# Synthesis and styrene copolymerization of novel dimethyl and dimethoxy ring-substituted isobutyl phenylcyanoacrylates

Alessandra Cimino, Ehxciquiel M. Camacho, Samantha M. Evans, Daniela Garza, Dylan A. Gregory, Julia C. Petrescu, Margaux J.E. Rocha, Brian J. Scannell, Katelyn M. Schreck, Mikal Zuljevic, Sara M. Rocus, William S. Schjerven and Gregory B. Kharas

DePaul University, Chemistry and Biochemistry Department, 1110 West Belden Avenue,
Chicago, IL 60614-3214
Contact E-mail: gkharas@depaul.edu

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## ABSTRACT

Novel dimethyl and dimethoxy ring-disubstituted isobutyl phenylcyanoacrylates, $RPhCH=C(CN)CO_2CH_2CH(CH_3)_2$, where R is 2,3-dimethyl, 2,4-dimethyl, 3,5-dimethyl, 2,3-dimethoxy, 2,4-dimethoxy, 2,5-dimethoxy, 2,6-dimethoxy, 3,4-dimethoxy, 3,5-dimethoxy were synthesized by the piperidine catalyzed Knoevenagel condensation of ring-disubstituted benzaldehydes and isobutyl cyanoacetate and characterized by CHN analysis, IR, $^{1}H$ and $^{13}C$ NMR. The acrylates were copolymerized with styrene in solution with radical initiation (ABCN) at 70°C. The compositions of the copolymers were calculated from nitrogen analysis and the structures were analyzed by FTIR, $^1$H and $^{13}$C NMR.

## 1. Introduction

Dimethyl ring-substituted phenylcyanoacrylates (PCA) are reported in a number of applications [1-12]. Thus, 2,3-dimethyl-phenyl ethyl PCA was prepared inside microflow reactor using polymer networks carrying tertiary amine as a catalyst [1], whereas 3,4-dimethyl-phenyl PCA was prepared with amine-functionalized polyacrylonitrile fiber [2]. This PCA was also reported in synthesis of highly substituted isoquinoline derivatives [3], in annulation/oxidation of cyclic amidines with activated olefins [4], and in asymmetric cyclopropanation of 2-cyano-3-arylacrylates with 2-bromomalonates [5]. 2,3-Dimethoxy ring-disubstituted ethyl PCA used in synthesis of pyranoquinoline [6], of polysubstituted cyclopropanes [7], of some derivatives of o-vanillin [8], as well as in microwave enhanced Knoevenagel condensation of ethyl cyanoacetate with aldehydes [9]. 3,4-Dimethoxy-phenyl ring-disubstituted isobutyl PCA was reported in esterification and amide formation via acid-catalyzed dehydration and Ritter reactions [10]. 3,5-Dimethoxy-phenyl methyl PCA was used in synthesis of pyrido[2,1-c]-1,2,4-triazine, 1,2,4-triazolo[4,3-a]pyridine and 2-(substituted-pyrazolyl)nicotinonitrile [11] and in synthesis of dihydrouracils spiro-fused to pyrrolidines [12].

We have reported synthesis and styrene copolymerization a number of dimethyl and dimethoxy ring-disubstituted PCAs, such esters as methyl [13,14], ethyl [15-17], propyl [18, 19], isopropyl [20-22], and butyl [23, 24], 2-methoxyethyl [25], and octyl [26].

In this work we have prepared dimethyl and dimethoxy ring-disubstituted isobutyl PCA, $RPhCH=C(CN)CO_2CH_2CH(CH_3)_2$, where R is 2,3-dimethyl, 2,4-dimethyl, 3,5-dimethyl, 2,3-dimethoxy, 2,4-dimethoxy, 2,5-dimethoxy, 2,6-dimethoxy, 3,4-dimethoxy, 3,5-dimethoxy, and radically copolymerized them with styrene. To the best of our knowledge, there have been no reports (except 3,4-dimethoxy [10]) on either synthesis of these compounds, nor their copolymerization with styrene [27].

