

# Synthesis and styrene copolymerization of novel fluoro and oxy ring-disubstituted isopropyl phenylcyanoacrylates

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## Abstract

Novel fluoro and oxy ring-disubstituted isopropyl phenylcyanoacrylates,  $RPhCH=C(CN)CO_2CH(CH_3)_2$  (where R is 2-fluoro-3-methoxy, 2-fluoro-4-methoxy, 2-fluoro-5-methoxy, 2-fluoro-6-methoxy, 3-fluoro-4-methoxy, 4-fluoro-3-methoxy, 5-fluoro-2-methoxy, 4-fluoro-3-phenoxy) were prepared and copolymerized with styrene. The monomers were synthesized by the piperidine catalyzed Knoevenagel condensation of ring-substituted benzaldehydes and isopropyl cyanoacetate and characterized by CHN elemental analysis, IR,  $^1H$ - and  $^{13}C$ -NMR. All the ethylenes 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,  $^1\text{H}$  and  $^{13}\text{C}$ -NMR, GPC, DSC, and TGA.

**Keywords:** ring-substituted phenylcyanoacrylates, Knoevenagel condensation, radical copolymerization, styrene copolymers

## 1. Introduction

Halogen and methoxy ring-functionalized esters of phenylcyanoacrylates attract attention as intermediates in synthesis of compounds for biomedical applications (1-4). Thus, 3-bromo-4-methoxy ring-disubstituted phenylcyanoacrylate was used in synthesis of thiazacridine derivatives as anticancer agents (1) and as a cell-active inhibitor of the cancer-promoting phosphatases (2). It also was applied in synthesis and studies of anti-inflammatory activity of new arylidene-thiazolidine-2,4-diones (3), as well as in design, synthesis and antitumor evaluation of novel celastrol derivatives (4).

We have reported synthesis and styrene copolymerization of a number of fluorine and methoxy ring-disubstituted propyl (5) and butyl phenylcyanoacrylates (6, 7). In continuation of research on synthesis and copolymerization of novel isopropyl phenylcyanoacrylates (8, 9) we have prepared fluoro and oxy ring-disubstituted isopropyl phenylcyanoacrylates (IPCA),  $\text{RPhCH}=\text{C}(\text{CN})\text{CO}_2\text{CH}(\text{CH}_3)_2$ , where R is 2-fluoro-3-methoxy, 2-fluoro-4-methoxy, 2-fluoro-5-methoxy, 2-fluoro-6-methoxy, 3-fluoro-4-methoxy, 4-fluoro-3-methoxy, 5-fluoro-2-methoxy, 4-fluoro-3-phenoxy, 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 phenylcyanoacrylates, nor their copolymerization with styrene (10).

## **2. Experimental**

### **2.1. Materials**

2-Fluoro-3-methoxy, 2-fluoro-4-methoxy, 2-fluoro-5-methoxy, 2-fluoro-6-methoxy, 3-fluoro-4-methoxy, 4-fluoro-3-methoxy, 5-fluoro-2-methoxy, 4-fluoro-3-phenoxy benzaldehydes, isopropyl cyanoacetate, piperidine, styrene, 1,1'-azobiscyclohexanecarbonitrile, (ABCN), and toluene supplied from Sigma-Aldrich Co., were used as received.

