

# Synthesis and styrene copolymerization of novel ring-disubstituted isopropyl cyanoarylacrylates

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Novel oxy ring-substituted isopropyl 2-cyano-3-arylacrylates,  $RPhCH=C(CN)CO_2CH(CH_3)_2$  (where R is 3,4-dibenzyloxy, 3-benzyloxy-4-methoxy, 4-benzyloxy-3-methoxy, 2,3-methylenedioxy, 3-iodo-4-methoxy, 5-iodo-2-methoxy, 3,4-difluoro, 3,5-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, FTIR,  $^1H$  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 FTIR,  $^1H$  and  $^{13}C$ -NMR. Thermal properties of the copolymers are characterized by DSC and TGA. Decomposition of the copolymers in nitrogen occurred in two steps, first in the 200-500°C range with a residue, which then decomposed in the 500-800°C range.

**Keywords:** cyanoarylacrylates, Knoevenagel condensation, radical copolymerization, styrene copolymers

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## 1. Introduction

Ring-functionalized trisubstituted ethylenes, esters of 2-cyano-3-arylacrylic acid,  $R^1\text{PhCH} = \text{C}(\text{CN})\text{CO}_2\text{R}^2$  have found various applications as functional compounds in organic and polymer synthesis. Thus, 3-methoxy-4-(phenylmethoxy) ( $R^1$ ) ring disubstituted ethyl ( $R^2$ ) ester of 2-cyano-3-arylacrylic acid (ECAA) was prepared by solvent-free microwave enhanced Knoevenagel condensation [1]. Other examples of ECAA applications are as follows, 4-methyl-2,5-bis(phenylmethoxy)-ring substituted ECAA was used in synthesis and oxidation of 3-(2,5-dihydroxyphenyl)propylamines [2]. 3-Benzodioxol-5-yl – ring substituted ECAA in studies of synthesis and antioxidant properties of novel pyrimidine-containing heterocycles [3], antitumor activity of novel pyridine, thiophene and thiazole derivatives [4], and highly enantioselective [4+2] cycloadditions of allenates and dual activated olefins catalyzed by N-acyl aminophosphines [5]. 4-Hydroxy-3,5-diiodophenyl ring-substituted ECAA was used in studies of electron transport inhibition of the cytochrome bc1 complex of rat-liver mitochondria by phenolic uncouplers [6]. 3,5-Difluoro ring-substituted ECAA is reported in studies of catalysis by layered double hydroxide anchored ionic liquids used as amphiphilic heterogeneous catalysts for the Knoevenagel condensation [7], whereas 3,4-difluorophenyl ring-substituted methyl arylcyanoacrylate was involved in synthesis and studies of histamine H2 agonistic activity of arpromidine analogs [8].

Our purposes in studies of new isopropyl cyanoarylacrylates were twofold: (1) to utilize aldol condensation for synthesis of trisubstituted ethylenes (TSE) with a variety of potentially reactive functional groups, and (2) to explore feasibility of conventional radical copolymerization with a commercial monomer styrene. Thus, in continuation of our exploration of novel TSE compounds we have prepared isopropyl oxy ring-substituted 2-cyano-3-arylacrylates, ICAA,  $RPhCH=C(CN)CO_2CH(CH_3)_2$ , where R is 3,4-dibenzyloxy, 3-benzyloxy-4-methoxy, 4-benzyloxy-3-methoxy, 2,3-(methylenedioxy), 3-iodo-4-methoxy, 5-iodo-2-methoxy, 3,4-difluoro, 3,5-difluoro), and explored the feasibility of their copolymerization with styrene. To the best of our knowledge there have been no reports on either synthesis of these compounds, nor their copolymerization with styrene.

## 2. Experimental

### 2.1 Materials

3,4-dibenzyloxy (98%), 3-benzyloxy-4-methoxy (97%), 4-benzyloxy-3-methoxy (98%), 2,3-(methylenedioxy) (97%), 3-iodo-4-methoxy (98%), 5-iodo-2-methoxy (98%), 3,4-difluoro (98%), 3,5-difluoro) (98%) - benzaldehydes, isopropyl cyanoacetate ( $\geq 98.0\%$ ), piperidine (99%), styrene ( $\geq 99\%$ ), 1,1'-azobiscyclohexanecarbonitrile (98%), (ABCN), and toluene (98%) supplied from Sigma-Aldrich Co., were used as received.

