Synthesis and copolymerization of novel oxy ring-substituted isopropyl cyanoarylacrylates

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Novel oxy ring-substituted isopropyl 2-cyano-3-arylacrylates,

\( R\text{PhCH}=C(\text{CN})\text{CO}_2\text{CH(CH}_3)_2 \) (where R is 3-phenoxy, 4-phenoxy, 2-benzyloxy, 3-benzyloxy, 4-benzyloxy, 4-acetyloxy, 3-acetyl, 4-acetyl, 4-acetylamino, 4-methoxy-2-methyl, 4-methoxy-3-methyl, 3-ethoxy-4-methoxy, 3,4-dibenzyloxy, 3-benzyloxy-4-methoxy, 4-benzyloxy-3-methoxy, 2,3-dimethyl-4-methoxy, 2,5-dimethyl-4-methoxy, 2,4-dimethoxy-3-methyl, 2,4-dimethoxy-6-methyl, 3,5-dimethoxy-4-hydroxy) were prepared and copolymerized with styrene. The acrylates were synthesized by the piperidine catalyzed Knoevenagel condensation of oxy ring-substituted benzaldehydes and isopropyl cyanoacetate and characterized by CHN elemental analysis, FTIR, \(^1\)H and \(^{13}\)C-NMR. All the acrylates were copolymerized with styrene in solution with radical initiation at 70°C. The composition of the copolymers was calculated from nitrogen analysis, and the structures were analyzed by FTIR, \(^1\)H 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 200-500ºC range with a residue, which then decomposed in the 500-800ºC range.

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

1. **Introduction**

Oxy ring–functionalized cyanoarylacrylates, RľPhCH = C(CN)CO₂R₂ have found various applications as functional compounds in organic and polymer synthesis. Thus, phenoxy ring-substituted ethyl cyanoarylacrylate (ECAA) was used in synthesis of tetrazoles compounds [1]; it was a product of condensations catalyzed by triazine-based microporous network [2], imidazolium chloride immobilized SBA-15 [3], and biocatalyst lipase, Aspergillus oryzae [4]. The ECAA was also used in N,N'-dioxide-lanthanum(III)-catalyzed asymmetric cyclopropanation with 2-bromomalonates [5]. It was employed in DBU-mediated [4 + 2] annulations of donor-acceptor cycloproanes [6], in synergistic NaBH₄ reduction/cyclization in synthesis of 3-oxabicyclo[3.1.0]hexane derivatives [7], as well as in studies on synthetic access to pyrano[3,2-c] quinoline and 3-substituted quinoline derivatives [8]. Benzyloxy ring-substituted ECAA was used in synthesis and biological evaluation of arylidene-thiazolidinediones with potential hypoglycemic and hypolipidemic activities [9]. Acetyl ring-substituted ECAA was involved in synthesis from nitriles with retention of the cyano group [10], in iridium hydride complex catalyzed addition of nitriles to carbon-nitrogen triple bonds of nitriles [11], and in synthesis (E)-
trisubstituted alkenes via bismuth triflate-catalyzed rearrangement of acetates [12].

Acetamido ring-substituted ECAA was used in heterocyclic syntheses of dihydropyridines [13] and in synthesis of polyimides from 4-aminophenylsuccinic acid and 3-(4-aminophenyl)glutaric acid [14]. 4-Acetylamino ring-substituted isopropyl 2-cyanophenylacrylate was reported as a nonlinear optical material [15]. Alkyl 2-cyanoacrylates are a family of vinyl monomers renowned for their high reactivity and instant adhesive properties [16]. Thus, isopropyl cyanoacrylate was reported in preparations of semipermeable membrane microcapsules [17] and as fissure sealant in dental application [18].

