-(2,5-difluorophenyl)-2-cyanoacrylate

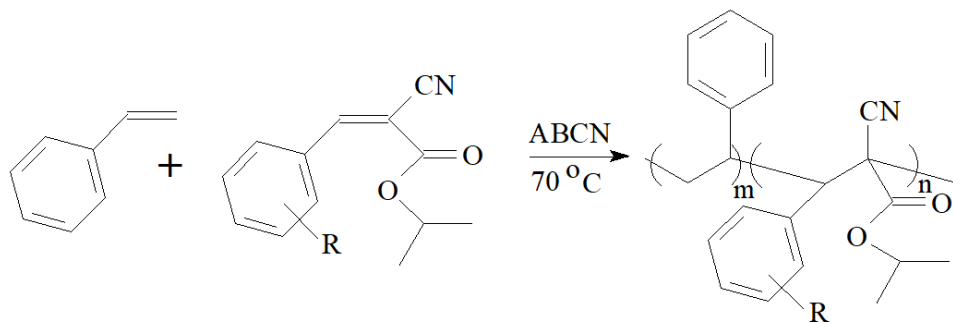
Yield 88; mp 58.9°C, $^1\text{H-NMR}$ δ 8.5 (s, 1H, CH=), 7.9-7.1 (m, 3H, Ph), 5.2 (m, 1H, OCH), 1.2 (d, 6H, CH₃); $^{13}\text{C-NMR}$ δ 163 (C=O), 151 (HC=), 137, 135, 127, 126 (Ph), 116 (CN), 104 (C=), 72 (OCH), 21 (CH₃); IR (cm⁻¹): 3146-2810 (m, C-H), 2236 (m, CN),

1715 (s, C=O), 1591 (s, C=C), 1261 (s, C-O-C), 892, 774 (s, C-H out of plane). Anal.

Calcd. for C₁₃H₁₁F₂NO₂: C, 62.15; H, 4.41; N, 5.58; Found: C, 60.69; H, 4.27; N, 5.51.

2.4. Copolymerization

Copolymers of the ST and the IPCA monomers were prepared in 25-mL glass screw cap vials at ST/ IPCA = 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 70°C. 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. The copolymers' yield was kept low to minimize copolymer compositional drift at given conversion.



Sch. 1. ST-IPCA copolymer synthesis, R = 2,5-dibromo, 3,5-dibromo, 2,3-dichloro, 2,4-dichloro, 2,5-dichloro, 2,6-dichloro, 3,4-dichloro, 3,5-dichloro, 2,4-difluoro, 2,5-difluoro, 2,6-difluoro.

2.4.1. ST- Isopropyl 3-(2,5-dibromophenyl)-2-cyanoacrylate Copolymer

Yield 14.6%; $^1\text{H-NMR}$ δ 7.8-6.5 (Ph), 5.2-4.9 (OCH), 3.8-2.8 (CHPh), 2.6-2.2 (CH, IPCA), 1.7-1.2 (CH_2), 1.4-1.2 (CH_3); $^{13}\text{C-NMR}$ δ 167-161 (C=O), 147-124 (Ph), 118-116 (CN), 76-71 (OCH), 46-35 (CH_2), 43-37 (CHPh, ST), 36-32 (CH, IPCA), 24-21 (CH_3); IR (cm^{-1}): 3845-2811 (m, C-H), 2243 (m, CN), 1738 (s, C=O), 1117 (s, C-O-C), 813, 747 (s, C-H out of plane). Anal. for N (wt%) 2.43.

2.4.2. ST- Isopropyl 3-(3,5-dibromophenyl)-2-cyanoacrylate Copolymer

Yield 13.8%; $^1\text{H-NMR}$ δ 7.9-6.4 (Ph), 5.1-4.8 (OCH), 3.7-2.7 (CHPh), 2.5-2.1 (CH, IPCA), 1.6-1.3 (CH_2), 1.3-1.1 (CH_3); $^{13}\text{C-NMR}$ δ 166-162 (C=O), 149-122 (Ph), 117-116 (CN), 75-72 (OCH), 45-33 (CH_2), 43-36 (CHPh, ST), 35-32 (CH, IPCA), 25-22 (CH_3); IR (cm^{-1}): 3802-2812 (m, C-H), 2239 (m, CN), 1742 (s, C=O), 1246 (s, C-O-C), 828, 746 (s, C-H out of plane). Anal. for N (wt%) 2.26.

2.4.3. ST- Isopropyl 3-(2,3-dichlorophenyl)-2-cyanoacrylate Copolymer

Yield 11.4%; $^1\text{H-NMR}$ δ 7.8-6.5 (Ph), 5.2-4.8 (OCH), 3.7-2.8 (CHPh), 2.5-2.2 (CH, IPCA), 1.7-1.2 (CH_2), 1.4-1.2 (CH_3); $^{13}\text{C-NMR}$ δ 167-161 (C=O), 147-123 (Ph), 118-116 (CN), 76-71 (OCH), 46-35 (CH_2), 43-37 (CHPh, ST), 36-32 (CH, IPCA), 24-21 (CH_3); IR (cm^{-1}): 3802-2812 (m, C-H), 2235 (m, CN), 1742 (s, C=O), 1247 (s, C-O-C), 823, 74 (s, C-H out of plane). Anal. for N (wt%) 2.92.