### 2.2 Instrumentation

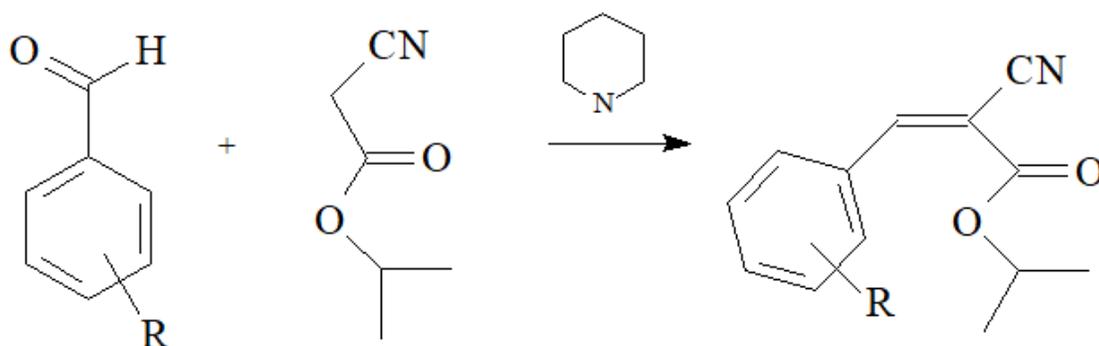
Infrared spectra of the ICAA compounds and polymers (KBr plates) were determined with an ABB FTLA 2000 FTIR spectrometer. The melting points of the ICAA compounds and the glass transition temperatures ( $T_g$ ), of the copolymers were measured with TA (Thermal Analysis, Inc.)

Model Q10 differential scanning calorimeter (DSC). The thermal scans were performed in a 25 to 150°C range on second heat 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 in the flow of nitrogen (20 mL/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 $\mu$  Linear column at 25°C and Viscotek 302 RI detector.  $^1\text{H}$  and  $^{13}\text{C}$ -NMR spectra were obtained on 10-25% (w/v) ICAA or polymer solutions in  $\text{CDCl}_3$  at ambient temperature using Bruker Avance 300 MHz spectrometer. Elemental analyses of ICAA compounds and the copolymers were performed by Midwest Microlab, LLC (IN).

### 3. Results and discussion

#### 3.1 Synthesis and characterization of isopropyl 2-cyano-3-arylacrylates

All isopropyl 2-cyano-3-arylacrylates (ICAA) were synthesized by were synthesized by Knoevenagel condensation [9] of appropriate benzaldehydes with isopropyl cyanoacetate, catalyzed by base, piperidine (Scheme 1).



**Scheme 1:** Synthesis of isopropyl 2-cyano-3-(R-aryl)acrylates where R is 3,4-dibenzyloxy, 3-benzyloxy-4-methoxy, 4-benzyloxy-3-methoxy, 2,3-methylenedioxy, 3-iodo-4-methoxy, 5-iodo-2-methoxy, 3,4-difluoro, 3,5-difluoro).

The preparation procedure was essentially the same for all the compounds. In a typical synthesis, equimolar amounts of isopropyl cyanoacetate and an appropriate 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. Melting points of the compounds in crystalline state were measured by DSC. The compounds were characterized by FTIR,  $^1\text{H}$  and  $^{13}\text{C}$ -NMR spectroscopies. No stereochemical analysis of the novel oxy ring-substituted ICPP was performed since no stereoisomers (*E* or/and *Z*) of known configuration were available.