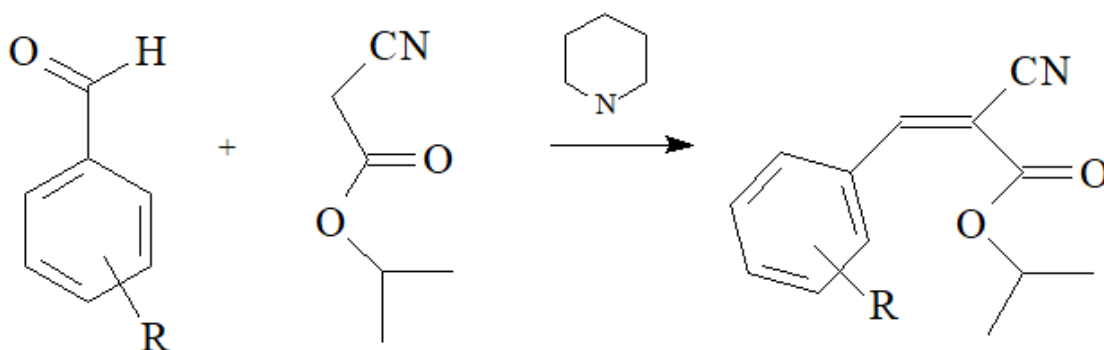
### **2.2. Instrumentation**

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 $\mu$  Linear column at 25°C and Viscotek 302 detector.  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR spectra were obtained on 10-25% (w/v) monomer or polymer solutions in  $\text{CDCl}_3$  at ambient temperature using Avance 300 MHz spectrometer. Elemental analyses were performed by Midwest Microlab, LLC (IN).

### 2.3. Synthesis of isopropyl phenylcyanoacrylates compounds

The ring-substituted isopropyl phenylcyanoacrylates (IPCA) were synthesized by Knoevenagel condensation (11) of a ring-substituted benzaldehyde with isopropyl cyanoacetate, catalyzed by base, piperidine (Sch. 1).



**Sch. 1.** Synthesis of isopropyl phenylcyanoacrylates compounds,

$\text{RPhCH}=\text{C}(\text{CN})\text{CO}_2\text{CH}(\text{CH}_3)_2$ , where R is 2-fluoro-3-methoxy, 2-fluoro-4-methoxy, 2-fluoro-5-methoxy, 2-fluoro-6-methoxy, 3-fluoro-4-methoxy, 4-fluoro-3-methoxy, 5-fluoro-2-methoxy, 4-fluoro-3-phenoxy.

The preparation procedure was essentially the same for all the monomers. In a typical synthesis, equimolar amounts of isopropyl cyanoacetate and an appropriate 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-fluoro-3-methoxyphenyl)-2-cyanoacrylate***

Yield 82%; mp 64.3°C,  $^1\text{H-NMR}$   $\delta$  8.6 (s, 1H, CH=), 7.9-6.7 (m, 3H, Ph), 5.2 (m, 1H, CH), 3.9 (s, 3H, OCH<sub>3</sub>), 1.4 (d, 6H, CH<sub>3</sub>);  $^{13}\text{C-NMR}$   $\delta$  166 (C=O), 146 (HC=), 162, 130, 124, 117 (Ph), 116 (CN), 107 (C=), 71 (OCH), 56 (OCH<sub>3</sub>), 22 (CH<sub>3</sub>); IR (cm<sup>-1</sup>): 3874-2834 (m, C-H), 2226 (m, CN), 1714 (s, C=O), 1587 (s, C=C), 1254 (s, C-O-C), 816, 734 (s, C-H out of plane). Anal. Calcd. for C<sub>14</sub>H<sub>14</sub>FNO<sub>3</sub>: C, 63.87; H, 5.36; N, 5.32; Found: C, 63.31; H, 5.62; N, 6.14.

### ***2.3.2. Isopropyl 3-(2-fluoro-4-methoxyphenyl)-2-cyanoacrylate***

Yield 97%; mp 88.0°C,  $^1\text{H-NMR}$   $\delta$  8.5 (s, 1H, CH=), 6.9-6.5 (m, 3H, Ph), 5.2 (m, 1H, CH), 3.9 (s, 3H, OCH<sub>3</sub>), 1.4 (d, 6H, CH<sub>3</sub>);  $^{13}\text{C-NMR}$   $\delta$  166 (C=O), 147 (HC=), 162, 131, 125, 123, 117, 112 (Ph), 116 (CN), 102 (C=), 71 (OCH), 57 (OCH<sub>3</sub>), 22 (CH<sub>3</sub>); IR (cm<sup>-1</sup>): 3112-2754 (m, C-H), 2222 (m, CN), 1717 (s, C=O), 1543 (s, C=C), 1254 (s, C-O-C), 874, 785 (s, C-H out of plane). Anal. Calcd. for C<sub>14</sub>H<sub>14</sub>FNO<sub>3</sub>: C, 63.87; H, 5.36; N, 5.32; Found: C, 62.87; H, 5.27; N, 4.76.