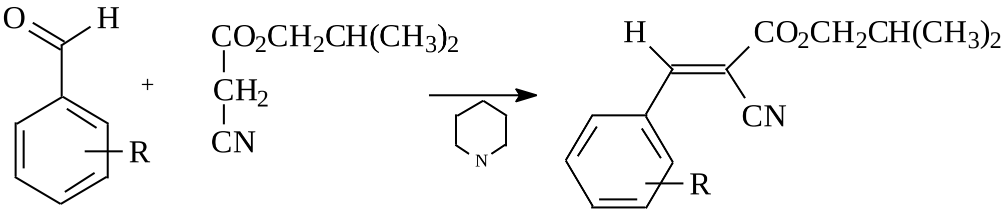
## 2. Experimental

2,3-Dimethyl, 2,4-dimethyl, 3,5-dimethyl, 2,3-dimethoxy, 2,4-dimethoxy, 2,5-dimethoxy, 2,6-dimethoxy, 3,4-dimethoxy, 3,5-dimethoxybenzaldehydes, isobutyl cyanoacetate, piperidine, styrene, 1,1'-azobis(cyclohexanecarbonitrile) (ABCN), and toluene supplied from Sigma-Aldrich Co., were used as received. Instrumentation is described in [28].

## 3. Results and discussion

### *3.1. Synthesis and characterization of isobutyl phenylcyanoacrylates*

All isobutyl phenylcyanoacrylates (IPCA) compounds were synthesized by Knoevenagel condensation [29] of appropriate benzaldehydes with isobutyl cyanoacetate, catalyzed by base, piperidine (Scheme 1).



Scheme 1. Synthesis of isobutyl R-phenylcyanoacrylates, where R is 2,3-dimethyl, 2,4-dimethyl, 3,5-dimethyl, 2,3-dimethoxy, 2,4-dimethoxy, 2,5-dimethoxy, 2,6-dimethoxy, 3,4-dimethoxy, 3,5-dimethoxy.

The preparation procedure was essentially the same for all the monomers. In a typical synthesis, equimolar amounts of isobutyl 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 IR, $^{1}$H and $^{13}$C NMR spectroscopies. No stereochemical analysis of the novel ring-substituted IPCA was performed since no stereoisomers (*E* or/and *Z*) of known configuration were available.

### 3.1.1. *Isobutyl 2,3-dimethylphenylcyanoacrylate*

Yield: 83.6%; mp 52.9°C; $^{1}$H NMR: $\delta$ 8.6 (s, 1H, CH=), 8.0-7.0 (m, 4H, Ph), 4.1 (d, 2H, $CH_2$), 2.3 (m, 1H, CH), 2.1 (s, 6H, $CH_3$), 1.0 (d, 6H, $CH_3$); $^{13}$C NMR: $\delta$ 162 (C=O), 155 (HC=), 137, 134, 130, 122 (Ph), 115 (CN), 107 (C=), 73 ($CH_2$), 63 ($OCH_3$), 28 (CH), 20 ($CH_3$) 16,20 ($PhCH_3$); IR: (cm$^{-1}$) 3024-2822 (m, C-H), 2225 (m, CN), 1728 (s, C=O), 1587 (s, C=C), 1286 (s, C-O-$CH_3$), 793, 760, 710 (s, C-H out of plane). Anal. calcd. for $C_{16}H_{19}NO_2$: C, 74.68; H, 7.44; N, 5.44; Found: C, 72.76; H, 7.21; N, 5.48.

### 3.1.2. *Isobutyl 2,4-dimethylphenylcyanoacrylate*

Yield 82%; mp 49.8°C; $^1$H NMR $\delta$ 8.5 (s, 1H, CH=), 8.2-6.8 (m, 4H, Ph), 4.1 (d, 2H, $CH_2$), 2.4 (m, 1H, CH), 2.3 (s, 6H, $CH_3$), 1.0 (d, 6H, $CH_3$); $^{13}$C NMR $\delta$ 163 (C=O), 152 (HC=), 143, 138, 133, 128, 124 (Ph), 117 (CN), 103 (C=), 72 ($CH_2$), 56 ($OCH_3$), 31 (CH), 19-15 ($CH_3$); IR (cm$^{-1}$): 3234-2887, 2224 (m, CN), 1726 (s, C=O), 1595 (C=C), 1288 (s, C-O-$CH_3$), 824, 784 (s, C-H out of plane). Anal. Calcd. for $C_{16}H_{19}NO_2$: C, 74.68; H, 7.44; N, 5.44; Found: C, 71.57; H, 7.33; N, 5.80.