### 3.1.1 Isopropyl 2-cyano-3-(3,4-dibenzyloxyaryl)acrylate

Yield 97%; mp 117°C;  $^1\text{H}$ -NMR:  $\delta$  8.1 (s, 1H, CH=), 8.0-6.9 (m, 13H, Ph), 5.2 (m, 1H, CH), 5.1 (s, 2H, CH<sub>2</sub>), 1.4 (d, 6H, CH<sub>3</sub>);  $^{13}\text{C}$ -NMR:  $\delta$  164 (C=O), 156 (HC=), 158, 157, 132, 130, 127, 123, 118, 114 (Ph), 116 (CN), 100 (C=), 72 (OCH), 31 (CH<sub>2</sub>), 22 (CH<sub>3</sub>); FTIR: (cm<sup>-1</sup>) 3021-2846 (m, C-H), 2226 (m, CN), 1724 (s, C=O), 1534 (C=C), 1263 (s, C-O-CH<sub>3</sub>), 824 (s, C-H out of plane). Anal. calcd. for C<sub>27</sub>H<sub>25</sub>NO<sub>4</sub>: C, 75.86; H, 5.89; N, 3.28; Found: C, 74.48; H, 5.92; N, 3.20.

### 3.1.2 Isopropyl 2-cyano-3-(3-benzyloxy-4-methoxyaryl)acrylate

Yield: 82%; mp 132.2°C;  $^1\text{H-NMR}$ :  $\delta$  8.1 (s, 1H, CH=), 7.8-6.8 (m, 8H, Ph), 5.2 (m, 1H, CH), 5.1 (s, 2H, CH<sub>2</sub>), 4.0 (s, 3H, OCH<sub>3</sub>), 1.4 (d, 6H, CH<sub>3</sub>);  $^{13}\text{C-NMR}$ :  $\delta$  164 (C=O), 154 (HC=), 157, 156, 131, 130, 125, 123, 118 (Ph), 116 (CN), 103 (C=), 71 (OCH), 58 (OCH<sub>3</sub>), 22 (CH<sub>3</sub>); FTIR: (cm<sup>-1</sup>) 3052-2865 (m, C-H), 2218 (m, CN), 1717 (s, C=O), 1253 (s, C-O-CH<sub>3</sub>), 767, 727 (s, C-H out of plane). Anal. calcd. for C<sub>21</sub>H<sub>21</sub>NO<sub>4</sub>: C, 71.78; H, 6.02; N, 3.99; Found: C, 71.14; H, 6.24; N, 3.83.

### 3.1.3 Isopropyl 2-cyano-3-(4-benzyloxy-3-methoxyaryl)acrylate

Yield 87%; mp 137.5°C;  $^1\text{H-NMR}$   $\delta$  8.2 (s, 1H, CH=), 7.8-6.8 (m, 9H, Ph), 5.3 (s, 2H, OCH<sub>2</sub>), 5.1 (m, 1H, CH), 4.0 (s, 3H, OCH<sub>3</sub>), 1.4 (d, 6H, CH<sub>3</sub>);  $^{13}\text{C-NMR}$   $\delta$  166 (C=O), 154 (HC=), 152, 137, 131, 130, 129, 128, 127, 122, 112 (Ph), 116 (CN), 103 (C=), 68 (OCH), 55 (OCH<sub>3</sub>), 22 (CH<sub>3</sub>); FTIR (cm<sup>-1</sup>): 3065-2758 (m, C-H), 2219 (m, CN), 1717 (s, C=O), 1576 (s, C=C), 1257 (s, C-O-CH<sub>3</sub>), 833, 762 (s, C-H out of plane). Anal. Calcd. for C<sub>21</sub>H<sub>21</sub>NO<sub>4</sub>: C, 71.77; H, 6.04; N, 3.99; Found: C, 69.75; H, 6.09; N, 4.03.

### 3.1.4 Isopropyl 2-cyano-3-3-(2,3-methylenedioxyaryl)acrylate

Yield 82%; mp 163°C,  $^1\text{H-NMR}$   $\delta$  8.4 (s, 1H, CH=), 7.9-6.9 (m, 9H, Ph), 6.1 (s, 2H, CH<sub>2</sub>), 5.3 (m, 1H, CH), 1.3 (d, 6H, CH<sub>3</sub>);  $^{13}\text{C-NMR}$   $\delta$  162 (C=O), 149 (HC=), 148, 147, 124, 120, 114 (Ph), 116 (CN), 101 (C=), 102 (CH<sub>2</sub>), 72 (CH), 22 (CH<sub>3</sub>); FTIR (cm<sup>-1</sup>): 3192-2826 (m, C-H), 2222 (m, CN), 1724 (s, C=O), 1558 (s, C=C), 1276 (s, C-O-CH<sub>3</sub>), 775, 723 (s, C-H out of plane). Anal. Calcd. for C<sub>14</sub>H<sub>13</sub>NO<sub>4</sub>: C, 64.86; H, 5.05; N, 5.40; Found: C, 64.61; H, 5.21; N, 5.24.