2.4.4. ST- Isopropyl 3-(2,4-dichlorophenyl)-2-cyanoacrylate Copolymer

Yield 12.6%; $^1\text{H-NMR}$ δ 7.8-6.5 (Ph), 5.2-4.9 (OCH), 3.8-2.8 (CHPh), 2.6-2.2 (CH, IPCA), 1.7-1.2 (CH_2), 1.4-1.2 (CH_3); $^{13}\text{C-NMR}$ δ 167-161 (C=O), 147-124 (Ph), 118-

116 (CN), 76-71 (OCH), 46-35 (CH₂), 43-37 (CHPh, ST), 36-32 (CH, IPCA), 24-21 (CH₃); IR (cm⁻¹): 3802-2812 (m, C-H), 2235 (m, CN), 1742 (s, C=O), 1247 (s, C-O-C), 823, 74 (s, C-H out of plane). Anal. for N (wt%) 3.24.

2.4.5. *ST- Isopropyl 3-(2,5-dichlorophenyl)-2-cyanoacrylate Copolymer*

Yield 14.2%; ¹H-NMR δ 7.9-6.7 (Ph), 5.4-4.9 (OCH), 3.9-2.8 (CHPh), 2.7-2.2 (CH, IPCA), 1.8-1.2 (CH₂), 1.4-1.1 (CH₃); ¹³C-NMR δ 169-166 (C=O), 149-124 (Ph), 118-116 (CN), 76-72 (OCH), 46-34 (CH₂), 43-36 (CHPh, ST), 36-32 (CH, IPCA), 24-22 (CH₃); IR (cm⁻¹): 3823-2842 (m, C-H), 2239 (m, CN), 1734 (s, C=O), 1267 (s, C-O-C), 829, 788 (s, C-H out of plane). Anal. for N (wt%) 2.76.

2.4.6. *ST- Isopropyl 3-(2,6-dichlorophenyl)-2-cyanoacrylate Copolymer*

Yield 12.3%; ¹H-NMR δ 8.0-6.5 (Ph), 5.2-4.9 (OCH), 3.8-2.8 (CHPh), 2.6-2.2 (CH, IPCA), 1.7-1.2 (CH₂), 1.4-1.2 (CH₃); ¹³C-NMR δ 167-161 (C=O), 147-124 (Ph), 118-116 (CN), 76-71 (OCH), 46-35 (CH₂), 43-37 (CHPh, ST), 36-32 (CH, IPCA), 24-21 (CH₃); IR (cm⁻¹): 3802-2812 (m, C-H), 2235 (m, CN), 1742 (s, C=O), 1247 (s, C-O-C), 823, 74 (s, C-H out of plane). Anal. for N (wt%) 1.91.

2.4.7. *ST- Isopropyl 3-(3,4-dichlorophenyl)-2-cyanoacrylate Copolymer*

Yield 13.3%; ¹H-NMR δ 7.8-6.5 (Ph), 5.2-4.9 (OCH), 3.8-2.8 (CHPh), 2.6-2.2 (CH, IPCA), 1.7-1.2 (CH₂), 1.4-1.2 (CH₃); ¹³C-NMR δ 167-161 (C=O), 147-124 (Ph), 118-116 (CN), 76-71 (OCH), 46-35 (CH₂), 43-37 (CHPh, ST), 36-32 (CH, IPCA), 24-21 (CH₃); IR (cm⁻¹): 3802-2812 (m, C-H), 2235 (m, CN), 1742 (s, C=O), 1247 (s, C-O-C), 823, 742 (s, C-H out of plane). Anal. for N (wt%) 2.88.

2.4.8. ST- Isopropyl 3-(3,5-dichlorophenyl)-2-cyanoacrylate Copolymer

Yield 11.7%; $^1\text{H-NMR}$ δ 7.9-6.5 (Ph), 5.3-4.8 (OCH), 3.9-2.8 (CHPh), 2.6-2.1 (CH, IPCA), 1.6-1.1 (CH_2), 1.3-1.0 (CH_3); $^{13}\text{C-NMR}$ δ 166-162 (C=O), 149-124 (Ph), 117-116 (CN), 75-71 (OCH), 46-34 (CH_2), 44-37 (CHPh, ST), 36-33 (CH, IPCA), 24-22 (CH_3); IR (cm^{-1}): 3832-2819 (m, C-H), 2239 (m, CN), 1738 (s, C=O), 1242 (s, C-O-C), 828, 747 (s, C-H out of plane). Anal. for N (wt%) 2.27.