**2.3.3. Isopropyl 3-(2-fluoro-5-methoxyphenyl)-2-cyanoacrylate**

Yield 87%; mp 83.3°C,  $^1\text{H-NMR}$   $\delta$  8.5 (s, 1H, CH=), 7.9-7.0 (m, 3H, Ph), 5.2 (m, 1H, CH), 3.9 (s, 3H, OCH<sub>3</sub>), 1.4 (d, 6H, CH<sub>3</sub>);  $^{13}\text{C-NMR}$   $\delta$  162 (C=O), 155 (HC=), 144, 123, 120, 117, 114, 111 (Ph), 116 (CN), 105 (C=), 70 (CH), 55 (OCH<sub>3</sub>), 22 (CH<sub>3</sub>); IR (cm<sup>-1</sup>): 3831-2902 (m, C-H), 2223 (m, CN), 1722 (s, C=O), 1621 (s, C=C), 1259 (s, C-O-C), 845, 726 (s, C-H out of plane). Anal. Calcd. for C<sub>14</sub>H<sub>14</sub>FNO<sub>3</sub>: C, 63.87; H, 5.36; N, 5.32; Found: C, 62.67; H, 5.51; N, 5.23.

**2.3.4. Isopropyl 3-(2-fluoro-6-methoxyphenyl)-2-cyanoacrylate**

Yield 88%; mp 42.5°C,  $^1\text{H-NMR}$   $\delta$  8.3 (s, 1H, CH=), 7.6-6.5 (m, 3H, Ph), 5.2 (m, 1H, CH), 4.0 (s, 3H, OCH<sub>3</sub>), 1.4 (d, 6H, CH<sub>3</sub>);  $^{13}\text{C-NMR}$   $\delta$  162 (C=O), 151 (HC=), 159, 146, 133, 122 (Ph), 116 (CN), 107 (C=), 71 (CH), 57 (OCH<sub>3</sub>), 22 (CH<sub>3</sub>); IR (cm<sup>-1</sup>): 3029-2777 (m, C-H), 2227 (m, CN), 1718 (s, C=O), 1576 (s, C=C), 1252 (s, C-O-C), 923, 828 (s, C-H out of plane). Anal. Calcd. for C<sub>14</sub>H<sub>14</sub>FNO<sub>3</sub>: C, 63.87; H, 5.36; N, 5.32; Found: C, 62.13; H, 5.52; N, 5.14.

**2.3.5. Isopropyl 3-(3-fluoro-4-methoxyphenyl)-2-cyanoacrylate**

Yield 82%; mp 102.8°C,  $^1\text{H-NMR}$   $\delta$  8.2 (s, 1H, CH=), 8.0-7.0 (m, 3H, Ph), 5.2 (m, 1H, CH), 4.0 (s, 3H, OCH<sub>3</sub>), 1.4 (d, 6H, CH<sub>3</sub>);  $^{13}\text{C-NMR}$   $\delta$  163 (C=O), 154 (HC=), 146, 132, 128, 127, 124 (Ph), 116 (CN), 101 (C=), 71 (CH), 57 (OCH<sub>3</sub>), 22 (CH<sub>3</sub>); IR (cm<sup>-1</sup>): 3018-2845 (m, C-H), 2224 (m, CN), 1718 (s, C=O), 1559 (s, C=C), 1269 (s, C-O-C), 844, 772 (s, C-H out of plane). Anal. Calcd. for C<sub>14</sub>H<sub>14</sub>FNO<sub>3</sub>: C, 63.87; H, 5.36; N, 5.32; Found: C, 63.23; H, 5.22; N, 5.27.