### 3.1.5 Isopropyl 2-cyano-3-(3-iodo-4-methoxyaryl)acrylate

Yield 86%; mp 142°C;  $^1\text{H-NMR}$   $\delta$  8.3 (s, 1H, CH=), 8.3-6.9 (m, 3H, Ph), 5.3 (m, 1H, CH), 4.0 (s, 3H, OCH<sub>3</sub>), 1.4 (d, 2H, CH<sub>3</sub>);  $^{13}\text{C-NMR}$   $\delta$  162 (C=O), 153 (HC=), 143, 133, 129, 88 (Ph), 116 (CN), 103 (C=), 72 (CH), 57 (OCH<sub>3</sub>), 22 (CH<sub>3</sub>); FTIR (cm<sup>-1</sup>): 3152-2824 (m, C-H), 2220 (m, CN), 1715 (s, C=O), 1276 (s, C-O-CH<sub>3</sub>), 814, 760 (s, C-H out of plane). Anal. Calcd. for C<sub>14</sub>H<sub>14</sub>INO<sub>3</sub>: C, 45.30; H, 3.80; N, 3.77; Found: C, 44.01; H, 3.93; N, 3.85.

### 3.1.6 Isopropyl 2-cyano-3-(5-iodo-2-methoxyaryl)acrylate

Yield 78%; mp 119°C;  $^1\text{H-NMR}$   $\delta$  8.7 (s, 1H, CH=), 8.6-6.7 (m, 3H, Ph), 5.2 (m, 1H, CH), 4.0 (s, 3H, OCH<sub>3</sub>), 1.3 (d, 6H, CH<sub>3</sub>);  $^{13}\text{C-NMR}$   $\delta$  159 (C=O), 154 (HC=), 147, 142, 87 (Ph), 116 (CN), 97 (C=), 71 (CH), 56 (OCH<sub>3</sub>), 22 (CH<sub>3</sub>); FTIR (cm<sup>-1</sup>): 3200-2800 (m, C-H), 2222 (m, CN), 1763 (s, C=O), 1593 (C=C), 1271 (s, C-O-CH<sub>3</sub>), 872, 910 (s, C-H out of plane). Anal. Calcd. for C<sub>14</sub>H<sub>14</sub>INO<sub>4</sub>: C, 45.30; H, 3.80; N, 3.77; Found: C, 43.72; H, 3.74; N, 3.45.

### 3.1.7 Isopropyl 2-cyano-3-(3,4-difluoroaryl)acrylate

Yield 91%; mp 116°C;  $^1\text{H-NMR}$   $\delta$  8.1 (s, 1H, CH=), 8.0-7.0 (m, 3H, Ph), 5.2 (m, 1H, CH), 1.4 (d, 2H, CH<sub>3</sub>);  $^{13}\text{C-NMR}$   $\delta$  166 (C=O), 153 (HC=), 150, 130, 118 (Ph), 115 (CN), 103 (C=), 67 (CH), 22 (CH<sub>3</sub>); FTIR (cm<sup>-1</sup>): 3075-2849 (m, C-H), 2223 (m, CN), 1765 (s, C=O), 1626 (C=C), 1281 (s, C-O-CH<sub>3</sub>), 837 (s, C-H out of plane). Anal. Calcd. for C<sub>13</sub>H<sub>11</sub>F<sub>2</sub>NO<sub>2</sub>: C, 62.15; H, 4.41; N, 5.58; Found: C, 62.29; H, 4.11; N, 5.42.