### 3.1.3. *Isobutyl 3,5-dimethylphenylcyanoacrylate*

Yield 78%; mp 122.3°C; $^1$H NMR $\delta$ 8.2 (s, 1H, CH=), 7.7-7.0 (m, 4H, Ph), 4.1 (d, 2H, $CH_2$), 2.3 (s, 6H, $CH_3$Ph), 2.1 (m, 1H, CH), 1.0 (d, 6H, $CH_3$); $^{13}$C NMR $\delta$ 163 (C=O), 153 (HC=), 139, 135, 133, 124, 119 (Ph), 115 (CN), 102 (C=), 72 ($CH_2$), 28 ($CH_3$), 28 (CH), 21 ($CH_3$Ph), 19 ($CH_3$); IR (cm$^{-1}$): 3045-2937 (m, C-H), 2216 (m, CN), 1713 (s, C=O), 1595 (C=C), 1229 (s, C-O-$CH_3$), 837 (s, C-H out of plane). Anal. Calcd. for $C_{16}H_{19}NO_2$: C, 74.68; H, 7.44; N, 5.44; Found: C, 74.23; H, 7.28; N, 5.89.

### 3.1.4. *Isobutyl 2,3-dimethoxyphenylcyanoacrylate*

Yield 88%; mp 78.3°C; $^1$H NMR $\delta$ 8.7 (s, 1H, CH=), 8.0-6.8 (m, 4H, Ph), 4.1 (m, 2H, $CH_2$), 3.8 (s, 6H, $OCH_3$), 2.1 (m, 1H, CH), 1.0 (d, 6H, $(CH_3)_2$); $^{13}$C NMR $\delta$ 163 (C=O), 152 (HC=), 149, 129, 123, 122 (Ph), 116 (CN), 103 (C=), 72 ($CH_2$), 61, 55 ($CH_3O$), 27 (CH), 18 $(CH_3)_2$; IR (cm$^{-1}$): 3120-2918 (m, C-H), 2222 (m, CN), 1728 (s, C=O), 1605 (s, C=C), 1242 (s, C-O-$CH_3$), 764 (s, C-H out of plane). Anal. Calcd. for $C_{16}H_{19}NO_4$: C, 66.42; H, 6.62; N, 4.84; Found: C, 65.07; H, 6.53; N, 4.88.

### 3.1.5. *Isobutyl 2,4-dimethoxyphenylcyanoacrylate*

Yield 91%; mp 82.7°C; $^1$H NMR $\delta$ 8.6 (s, 1H, CH=), 8.5-8.3 (m, 4H, Ph), 4.1 (m, 2H, $CH_2$), 3.9 (s, 6H, $OCH_3$), 2.1 (m, 1H, CH), 1.0 (d, 6H, $(CH_3)_2$); $^{13}$C NMR $\delta$ 166 (C=O), 162 (HC=), 161, 148, 131 (Ph), 117 (CN), 106 (C=), 72 ($CH_2$), 56 ($CH_3O$), 28 (CH), 20 $(CH_3)_2$; IR (cm$^{-1}$): 2910(m, C-H), 2223 (m, CN), 1722 (s, C=O), 1607 (s, C=C), 1261 (s, C-O-$CH_3$), 781, 762 (s, C-H out of plane). Anal. Calcd. for $C_{16}H_{19}NO_4$: C, 66.42; H, 6.62; N, 4.84; Found: C, 66.07; H, 6.54; N, 4.98.

### 3.1.6. *Isobutyl 2,5-dimethoxyphenylcyanoacrylate*

Yield 76%; mp 78.1°C; $^1$H NMR $\delta$ 8.7 (s, 1H, CH=), 7.8-7.2 (m, 4H, Ph), 4.4 (m, 2H, $CH_2$), 3.8 (s, 6H, $OCH_3$), 2.4 (m, 1H, CH), 1.0 (d, 6H, $(CH_3)_2$); $^{13}$C NMR $\delta$ 163 (C=O), 152 (HC=), 152, 148, 131, 127 (Ph), 115 (CN), 102 (C=), 71 ($CH_2$), 56 ($CH_3O$), 28 (CH), 19 $(CH_3)_2$; IR (cm$^{-1}$): 2918(m, C-H), 2223 (m, CN), 1729 (s, C=O), 1647 (s, C=C), 1263 (s, C-O-$CH_3$), 786 (s, C-H out of plane). Anal. Calcd. for $C_{16}H_{19}NO_4$: C, 66.42; H, 6.62; N, 4.84; Found: C, 65.73; H, 6.53; N, 4.99.