**2.3.6. Isopropyl 3-(4-fluoro-3-methoxyphenyl)-2-cyanoacrylate**

Yield 76%; mp 99.2°C;  $^1\text{H-NMR}$   $\delta$  8.2 (s, 1H, CH=), 7.9-7.0 (m, 3H, Ph), 5.2 (m, 1H, CH), 4.0 (s, 3H, OCH<sub>3</sub>), 1.4 (d, 6H, CH<sub>3</sub>);  $^{13}\text{C-NMR}$   $\delta$  163 (C=O), 144 (HC=), 138, 130, 128, 126, 125, 121 (Ph), 115 (CN), 103 (C=), 72 (OCH<sub>3</sub>), 57 (CH), 22 (CH<sub>3</sub>); IR (cm<sup>-1</sup>): 3041-2762 (m, C-H), 2222 (m, CN), 1734 (s, C=O), 1621 (s, C=C), 1228 (s, C-O-C), 813, 767 (s, C-H out of plane). Anal. Calcd. for C<sub>14</sub>H<sub>14</sub>FNO<sub>3</sub>: C, 63.87; H, 5.36; N, 5.32; Found: C, 60.85; H, 5.10; N, 5.17.

**2.3.7. Isopropyl 3-(5-fluoro-2-methoxyphenyl)-2-cyanoacrylate**

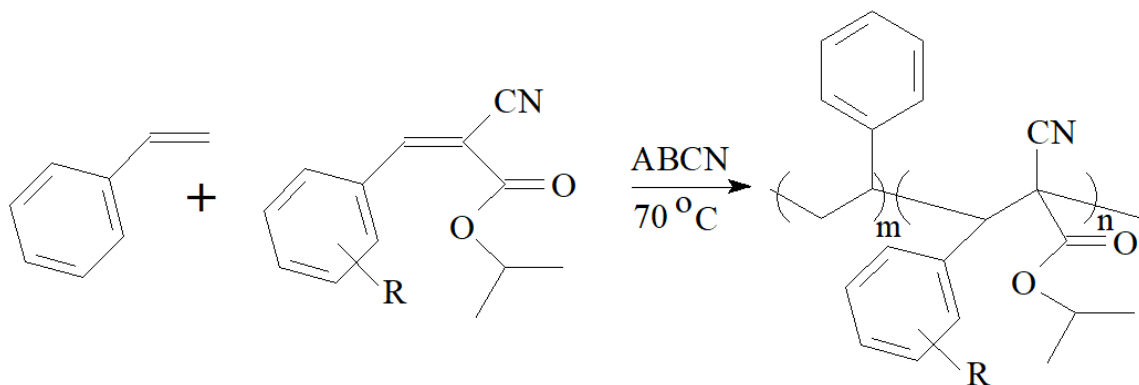
Yield 88%; mp 110.0°C,  $^1\text{H-NMR}$   $\delta$  8.7 (s, 1H, CH=), 8.1-6.8 (m, 3H, Ph), 5.2 (m, 1H, CH), 3.9 (s, 3H, OCH<sub>3</sub>), 1.4 (d, 6H, CH<sub>3</sub>);  $^{13}\text{C-NMR}$   $\delta$  161 (C=O), 152 (HC=), 155, 145, 130, 128, 125 (Ph), 115 (CN), 107 (C=), 71 (CH), 51 (OCH<sub>3</sub>), 22 (CH<sub>3</sub>); IR (cm<sup>-1</sup>): 3098-2787 (m, C-H), 2226 (m, CN), 1741 (s, C=O), 1601 (s, C=C), 1254 (s, C-O-C), 832, 787 (s, C-H out of plane). Anal. Calcd. for C<sub>14</sub>H<sub>14</sub>FNO<sub>3</sub>: C, 63.87; H, 5.36; N, 5.32; Found: C, 62.04; H, 5.58; N, 5.92.

**2.3.8. Isopropyl 3-(4-fluoro-3-phenoxyphenyl)-2-cyanoacrylate**

Yield 84%; mp 76.7°C,  $^1\text{H-NMR}$   $\delta$  8.1 (s, 1H, CH=), 7.8-7.0 (m, 8H, Ph), 5.2 (m, 1H, CH), 1.4 (d, 6H, CH<sub>3</sub>);  $^{13}\text{C-NMR}$   $\delta$  161 (C=O), 154 (HC=), 152, 130, 129, 128, 124, 123, 118 (Ph), 115 (CN), 103 (C=), 71 (CH), 51 (OCH<sub>3</sub>), 21 (CH<sub>3</sub>); IR (cm<sup>-1</sup>): 3027-2813 (m, C-H), 2226 (m, CN), 1724 (s, C=O), 1594 (s, C=C), 1262 (s, C-O-C), 844, 798 (s, C-H out of plane). Anal. Calcd. for C<sub>19</sub>H<sub>16</sub>FNO<sub>3</sub>: C, 70.14; H, 4.96; N, 4.31; Found: C, 69.20; H, 4.82; N, 4.21.