### 3.1.8 Isopropyl 2-cyano-3-(3,5-difluoroaryl)acrylate

Yield 76%; mp 91°C;  $^1\text{H-NMR}$   $\delta$  8.1 (s, 1H, CH=), 7.8 (m, 3H, Ph), 5.3 (m, 1H, CH), 1.4 (d, 6H, CH<sub>3</sub>);  $^{13}\text{C-NMR}$   $\delta$  166 (C=O), 154 (HC=), 158, 142, 131, 129, 125 (Ph), 116 (CN), 104 (C=), 68

(OCH), 22 (CH<sub>3</sub>); FTIR (cm<sup>-1</sup>): 3175-2851 (m, C-H), 2218 (m, CN), 1732 (s, C=O), 1607 (C=C), 1268 (s, C-O-CH<sub>3</sub>), 843 (s, C-H out of plane). Anal. Calcd. for C<sub>13</sub>H<sub>11</sub>F<sub>2</sub>NO<sub>2</sub>: C, 62.15; H, 4.41; N, 5.58; Found: C, 62.09; H, 4.28; N, 5.31.

### 3.2. Synthesis and characterization of styrene – ICAA copolymers

Copolymers of the ST and the ICAA compounds, P(ST-*co*-ICAA) were prepared in 25-mL glass screw cap vials at ST/ICAA=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 (cyano group in ICAA monomers). The compounds were characterized by nitrogen elemental analysis, FTIR, <sup>1</sup>H and <sup>13</sup>C-NMR spectroscopies.

#### 3.2.1 Styrene - isopropyl 2-cyano-3-(3,4-dibenzyloxyaryl)acrylate copolymer

Yield 12%; <sup>1</sup>H-NMR: δ 8.0-6.9 (Ph), 5.2-5.1 (CH), 5.1 (CH<sub>2</sub>), 1.4 (CH<sub>3</sub>); <sup>13</sup>C-NMR: δ 164 (C=O), 158-112 (Ph), 116 (CN), 72-70 (CH), 31-29 (CH<sub>2</sub>), 22-20 (CH<sub>3</sub>); IR: (cm<sup>-1</sup>) 3150-2800 (m, C-H), 2224 (m, CN), 1754 (s, C=O), 1256 (s, C-O-CH<sub>3</sub>), 758-723 (s, C-H out of plane).  
Anal. for N, 2.39.

#### 3.2.2 Styrene - isopropyl 2-cyano-3-(3-benzyloxy-4-methoxyaryl)acrylate copolymer

Yield: 14%; <sup>1</sup>H-NMR: δ 7.8-6.7 (Ph), 5.1-4.9 (CH), 5.0-4.8 (CH<sub>2</sub>), 4.1-3.9 (OCH<sub>3</sub>), 1.3-1.1 (CH<sub>3</sub>); <sup>13</sup>C-NMR: δ 173-168 (C=O), 158-117 (Ph), 118-116 (CN), 72-70 (OCH), 60-34 (CH),

55 (OCH<sub>3</sub>), 37-32 (CH<sub>2</sub>), 25-19 (CH<sub>3</sub>); FTIR: (cm<sup>-1</sup>) 3152-2825 (m, C-H), 2231 (m, CN), 1734 (s, C=O), 1267 (s, C-O-CH<sub>3</sub>), 754, 698 (s, C-H out of plane). Anal. calcd. for N, 2.06.

### 3.2.3 Styrene - isopropyl 2-cyano-3-(4-benzyloxy-3-methoxyaryl)acrylate copolymer

Yield 11%; <sup>1</sup>H-NMR δ 7.8-6.8 (Ph), 5.3-4.8 (CH), 5.0-4.8 (CH<sub>2</sub>), 4.1-3.9 (OCH<sub>3</sub>), 1.3-1.1 (CH<sub>3</sub>); <sup>13</sup>C-NMR: δ 172-166 (C=O), 159-118 (Ph), 118-116 (CN), 68-65 (CH), 55 (OCH<sub>3</sub>), 38-33 (CH<sub>2</sub>), 26-18 (CH<sub>3</sub>); FTIR (cm<sup>-1</sup>): 3105-2851 (m, C-H), 2244 (m, CN), 1738 (s, C=O), 1265 (s, C-O-CH<sub>3</sub>), 754, 698 (s, C-H out of plane). Anal. Calcd. for N, 1.96.