We have reported earlier synthesis and styrene copolymerization of oxy ring-substituted methyl [19-24], ethyl [25-27], propyl [28-31], butyl [32-34], isobutyl [35-37], methoxyethyl [38,39], and octyl [40-42] cyanoarylacrylates. In continuation of our exploration of novel trisubstituted ethylene compounds we have prepared isopropyl oxy ring-substituted cyanoarylacrylates, ICAA, RPhCH=C(CN)CO₂CH(CH₃)₂, where R is 3-phenoxy, 4-phenoxy, 2-benzyloxy, 3-benzyloxy, 4-benzyloxy, 4-acetyloxy, 3-acetyl, 4-acetyl, 4-acetylamino, 4-methoxy-2-methyl, 4-methoxy-3-methyl, 3-ethoxy-4-methoxy, 3,4-dibenzylloxy, 3-benzyloxy-4-methoxy, 4-benzyloxy-3-methoxy, 2,3-dimethyl-4-methoxy, 2,5-dimethyl-4-methoxy, 2,4-dimethoxy-3-methyl, 2,4-dimethoxy-6-methyl, 3,5-dimethoxy-4-hydroxy, and copolymerized with styrene. To the best of our knowledge there have been no reports on either synthesis of these compounds (except 4-acetylamino [15]), nor their copolymerization with styrene [43].
2. Experimental

3-Phenoxy, 4-phenoxy, 2-benzyl(xo), 3-benzyl(xo), 4-benzyl(xo), 4-acetoxy, 3-acetyl, 4-acetyl (90%), 4-acetamido (97%), 4-methoxy-2-methyl, 4-methoxy-3-methyl, 3-ethoxy-4-methoxy, 3,4-dibenzyl(xo), 3-benzyl(xo)-4-methoxy, 4-benzyl(xo)-3-methoxy, 2,3-dimethyl-4-methoxy, 2,5-dimethyl-4-methoxy, 2,4-dimethoxy-3-methyl, 2,4-dimethoxy-6-methyl, 3,5-dimethoxy-4-hydroxybenzaldehydes, isopropyl cyanoacetate, piperidine, styrene, 1,1'-azobiscyclohexanecarbonitrile, (ABCN), and toluene supplied from Sigma-Aldrich Co., were used as received. Instrumentation is described in the first paper of this isopropyl esters’ series [44].

3. Synthesis and characterization of isopropyl 2-cyano-3-arylacrylates

All isopropyl 2-cyano-3-arylacrylates (ICAA) were synthesized by Knoevenagel condensation [45] 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-phenoxy, 4-phenoxy, 2-benzyl(xo), 3-benzyl(xo), 4-benzyl(xo), 4-acetoxy, 3-acetyl, 4-acetyl, 4-]
acetylamino, 4-methoxy-2-methyl, 4-methoxy-3-methyl, 3-ethoxy-4-methoxy, 3,4-dibenzyloxy, 3-benzyloxy-4-methoxy, 4-benzyloxy-3-methoxy, 2,3-dimethyl-4-methoxy, 2,5-dimethyl-4-methoxy, 2,4-dimethoxy-3-methyl, 2,4-dimethoxy-6-methyl, 3,5-dimethoxy-4-hydroxy.

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 [44]. No stereochemical analysis of the novel oxy ring-substituted ICAA was performed since no stereoisomers (E or/and Z) of known configuration were available.

3.1. Isopropyl 2-cyano-3-(3-phenoxyaryl)acrylate

Yield 78%; mp 80.4°C; $^1$H-NMR: $\delta$ 8.2 (s, 1H, CH=), 8.0-7.1 (m, 9H, Ph), 5.2 (m, 1H, CH), 1.4 (d, 6H, CH$_3$); $^{13}$C-NMR: $\delta$ 167 (C=O), 154 (HC=), 158, 157, 132, 130, 127, 123, 118, 114 (Ph), 116 (CN), 104 (C=), 68 (OCH), 22 (CH$_3$); FTIR: (cm$^{-1}$) 3021-2846 (m, C-H), 2226 (m, CN), 1724 (s, C=O), 1534 (C=C), 1263 (s, C-O-CH$_3$), 824 (s, C-H out of plane). Anal. calcd. for C$_{19}$H$_{17}$NO$_3$: C, 74.25; H, 5.58; N, 4.56; Found: C, 76.38; H, 5.90; N, 4.64.