### 3.1.7. *Isobutyl 2,6-dimethoxyphenylcyanoacrylate*

Yield 76%; mp 85.4°C; $^1$H NMR $\delta$ 8.4 (s, 1H, CH=), 7.7-6.4 (m, 4H, Ph), 4.1 (m, 2H, $CH_2$), 3.9 (s, 6H, $OCH_3$), 2.1 (m, 1H, CH), 1.0 (d, 6H, $(CH_3)_2$; $^{13}$C NMR $\delta$ 163 (C=O), 159 (HC=), 148, 133, 110, 107 (Ph), 115 (CN), 104 (C=), 72 ($CH_2$), 55 ($CH_3O$), 28 (CH), 19 $(CH_3)_2$; IR (cm$^{-1}$): 3120-2818 (m, C-H), 2225 (m, CN), 1722 (s, C=O), 1607 (s, C=C), 1288 (s, C-O-$CH_3$), 781, 762 (s, C-H out of plane). Anal. Calcd. for $C_{16}H_{19}NO_4$: C, 66.42; H, 6.62; N, 4.84; Found: C, 64.03; H, 6.43; N, 4.76.

### 3.1.8. *Isobutyl 2,5-dimethoxyphenylcyanoacrylate*

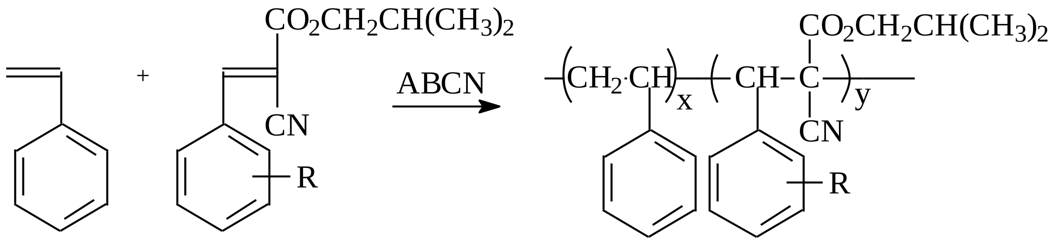
Yield 76%; mp 86.9°C; $^1H$ NMR $\delta$ 8.2 (s, 1H, CH=), 8.0-6.9 (m, 4H, Ph), 4.5 (m, 2H, $CH_2$), 4.0 (s, 6H, $OCH_3$), 2.1 (m, 1H, CH), 1.0 (d, 6H, $(CH_3)_2$; $^{13}C$ NMR $\delta$ 162 (C=O), 154 (HC=), 153, 148, 131, 127, 124, 110 (Ph), 115 (CN), 99 (C=), 71 ($CH_2$), 55 ($CH_3O$), 27 (CH), 19 $(CH_3)_2$; IR ($cm^{-1}$): 3102 – 2818 (m, C-H), 2217 (m, CN), 1722 (s, C=O), 1589 (s, C=C), 1263 (s, C-O-$CH_3$), 786 (s, C-H out of plane). Anal. Calcd. for $C_{16}H_{19}NO_4$: C, 66.42; H, 6.62; N, 4.84; Found: C, 64.71; H, 6.53; N, 4.45.

### 3.1.9. *Isobutyl 3,5-dimethoxyphenylcyanoacrylate*

Yield 84%; mp 104.1°C; $^1H$ NMR $\delta$ 8.2 (s, 1H, CH=), 7.4-6.5 (m, 4H, Ph), 4.1 (m, 2H, $CH_2$), 4.0 (s, 6H, $OCH_3$), 2.1 (m, 1H, CH), 1.0 (d, 6H, $(CH_3)_2$); $^{13}C$ NMR $\delta$ 162 (C=O), 155 (HC=), 154, 133, 108, 106 (Ph), 115 (CN), 103 (C=), 73 ($CH_2$), 56 ($CH_3O$), 28 (CH), 19 $(CH_3)_2$; IR ($cm^{-1}$): 3215 – 2812 (m, C-H), 2221 (m, CN), 1717 (s, C=O), 1609 (s, C=C), 1240 (s, C-O-$CH_3$), 785, 761 (s, C-H out of plane). Anal. Calcd. for $C_{16}H_{19}NO_4$: C, 66.42; H, 6.62; N, 4.84; Found: C, 65.18; H, 6.46; N, 4.80.