### 3.2.4 Styrene - isopropyl 2-cyano-3-(2,3-methylenedioxyaryl)acrylate copolymer

Yield 12%; <sup>1</sup>H-NMR δ 7.7-6.7 (Ph), 6.2-6.0 (CH<sub>2</sub>), 5.1 (CH), 1.3-1.1 (CH<sub>3</sub>); <sup>13</sup>C-NMR: δ 172-166 (C=O), 159-118 (Ph), 118-116 (CN), 74-64 (OCH, OCH<sub>2</sub>), 61-35 (CH), 38-33 (CH<sub>2</sub>), 26-18 (CH<sub>3</sub>); FTIR (cm<sup>-1</sup>): 3200-2800 (m, C-H), 2240 (m, CN), 1736 (s, C=O), 1261 (s, C-O-CH<sub>3</sub>), 735, 698 (s, C-H out of plane). Anal. Calcd. for N, 2.60.

### 3.2.5 Styrene - isopropyl 2-cyano-3-(3-iodo-4-methoxyaryl)acrylate copolymer

Yield 16%; <sup>1</sup>H-NMR δ 7.9-6.5 (Ph), 5.0-4.9 (CH), 4.1-3.9 (OCH<sub>3</sub>), 1.3-1.0 (CH<sub>3</sub>); <sup>13</sup>C-NMR: δ 173-165 (C=O), 156-119 (Ph), 118-116 (CN), 73-70 (CH), 55 (OCH<sub>3</sub>), 23-19 (CH<sub>3</sub>); FTIR (cm<sup>-1</sup>): 3172-2822 (m, C-H), 2231 (m, CN), 1732 (s, C=O), 1265 (s, C-O-CH<sub>3</sub>), 737, 698 (s, C-H out of plane). Anal. Calcd. for N, 2.23.

### 3.2.6 Styrene - isopropyl 2-cyano-3-(5-iodo-2-methoxyaryl)acrylate copolymer

Yield 16%;  $^1\text{H-NMR}$   $\delta$  7.3-6.5 (Ph), 5.3-4.8 (CH), 4.2-4.0 ( $\text{CH}_3\text{O}$ ), 1.3-1.1 ( $\text{CH}_3$ );  $^{13}\text{C-NMR}$ :  $\delta$  172-165 (C=O), 151-119 (Ph), 117-115 (CN), 72-62 (CH), 57-32 (CH), 36-31 ( $\text{CH}_2$ ), 28-17 ( $\text{CH}_3$ ); FTIR ( $\text{cm}^{-1}$ ): 3200-2800 (m, C-H), 2244 (m, CN), 1736 (s, C=O), 1203 (s, C-O- $\text{CH}_3$ ), 772, 698 (s, C-H out of plane). Anal. Calcd. for N, 2.12.

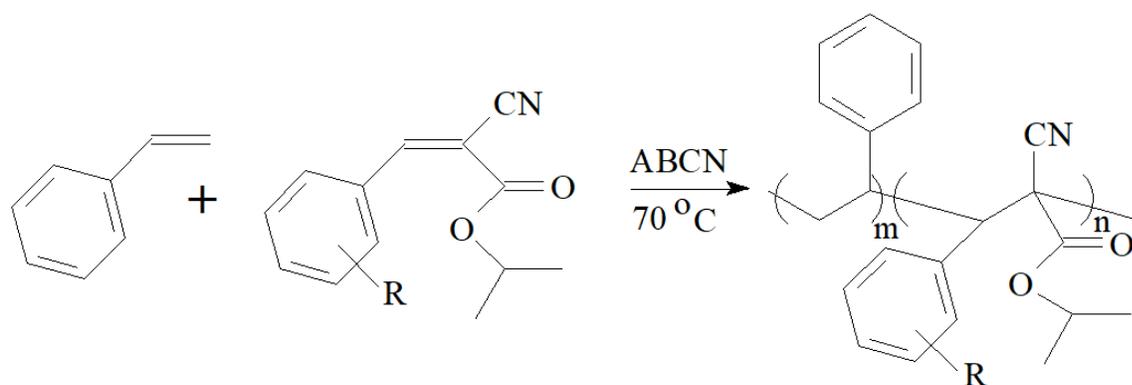
### 3.2.7 Styrene - isopropyl 2-cyano-3-(3,4-difluoroaryl)acrylate copolymer