2.4.9. ST- Isopropyl 3-(2,4-difluorophenyl)-2-cyanoacrylate Copolymer

Yield 14.8%; $^1\text{H-NMR}$ δ 7.8-6.4 (Ph), 5.2-4.9 (OCH), 3.8-2.7 (CHPh), 2.7-2.2 (CH, IPCA), 1.7-1.2 (CH_2), 1.4-1.2 (CH_3); $^{13}\text{C-NMR}$ δ 168-162 (C=O), 147-124 (Ph), 118-116 (CN), 76-71 (OCH), 46-35 (CH_2), 43-37 (CHPh, ST), 36-32 (CH, IPCA), 24-21 (CH_3); IR (cm^{-1}): 3842-2810 (m, C-H), 2243 (m, CN), 1747 (s, C=O), 1245 (s, C-O-C), 822, 721 (s, C-H out of plane). Anal. for N (wt%) 2.82.

2.4.10. ST- Isopropyl 3-(2,5-difluorophenyl)-2-cyanoacrylate Copolymer

Yield 12.8%; $^1\text{H-NMR}$ δ 7.8-6.5 (Ph), 5.2-4.9 (OCH), 3.8-2.8 (CHPh), 2.6-2.2 (CH, IPCA), 1.7-1.2 (CH_2), 1.4-1.2 (CH_3); $^{13}\text{C-NMR}$ δ 167-161 (C=O), 147-124 (Ph), 118-116 (CN), 76-71 (OCH), 46-35 (CH_2), 43-37 (CHPh, ST), 36-32 (CH, IPCA), 24-21 (CH_3); IR (cm^{-1}): 3802-2812 (m, C-H), 2235 (m, CN), 1742 (s, C=O), 1247 (s, C-O-C), 823, 745 (s, C-H out of plane). Anal. for N (wt%) 2.81.

2.4.11. ST- Isopropyl 3-(2,6-difluorophenyl)-2-cyanoacrylate Copolymer

Yield 12.0%; $^1\text{H-NMR}$ δ 7.9-6.5 (Ph), 5.3-4.8 (OCH), 3.7-2.7 (CHPh), 2.5-2.2 (CH, IPCA), 1.6-1.3 (CH_2), 1.2-1.0 (CH_3); $^{13}\text{C-NMR}$ δ 168-164 (C=O), 146-126 (Ph), 117-

116 (CN), 75-71 (OCH), 46-37 (CH₂), 43-35 (CHPh, ST), 37-33 (CH, IPCA), 23-21 (CH₃); IR (cm⁻¹): 3812-2800 (m, C-H), 2245 (m, CN), 1747 (s, C=O), 1222 (s, C-O-C), 821, 748 (s, C-H out of plane). Anal. for N (wt%) 2.74.

Copolymerization (Sch. 1) of ST and the dihalogen ring-disubstituted IPCA resulted in formation of copolymers (Table 1) with weight-average molecular masses 29.1 to 59.4 kD. According to elemental analysis, between 18.8 and 41.3 mol% of IPCA monomer is present in the copolymers prepared at ST/ IPCA = 3 (mol), which is indicative of relatively high reactivity of the monomers towards ST. The copolymers prepared in the present work are all soluble in ethyl acetate, THF, DMF and CHCl₃ and insoluble in methanol, ethyl ether, and petroleum ether.

The ST- IPCA copolymers are amorphous and show no crystalline DSC endotherm. Results of thermal analysis of ST- IPCA copolymers are presented in Table 1. Information on the degradation of the copolymers was obtained from thermogravimetric analysis.

Decomposition of the copolymers in nitrogen occurred in two steps, first in the 200-500°C range with residue (1-6% wt.), which then decomposed in the 500-800°C range.

3. Conclusions

Novel isopropyl cyanophenylacrylates were prepared and copolymerized with styrene. The compositions of novel copolymers were calculated from nitrogen analysis and the structures were analyzed by IR, H¹ and ¹³C-NMR. The thermal gravimetric analysis indicated that the copolymers decompose in in two steps, first in the 200-500°C range with residue (1-6% wt), which then decomposed in the 500-800°C range.

Table 1. Copolymerization of styrene and dihalogen ring-substituted isopropyl phenyl cyanoacrylates.

						<i>TGA</i>			
R	Yield ^a (wt%)	N (wt%)	m ₂ in copol. (mol%)	M _w (kD)	T _g (°C)	Onset of decomp. (°C)	10 wt% loss (°C)	50 wt% loss (°C)	Residue wt%
2,5-Dibromo	14.6	2.43	33.9	57.7	117	126	280	351	6
3,5-Dibromo	13.8	2.26	29.7	81.7	175	164	276	339	6
2,3-Dichloro	11.4	2.92	34.7	66.5	86	166	276	316	4
2,4-Dichloro	12.6	3.24	41.3	60.7	145	170	281	321	4
2,5-Dichloro	14.2	2.76	31.8	60.7	90	159	276	317	4
2,6-Dchloro	12.3	1.91	18.8	55.3	100	114	272	334	2
3,4-Dichloro	13.3	2.88	34.0	59.8	130	237	255	341	4
3,5-Dichloro	11.7	2.27	23.8	64.5	131	102	277	337	3
2,4-Difluoro	14.8	2.82	29.8	72.1	110	172	289	321	1
2,5-Difluoro	12.8	2.81	29.6	70.1	88	161	276	322	2
2,6-Difluoro	12.0	2.74	28.6	64.9	158	234	281	323	2

^aPolymerization time was 8 h.

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