3.2 Isopropyl 2-cyano-3-(4-phenoxyaryl)acrylate
Yield: 89%; mp 74.6°C; $^1$H-NMR: $\delta$ 8.2 (s, 1H, CH=), 8.0-6.9 (m, 9H, Ph), 5.2 (m, 1H, CH), 1.4 (d, 6H, CH$_3$); $^{13}$C-NMR: $\delta$ 167 (C=O), 154 (HC=), 157, 156, 131, 130, 125, 123, 118 (Ph), 116 (CN), 100 (C=), 68 (OCH), 22 (CH$_3$); FTIR: (cm$^{-1}$) 3052-2865 (m, C-H), 2222 (m, CN), 1720 (s, C=O), 1253 (s, C-O-CH$_3$), 767, 727 (s, C-H out of plane).

Anal. calcd. for C$_{19}$H$_{17}$NO$_3$: C, 74.25; H, 5.58; N, 4.56; Found: C, 74.07; H, 5.55; N, 4.53.

3.3 Isopropyl 2-cyano-3-(2-phenylmethoxyaryl)acrylate

Yield 87%; mp 55.7°C; $^1$H-NMR $\delta$ 8.2 (s, 1H, CH=), 8.1-7.0 (m, 9H, Ph), 5.2 (s, 2H, OCH$_2$), 5.1 (m, 1H, CH), 1.5 (CH$_3$); $^{13}$C-NMR $\delta$ 167 (C=O), 154 (HC=), 137, 131, 130, 129, 128, 127, 122, 112 (Ph), 116 (CN), 111 (C=), 71 (OCH$_2$), 68 (OCH), 22 (CH$_3$); FTIR (cm$^{-1}$): 3065-2758 (m, C-H), 2221 (m, CN), 1718 (s, C=O), 1580 (s, C=C), 1257 (s, C-O-CH$_3$), 833, 762 (s, C-H out of plane). Anal. Calcd. for C$_{20}$H$_{19}$NO$_3$: C, 74.75; H, 5.96; N, 4.36; Found: C, 73.49; H, 6.01; N, 4.65.

3.4 Isopropyl 2-cyano-3-3-(phenylmethoxyaryl)acrylate

Yield 82%; mp 100.8°C, $^1$H-NMR $\delta$ 8.2 (s, 1H, CH=), 7.8-7.1 (m, 9H, Ph), 5.3 (m, 1H, CH), 5.2 (s, 2H, CH$_2$), 1.3 (d, 6H, CH$_3$); $^{13}$C-NMR $\delta$ 166 (C=O), 154 (HC=), 159, 137, 133, 130, 129, 128, 127, 114 (Ph), 116 (CN), 104 (C=), 70 (CH$_2$), 68 (CH), 22 (CH$_3$); FTIR (cm$^{-1}$): 3192-2826 (m, C-H), 2226 (m, CN), 1724 (s, C=O), 1576 (s, C=C), 1276 (s, C-O-CH$_3$), 730, 684 (s, C-H out of plane). Anal. Calcd. for C$_{20}$H$_{19}$NO$_3$: C, 74.75; H, 5.96; N, 4.36; Found: C, 74.99; H, 6.12; N, 4.45.

3.5 Isopropyl 2-cyano-3-(4-phenylmethoxyaryl)acrylate
Yield 86%; mp 108.4°C; $^1$H-NMR $\delta$ 8.2 (s, 1H, CH=), 8.0-6.9 (m, 9H, Ph), 5.3 (m, 1H, CH), 5.2 (s, 2H, CH$_3$); $^{13}$C-NMR $\delta$ 166 (C=O), 154 (HC=), 156, 137, 131, 129, 128, 127, 115 (Ph), 116 (CN), 100 (C=), 70 (CH$_2$), 68 (CH), 22 (CH$_3$); FTIR (cm$^{-1}$): 3152-2824 (m, C=H), 2220 (m, CN), 1715 (s, C=O), 1276 (s, C-O-CH$_3$), 814, 760 (s, C-H out of plane).

Anal. Calcd. for C$_{20}$H$_{19}$NO$_3$: C, 74.75; H, 5.96; N, 4.36; Found: C, 74.76; H, 6.00; N, 4.35.