Yield 12%;  $^1\text{H-NMR}$   $\delta$  7.3-6.7 (Ph), 5.1-4.9 (CH), 1.3-1.1 ( $\text{CH}_3$ );  $^{13}\text{C-NMR}$ :  $\delta$  173-168 (C=O), 151-121 (Ph), 119-116 (CN), 72-62 (CH), 28-17 ( $\text{CH}_3$ ); FTIR ( $\text{cm}^{-1}$ ): 3026-2812 (m, C-H), 2239 (m, CN), 1738 (s, C=O), 1281 (s, C-O- $\text{CH}_3$ ), 697 (s, C-H out of plane). Anal. Calcd. for N, 2.53.

### 3.2.8 Styrene - isopropyl 2-cyano-3-(3,5-difluoroaryl)acrylate copolymer

Yield 13%;  $^1\text{H-NMR}$   $\delta$  7.4-6.8 (Ph), 5.2-4.7 (CH), 1.3-1.0 ( $\text{CH}_3$ );  $^{13}\text{C-NMR}$ :  $\delta$  172-167 (C=O), 152-120 (Ph), 118-116 (CN), 71-62 (CH), 27-17 ( $\text{CH}_3$ ); FTIR ( $\text{cm}^{-1}$ ): 3175-2851 (m, C-H), 2244 (m, CN), 1734 (s, C=O), 1276 (s, C-O- $\text{CH}_3$ ), 908 (s, C-H out of plane). Anal. Calcd. for N, 2.64.

The novel synthesized ICAA compounds copolymerized readily with ST under free-radical conditions (Scheme 2) forming white flaky precipitates when their solutions were poured into methanol. The conversion of the copolymers was kept below 15% to minimize compositional drift (Table 1). Nitrogen elemental analysis showed that between 22 and 29 mol% of ICAA is present in the copolymers prepared at ST/ICAA = 3 (mol), which is indicative of relatively high reactivity of the ICAA monomers towards ST radical. Since ICAA monomers do not homopolymerize, the most likely structure of the copolymers would be short ( $m = 1-4$ ) ST sequences alternating with isolated ICAA monomer units ( $n = 1$ ) (Scheme 2).



**Scheme 2:** Copolymerization of ST and the ring-substituted isopropyl 2-cyano-3-(R-aryl)acrylates. R is 3,4-dibenzyloxy, 3-benzyloxy-4-methoxy, 4-benzyloxy-3-methoxy, 2,3-methylenedioxy, 3-iodo-4-methoxy, 5-iodo-2-methoxy, 3,4-difluoro, 3,5-difluoro.

**Table 1.** Molecular characteristics of P(ST-co-ICAA) copolymers<sup>a</sup>.

R	Nitrogen wt%	% mole ST	% mole ICAA	1/r <sub>1</sub>	M <sub>w</sub> <sup>b</sup> kD
3,4-dibenzyloxy	2.39	76	24	1.39	19.6
3-benzyloxy-4-methoxy	2.06	78	22	1.20	13.5
4-benzyloxy-3-methoxy	1.96	73	27	1.78	20.8
2,3-methylenedioxy	2.60	71	29	2.04	34.2
3-iodo-4-methoxy	2.23	74	26	1.68	18.3
5-iodo-2-methoxy	2.12	74	26	1.57	18.6
3,4-difluoro	2.53	73	27	1.78	15.7
3,5-difluoro	2.64	76	24	1.39	21.2

<sup>a</sup>Conditions: ST/ICAA: 3 (mol) / Toluene / 70°C / 5 hrs. <sup>b</sup>by GPC in THF

The copolymers prepared in the present work are all soluble in ethyl acetate, THF, DMF and CHCl<sub>3</sub> and insoluble in methanol, ethyl ether, and petroleum ether. The molecular weights were measured

by GPC in THF. According to GPC analysis the copolymers had weight-average molecular masses 13.5 to 34.2 kD (Table 1).