## 3.2. *Synthesis and characterization of styrene – IPCA copolymers*

Copolymers of the styrene (ST) and the IPCA compounds, P(ST-co-IPCA) 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 70ºC. 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 novel synthesized IPCA 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 between 10 and 20% to minimize compositional drift (Table 1). Nitrogen elemental analysis showed that between 18.1 and 30.1 mol% of IPCA is present in the copolymers, which is indicative of relatively high reactivity of the IPCA monomers towards ST radical which is typical of dimethyl and dimethoxy ring-disubstituted different esters PCA [13-26]. Since IPCA monomers do not homopolymerize, the most likely structure of the copolymers would be isolated IPCA monomer (y = 1) units alternating with short ST sequences (x > 1) (Scheme 2).



**Scheme 2.** Copolymerization of ST and the ring-disubstituted isobutyl phenylcyanoacrylates, $RPhCH = C(CN)CO_2CH_2CH(CH_3)_2$, R = 2,3-dimethyl, 2,4-dimethyl, 3,5-dimethyl, 2,3-dimethoxy, 2,4-dimethoxy, 2,5-dimethoxy, 2,6-dimethoxy, 3,4-dimethoxy, 3,5-dimethoxy.

### 3.2.1. Styrene- Isobutyl 2,3-dimethylphenylcyanoacrylate copolymer

Yield 11%; $^{1}$H-NMR $\delta$ 7.4 – 6.3 (8H, Ph), 5.2-5.0 (1H, OCH), 4.1 – 3.7 (1H, CHPh – ST), 1.6 - 1.4 (2H, $CH_2$), 2.7-2.4 (6H, $PhCH_3$), 2.7 - 2.4 (1H, CH-ICPP), 1.5-1.0 (6H, $CH(CH_3)_2$); $^{13}$C-NMR $\delta$ 174-165 (C=O), 152 - 100 (Ph), 118 - 114 (CN), 68-58 (OCH), 51-41 (CH, $CH_2$), 24-19 ($CH(CH_3)_2$), 21 - 14 ($CH_3$); IR (cm$^{-1}$): 3023-2822 (m, C-H), 2239 (m, CN), 1741 (s, C=O), 1249 (s, C-O-C), 778 (s, C-H out of plane). Nitrogen content 2.12%.

### 3.2.2. Styrene - Isobutyl 2,4-dimethylphenylcyanoacrylate copolymer

Yield 13%; $^{1}$H-NMR $\delta$ 7.5 – 6.6 (8H, Ph), 5.3 - 5.1 (1H, OCH), 4.0 – 3.6 (1H, CHPh – ST), 1.5 - 1.3 (2H, $CH_2$), 2.6 - 2.3 (6H, $PhCH_3$), 2.6 - 2.4 (1H, CH-ICPP), 1.4 - 0.9 (6H, $CH(CH_3)_2$); $^{13}$C-NMR $\delta$ 173-164 (C=O), 151 - 101 (Ph), 119 - 112 (CN), 68 - 57 (OCH), 51 - 40 (CH, $CH_2$), 25 - 20 ($CH(CH_3)_2$), 21 - 14 ($CH_3$); IR (cm$^{-1}$): 3012-2825 (m, C-H), 2242 (m, CN), 1740 (s, C=O), 1229 (s, C-O-C), 750 (s, C-H out of plane). Nitrogen content 1.92%.

### 3.2.3. Styrene - Isobutyl 3,5-dimethylphenylcyanoacrylate copolymer

Yield 12%; $^{1}$H-NMR $\delta$ 7.6 – 6.5 (8H, Ph), 5.3-5.0 (1H, OCH), 4.0 – 3.7 (1H, CHPh – ST), 1.6 - 1.4 (2H, $CH_2$), 2.7-2.4 (6H, $PhCH_3$), 2.6 - 2.5 (1H, CH-ICPP), 1.4-1.0 (6H, $CH(CH_3)_2$); $^{13}$C-NMR $\delta$ 171-165 (C=O), 152 - 100 (Ph), 118 - 116 (CN), 68-58 (OCH), 51-41 (CH, $CH_2$), 24-19 ($CH(CH_3)_2$), 22 - 14 ($CH_3$); IR (cm$^{-1}$): 3128-2832 (m, C-H), 2243 (m, CN), 1742 (s, C=O), 1268 (s, C-O-C), 853, 760, 738 (s, C-H out of plane). Nitrogen content 2.63%.