## 2.4. Synthesis of styrene – isopropyl phenylcyanoacrylate copolymers

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. Copolymerization (Sch. 1) of ST and the ring-disubstituted IPCA resulted in formation of copolymers (Table 1) with weight-average molecular masses 38.1 to 46.7 kD.



**Sch. 1.** ST-IPCA copolymer synthesis, R = 2-fluoro-3-methoxy, 2-fluoro-4-methoxy, 2-fluoro-5-methoxy, 2-fluoro-6-methoxy, 3-fluoro-4-methoxy, 4-fluoro-3-methoxy, 5-fluoro-2-methoxy, 4-fluoro-3-phenoxy.

### 2.4.1. ST-Isopropyl 3-(2-fluoro-3-methoxyphenyl)-2-cyanoacrylate



Yield 11.6%;  $^1\text{H-NMR}$   $\delta$  7.8-6.6 (Ph), 5.3-5.1 (OCH), 4.2-3.8 (OCH<sub>3</sub>), 3.9-2.7 (CHPh, ST), 2.7-2.5 (CH, IPCA), 1.6-1.4 (CH<sub>2</sub>), 1.5-1.2 (CH<sub>3</sub>);  $^{13}\text{C-NMR}$   $\delta$  173-169 (C=O), 148-126 (Ph), 122-118 (CN), 78-71 (OCH), 59-54 (OCH<sub>3</sub>), 45-36 (CH<sub>2</sub>), 41-38 (CHPh, ST), 34-31(CH, IPCA), 24-21 (CH<sub>3</sub>); IR (cm<sup>-1</sup>): 3802-2832 (m, C-H), 2236 (m, CN), 1744 (s, C=O), 1258 (s, C-O-C), 822, 746 (s, C-H out of plane). Anal. for N (wt%) 2.91.

#### ***2.4.2. ST-Isopropyl 3-(2-fluoro-4-methoxyphenyl)-2-cyanoacrylate***

Yield 11.2%;  $^1\text{H-NMR}$   $\delta$  7.9-6.7 (Ph), 5.3-5.1 (OCH), 4.2-3.7 (OCH<sub>3</sub>), 3.9-2.8 (CHPh), 2.7-2.4 (CH, IPCA), 1.7-1.4 (CH<sub>2</sub>), 1.5-1.1 (CH<sub>3</sub>);  $^{13}\text{C-NMR}$   $\delta$  169-163 (C=O), 148-127 (Ph), 119-117 (CN), 78-71 (OCH), 59-54 (OCH<sub>3</sub>), 45-35 (CH<sub>2</sub>), 41-37 (CHPh, ST), 34-31 (CH, IPCA), 24-22 (CH<sub>3</sub>); IR (cm<sup>-1</sup>): 3876-2839 (m, C-H), 2234 (m, CN), 1738 (s, C=O), 1252 (s, C-O-C), 825, 749 (s, C-H out of plane). Anal. for N (wt%) 2.36.

#### ***2.4.3. ST-Isopropyl 3-(2-fluoro-5-4-methoxyphenyl)-2-cyanoacrylate***

Yield 10.3%;  $^1\text{H-NMR}$   $\delta$  7.8-6.6 (Ph), 5.2-5.1 (OCH), 4.3-3.7 (OCH<sub>3</sub>), 3.9-2.7 (CHPh), 2.7-2.3 (CH, IPCA), 1.8-1.4 (CH<sub>2</sub>), 1.5-1.2 (CH<sub>3</sub>);  $^{13}\text{C-NMR}$   $\delta$  169-161 (C=O), 148-125 (Ph), 119-116 (CN), 77-71 (OCH), 58-54 (OCH<sub>3</sub>), 45-35 (CH<sub>2</sub>), 42-37 (CHPh, ST), 34-30 (CH, IPCA), 24-21 (CH<sub>3</sub>); IR (cm<sup>-1</sup>): 3883-2845 (m, C-H), 2233 (m, CN), 1742 (s, C=O), 1258 (s, C-O-C), 823, 745 (s, C-H out of plane). Anal. for N (wt%) 2.88.