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

$$m_1/m_2 = [M_1] (r_1 [M_1] + [M_2]) / [M_2] ([M_1] + r_2 [M_2]) \quad (1)$$

where  $m_1$  and  $m_2$  are mole fractions of ST and ICAA monomer units in the copolymer,  $[M_1]$  and  $[M_2]$  are concentrations of ST and an ICAA in the monomer feed, and  $r_1$  and  $r_2$  are monomer reactivity ratios,  $r_1 = k_{ST-ST}/k_{ST-ICAA}$  and  $r_2 = k_{ICAA-ICAA}/k_{ICAA-ST}$ . In the absence of self-propagation of ICAA monomers ( $k_{ICAA-ICAA} = 0$ ,  $r_2 = 0$ ), the Eq. 1 yields

$$m_1/m_2 = r_1 ([M_1]/[M_2]) + 1 \quad (2)$$

Equation 2 assumes a minimal copolymer compositional drift during a copolymerization reaction, i.e., a low conversion. The fact that ICAA monomers do not self-propagate allows the use of Eq. 2 for a single-point estimation of the relative reactivity of ICAA monomers with respect to ST; it is represented by the  $1/r_1 = k_{ST-ICAA}/k_{ST-ST}$  ratio (the rate constant ratio of attaching an ICAA molecule vs. a ST molecule to a ST-ending growing polymer chain). Taking into account that the  $[M_1]/[M_2]$  ratio in all the experiments was equal to 3.0, relative reactivities ( $1/r_1$ ) for the ICAA monomers decrease in the following row R = 3,4-dibenzyloxy (5.80) > 3-iodo-4-methoxy (2.04) > 2,3-methylenedioxy (1.78) = 3,5-difluoro (1.78) > 5-iodo-2-methoxy (1.68) > 3,4-difluoro (1.57) > 3-benzyloxy-4-methoxy (1.39) > 4-benzyloxy-3-methoxy (1.20). These ratios signify that most ICAA monomers are slightly more reactive than styrene in the addition to a ST-ended polymer radical.

### 3.3. Thermal behavior

Thermal transitions of the ST-ICAA copolymers were analyzed by differential scanning calorimetry. All the copolymers were amorphous and show no crystalline DSC endotherm on repeated heating and cooling cycles. The glass transition temperatures  $T_g$  of the copolymers were measured by DSC. The second heating results were obtained in all cases so that the samples become more dry without “thermal memory”. Table 2 shows glass transition values for the ST-ICAA copolymers prepared in this work with no correlation to the size and position of the ICAA ring substitution apparently due to non-uniform composition, monomer unit distribution, and/or molecular weight and MWD. A single  $T_g$  value was observed for all the copolymers with values close or higher than polystyrene (104°C).

**Table 2:** Thermal behavior of P(ST-co-ICAA) copolymers.

R	$T_g$ °C	TGA			
		Onset of decomp., °C	10% wt loss, °C	50% wt loss, °C	Residue at 500 °C, wt%
3,4-dibenzyloxy	65	116	263	319	8
3-benzyloxy-4-methoxy	95	122	294	352	10
4-benzyloxy-3-methoxy	62	125	276	343	9
2,3-methylenedioxy	148	143	292	359	12
3-iodo-4-methoxy	118	127	286	361	10
5-iodo-2-methoxy	162	243	297	350	12
3,4-difluoro	75	21	46	320	2
3,5-difluoro	79	193	253	324	3

Information on thermal stability of the copolymers (Table 2) was obtained from thermogravimetric analysis (Table 2). Decomposition of the copolymers in nitrogen occurred in two steps, first in the 250-500°C range with residue (2-12% wt), which then decomposed in the 500-800°C range. The

decomposition products were not analyzed in this study, and the mechanism has yet to be investigated.

#### **4 Conclusions**

Novel trisubstituted ethylenes, oxy ring-substituted isopropyl 2-cyano-3-arylacrylates 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 two steps, first in the 250-500°C range with residue (2-5% wt), which then decomposed in the 500-800°C range.

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