### 3.2.4. Styrene - Isobutyl 2,3-dimethoxyphenylcyanoacrylate copolymer

Yield 12%; $^1$H-NMR $\delta$ 7.5 – 6.6 (8H, Ph), 5.3-5.1 (1H, OCH), 4.1 – 3.7 (1H, CHPh – ST), 3.8-3.5 (6H, $PhOCH_3$), 2.7 - 2.5 (1H, CH-ICPP), 1.5 - 1.3 (2H, $CH_2$), 1.6-1.1 (6H, $CH(CH_3)_2$); $^{13}$C-NMR $\delta$ 176-166 (C=O), 151 - 99 (Ph), 117 - 115 (CN), 69-58 (OCH), 61-54 ($CH_3OPh$), 52-42 (CH, $CH_2$), 23-18 ($CH(CH_3)_2$); IR (cm$^{-1}$): 3145-2812 (m, C-H), 2239 (m, CN), 1742 (s, C=O), 1266 (s, C-O-C), 754, 698 (s, C-H out of plane). Nitrogen content 2.3%.

### 3.2.5. Styrene - Isobutyl 2,4-dimethoxyphenylcyanoacrylate copolymer

Yield 10%; $^1$H-NMR $\delta$ 7.6 – 6.6 (8H, Ph), 5.3 - 5.1 (1H, OCH), 4.0 – 3.6 (1H, CHPh – ST), 3.7-3.5 (6H, $PhOCH_3$), 2.7 - 2.5 (1H, CH-ICPP), 1.5 - 1.3 (2H, $CH_2$), 1.4 - 0.9 (6H, $CH(CH_3)_2$); $^{13}$C-NMR $\delta$ 172-165 (C=O), 154 - 101 (Ph), 118 - 114 (CN), 68 - 57 (OCH), 61-54 ($CH_3OPh$), 51 - 42 (CH, $CH_2$), 25 - 21 ($CH(CH_3)_2$); IR (cm$^{-1}$): 3068-2832 (m, C-H), 2239 (m, CN), 1742 (s, C=O), 1245 (s, C-O-C), 767 (s, C-H out of plane). Nitrogen content 1.87%.

### 3.2.6. Styrene - Isobutyl 2,5-dimethoxyphenylcyanoacrylate copolymer

Yield 12%; $^1$H-NMR $\delta$ 7.5 – 6.5 (8H, Ph), 5.4 - 5.1 (1H, OCH), 4.1 – 3.6 (1H, CHPh – ST), 3.7-3.5 (6H, $PhOCH_3$), 1.6 - 1.3 (2H, $CH_2$), 2.5 - 2.3 (6H, $PhCH_3$), 2.6 - 2.3 (1H, CH-ICPP), 1.3 - 0.9 (6H, $CH(CH_3)_2$); $^{13}$C-NMR $\delta$ 173-163 (C=O), 153 - 101 (Ph), 118 - 114 (CN), 68 - 58 (OCH), 61-54 ($CH_3OPh$), 51 - 42 (CH, $CH_2$), 25 - 21 ($CH(CH_3)_2$), 21 - 14 ($CH_3$); FTIR (cm$^{-1}$): 3147-2835 (m, C-H), 2239 (m, CN), 1740 (s, C=O), 1223 (s, C-O-C), 767 (s, C-H out of plane). Nitrogen content 2.37%.