#### ***2.4.4. ST-Isopropyl 3-(2-fluoro-6-methoxyphenyl)-2-cyanoacrylate***

Yield % 18;  $^1\text{H-NMR}$   $\delta$  7.9-6.6 (Ph), 5.3-5.0 (OCH), 4.3-3.8 (OCH<sub>3</sub>), 3.9-2.6 (CHPh, ST), 2.8-2.5 (CH, IPCA), 1.7-1.4 (CH<sub>2</sub>), 1.6-1.2 (CH<sub>3</sub>);  $^{13}\text{C-NMR}$   $\delta$  174-168 (C=O), 147-126 (Ph), 121-117 (CN), 77-71 (OCH), 58-54 (OCH<sub>3</sub>), 44-34 (CH<sub>2</sub>), 42-38 (CHPh, ST),

35-32(CH, IPCA), 25-20 (CH<sub>3</sub>); IR (cm<sup>-1</sup>): 3817-2821 (m, C-H), 2232 (m, CN), 1741 (s, C=O), 1256 (s, C-O-C), 820, 742 (s, C-H out of plane). Anal. for N (wt%) 2.50.

**2.4.5. Isopropyl 3-(3-fluoro-4-methoxyphenyl)-2-cyanoacrylate**

Yield 17.7%; <sup>1</sup>H-NMR δ 7.8-6.6 (Ph), 5.2-5.0 (OCH), 4.3-3.6 (OCH<sub>3</sub>), 3.8-2.7 (CHPh), 2.8-2.5 (CH, IPCA), 1.6-1.4 (CH<sub>2</sub>), 1.5-1.2 (CH<sub>3</sub>); <sup>13</sup>C-NMR δ 169-163 (C=O), 148-128 (Ph), 118-117 (CN), 78-71 (OCH), 59-54 (OCH<sub>3</sub>), 45-35 (CH<sub>2</sub>), 41-37 (CHPh, ST), 34-31 (CH, IPCA), 24-22 (CH<sub>3</sub>); IR (cm<sup>-1</sup>): 3875-2835 (m, C-H), 2235 (m, CN), 1736 (s, C=O), 1256 (s, C-O-C), 825, 747 (s, C-H out of plane). Anal. for N (wt%) 2.71.

**2.4.6. Isopropyl 3-(4-fluoro-3-methoxyphenyl)-2-cyanoacrylate**

Yield 12.7%; <sup>1</sup>H-NMR δ 7.7-6.6 (Ph), 5.2-4.9 (OCH), 4.2-3.7 (OCH<sub>3</sub>), 3.8-2.7 (CHPh), 2.6-2.2 (CH, IPCA), 1.7-1.4 (CH<sub>2</sub>), 1.4-1.2 (CH<sub>3</sub>); <sup>13</sup>C-NMR δ 167-161 (C=O), 147-124 (Ph), 118-116 (CN), 76-71 (OCH), 59-54 (OCH<sub>3</sub>), 46-35 (CH<sub>2</sub>), 43-37 (CHPh, ST), 36-30 (CH, IPCA), 24-21 (CH<sub>3</sub>); IR (cm<sup>-1</sup>): 3892-2823 (m, C-H), 2237 (m, CN), 1748 (s, C=O), 1245 (s, C-O-C), 828, 748 (s, C-H out of plane). Anal. for N (wt%) 2.62.