### 3.2.7. Styrene - Isobutyl 2,6-dimethoxyphenylcyanoacrylate copolymer

Yield 12%; $^1$H-NMR $\delta$ 7.5 – 6.6 (8H, Ph), 5.3-5.1 (1H, OCH), 4.1 – 3.7 (1H, CHPh – ST), 3.7-3.5 (6H, $PhOCH_3$), 1.5 - 1.3 (2H, $CH_2$), 2.8-2.5 (6H, $PhCH_3$), 2.7 - 2.5 (1H, CH-ICPP), 1.6-1.1 (6H, $CH(CH_3)_2$); $^{13}$C-NMR $\delta$ 176-166 (C=O), 151 - 99 (Ph), 117 - 115 (CN), 69-58 (OCH), 61-54 ($CH_3OPh$), 52-42 (CH, $CH_2$), 23-18 ($CH(CH_3)_2$), 21 - 14 ($CH_3$); FTIR (cm$^{-1}$): 3145-2812 (m, C-H), 2239 (m, CN), 1742 (s, C=O), 1266 (s, C-O-C), 754, 698 (s, C-H out of plane). Nitrogen content 1.87%.

### 3.2.8. Styrene - Isobutyl 3,4-dimethoxyphenylcyanoacrylate copolymer

Yield 12%; $^1$H-NMR $\delta$ 7.5 – 6.6 (8H, Ph), 5.3-5.1 (1H, OCH), 4.1 – 3.7 (1H, CHPh – ST), 3.7-3.5 (6H, $PhOCH_3$), 1.5 - 1.3 (2H, $CH_2$), 2.8-2.5 (6H, $PhCH_3$), 2.7 - 2.5 (1H, CH-ICPP), 1.6-1.1 (6H, $CH(CH_3)_2$); $^{13}$C-NMR $\delta$ 176-166 (C=O), 151 - 99 (Ph), 117 - 115 (CN), 69-58 (OCH), 61-54 ($CH_3OPh$), 52-42 (CH, $CH_2$), 23-18 ($CH(CH_3)_2$), 21 - 14 ($CH_3$); FTIR (cm$^{-1}$): 3141-2800 (m, C-H), 2243 (m, CN), 1741 (s, C=O), 1263 (s, C-O-C), 761, 737, 699 (s, C-H out of plane). Nitrogen content 2.15%.

### 3.2.9. Styrene - Isobutyl 3,5-dimethoxyphenylcyanoacrylate copolymer

Yield 11%; $^1$H-NMR $\delta$ 7.6 – 6.3 (8H, Ph), 5.4 - 5.2 (1H, OCH), 4.2 – 3.5 (1H, CHPh – ST), 3.9-3.5 (6H, $CH_3O$), 3.7-3.5 (6H, $PhOCH_3$), 1.6 - 1.3 (2H, $CH_2$), 2.7 - 2.4 (1H, CH-ICPP), 1.5 - 1.2 (6H, $CH(CH_3)_2$); $^{13}$C-NMR $\delta$ 174-166 (C=O), 152 - 100 (Ph), 117 - 115 (CN), 68 - 58 (OCH), 60 - 54 ($OCH_3$), 54 - 41 (CH, $CH_2$), 25 - 23 ($CH(CH_3)_2$); FTIR (cm$^{-1}$): 3077-2869 (m, C-H), 2222 (m, CN), 1740 (s, C=O), 1238 (s, C-O-C), 978 (s, C-H out of plane). Nitrogen content 2.64%.

**Table 1.** Molecular characteristics of ST-IPCA copolymers

| R | Conversion % | Nitrogen wt% | % mole ST | % mole IPCA |
|---|---|---|---|---|
| 2,3-$(CH_3)_2$ | 12.1 | 0.15 | 79.5 | 20.5 |
| 2,4-$(CH_3)_2$ | 14.2 | 0.14 | 81.9 | 18.1 |
| 3,5-$(CH_3)_2$ | 12.8 | 0.19 | 72.6 | 27.4 |
| 2,3-$(CH_3O)_2$ | 12.7 | 0.16 | 75.5 | 24.5 |
| 2,4-$(CH_3O)_2$ | 11.2 | 0.13 | 81.5 | 18.5 |
| 2,5-$(CH_3O)_2$ | 13.4 | 0.17 | 74.4 | 25.6 |
| 2,6-$(CH_3O)_2$ | 15.1 | 0.13 | 81.5 | 18.5 |
| 3,4-$(CH_3O)_2$ | 14.1 | 0.15 | 77.7 | 22.3 |
| 3,5-$(CH_3O)_2$ | 12.7 | 0.19 | 69.9 | 30.1 |

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.

## 4 Conclusions

Novel dimethyl and dimethoxy ring-disubstituted isobutyl phenylcyanoacrylates 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.

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