**2.4.7. Isopropyl 3-(5-fluoro-2-methoxyphenyl)-2-cyanoacrylate**

Yield % 12.2; <sup>1</sup>H-NMR δ 8.1-6.5 (Ph), 5.2-4.8 (OCH), 4.3-3.7 (OCH<sub>3</sub>), 3.9-2.7 (CHPh, ST), 2.8-2.4 (CH, IPCA), 1.8-1.3 (CH<sub>2</sub>), 1.5-1.3 (CH<sub>3</sub>); <sup>13</sup>C-NMR δ 175-167 (C=O), 146-125 (Ph), 121-117 (CN), 78-71 (OCH), 58-53 (OCH<sub>3</sub>), 43-34 (CH<sub>2</sub>), 42-37 (CHPh, ST), 35-31 (CH, IPCA), 25-20 (CH<sub>3</sub>); IR (cm<sup>-1</sup>): 3823-2829 (m, C-H), 2233 (m, CN), 1743 (s, C=O), 1254 (s, C-O-C), 823, 741 (s, C-H out of plane). Anal. for N (wt%) 2.77.

**2.3.8. Isopropyl 3-(4-fluoro-3-phenoxyphenyl)-2-cyanoacrylate**

Yield 14.1%;  $^1\text{H-NMR}$   $\delta$  7.8-6.5 (Ph), 5.2-4.9 (OCH), 3.8-2.8 (CHPh), 2.6-2.2 (CH, IPCh), 1.7-1.2 ( $\text{CH}_2$ ), 1.4-1.2 ( $\text{CH}_3$ );  $^{13}\text{C-NMR}$   $\delta$  167-161 (C=O), 147-124 (Ph), 118-116 (CN), 76-71 (OCH), 46-35 ( $\text{CH}_2$ ), 43-37 (CHPh, ST), 36-32 (CH, IPCh), 24-21 ( $\text{CH}_3$ ); IR ( $\text{cm}^{-1}$ ): 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%) 2.82.

**Table 1.** Copolymerization of Styrene and Ring-disubstituted isopropyl 3-phenyl 2-cyanoacrylates,  $\text{RPhCH}=\text{C}(\text{CN})\text{CO}_2\text{CH}(\text{CH}_3)$  [ $\text{M}_2$ ].

						TGA			
R	Yield <sup>a</sup> (wt%)	N (wt %)	$m_2$ in copol. (mol %)	$M_w$ (kD)	$T_g$ ( $^{\circ}\text{C}$ )	Onset of decomp. ( $^{\circ}\text{C}$ )	10 wt% loss ( $^{\circ}\text{C}$ )	50 wt% loss ( $^{\circ}\text{C}$ )	Residue at 500 $^{\circ}\text{C}$ wt%
2-F-3- $\text{CH}_3\text{O}$	11.6	2.91	32	38.1	138	253	284	345	5.0
2-F-4- $\text{CH}_3\text{O}$	11.2	2.36	24	42.3	135	252	282	349	4.8
2-F-5- $\text{CH}_3\text{O}$	10.3	2.88	32	42.4	138	249	284	336	4.9
2-F-6- $\text{CH}_3\text{O}$	18.1	2.50	26	45.3	136	250	289	330	3.1
3-F-4- $\text{CH}_3\text{O}$	17.7	2.71	29	43.8	137	249	288	332	3.0
4-F-3- $\text{CH}_3\text{O}$	12.7	2.62	28	41.4	137	253	283	341	5.1
5-F-2- $\text{CH}_3\text{O}$	12.2	2.77	30	39.1	132	250	288	333	3.6
4-F-3-PhO	14.1	2.82	38	46.7	116	251	287	356	3.0

<sup>a</sup>Polymerization time was 8 h.

According to elemental analysis, between 24 and 38 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  $\text{CHCl}_3$  and insoluble in methanol, ethyl ether, and petroleum ether. They are amorphous and show no crystalline DSC endotherm. Results of thermal analysis of 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 (3.0-5.1 % 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, fluorine and oxy ring-disubstituted isopropyl 2 isopropyl phenylcyanoacrylates were prepared and copolymerized with styrene. The compositions of the copolymers were calculated from nitrogen analysis and the structures were analyzed by IR,  $\text{H}^1$  and  $^{13}\text{C}$ -NMR. The thermal gravimetric analysis indicated that the copolymers decompose in in two steps, first in the 200-500°C range with residue, which then decomposed in the 500-800°C range.

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