### 3.6 Isopropyl 2-cyano-3-(4-acetoxyaryl)acrylate

Yield 78%; mp 78.3°C; $^1$H-NMR $\delta$ 8.2 (s, 1H, CH=), 8.1-7.0 (d, 4H, Ph), 5.2 (m, 1H, CH), 2.4 (s, 3H, CH$_3$CO), 1.3 (d, 6H, OCHCH$_3$); $^{13}$C-NMR $\delta$ 169 (O=CCH$_3$), 167 (C=O), 154 (HC=), 153, 131, 125, 122 (Ph), 116 (CN), 100 (C=), 68 (CH), 22 (CH$_3$)$_2$ 21 (Ph-OCOCH$_3$); FTIR (cm$^{-1}$): 3200-2800 (m, C=H), 2222 (m, CN), 1763 (s, C=O), 1593 (C=C), 1271 (s, C-O-CH$_3$), 872, 910 (s, C-H out of plane). Anal. Calcd. for C$_{19}$H$_{15}$NO$_4$: C, 65.92; H, 5.53; N, 5.13; Found: C, 63.88; H, 5.78; N, 5.17.

### 3.7 Isopropyl 2-cyano-3-(3-acetylaryl)acrylate

Yield 91%; mp 145.7°C; $^1$H-NMR $\delta$ 8.5 (s, 1H, CH=), 8.4-7.0 (m, 4H, Ph), 5.2 (m, 1H, CH), 2.7 (s, 3H, CH$_3$CO), 1.2 (d, 2H, CH$_3$); $^{13}$C-NMR $\delta$ 197 (O=CCH$_3$) 166 (C=O), 154 (HC=), 137, 134, 129, 125 (Ph), 116 (CN), 104 (C=), 68 (CH), 26 (CH$_3$CO), 22 (CH$_3$); FTIR (cm$^{-1}$): 3075-2849 (m, C-H), 2226 (m, CN), 1734 (s, C=O), 1612 (C=C), 1281 (s, C-O-CH$_3$), 837 (s, C-H out of plane). Anal. Calcd. for C$_{15}$H$_{13}$NO$_3$: C, 70.02; H, 5.88; N, 5.44; Found: C, 69.22; H, 6.11; N, 5.52.
3.8 Isopropyl 2-cyano-3-(4-acetylaryl)acrylate

Yield 76%; mp 133.1°C; $^1$H-NMR $\delta$ 8.3 (s, 1H, CH=), 8.1 (s, 4H, Ph), 5.3 (m, 1H, CH), 2.7 (s, 3H, CH$_3$CO), 1.4 (d, 6H, CH$_3$); $^{13}$C-NMR $\delta$ 197 (C=CH$_3$) 166 (C=O), 154 (HC=), 142, 131, 129, 125 (Ph), 116 (CN), 104 (C=), 68 (OCH), 26 (CH$_3$CO), 22 (CH$_3$); FTIR (cm$^{-1}$): 3175-2851 (m, C-H), 2218 (m, CN), 1732 (s, C=O), 1607 (C=C), 1268 (s, C-O-CH$_3$), 843 (s, C-H out of plane). Anal. Calcd. for C$_{15}$H$_{15}$NO$_3$: C, 70.02; H, 5.88; N, 5.44; Found: C, 69.01; H, 5.97; N, 5.36.

3.9 Isopropyl 2-cyano-3-(4-acetamidoaryl)acrylate

Yield 82%; mp 160.1°C; $^1$H-NMR $\delta$ 9.5 (s, 1H, NH), 8.2 (s, 1H, CH=), 8.1-7.1 (m, 4H, Ph), 5.2 (m, 1H, CH), 2.2 (s, 3H, CH$_3$CO), 1.3 (d, 6H, CH$_3$); $^{13}$C-NMR $\delta$ 169 (NHC=O), 166 (C=O), 154 (HC=), 151, 134, 121, 119 (Ph), 116 (CN), 96 (C=), 68 (CH), 24 (CH$_3$CO), 22 (CH$_3$); FTIR (cm$^{-1}$): 3057-2832 (m, C-H), 2220 (m, CN), 1705 (s, C=O), 1585 (C=C), 1254 (s, C-O-CH$_3$), 858 (s, C-H out of plane). Anal. Calcd. for C$_{15}$H$_{16}$N$_2$O$_3$: C, 66.16; H, 5.92; N, 10.29; Found: C, 66.24; H, 5.96; N, 10.35.

3.10 Isopropyl 2-cyano-3-(4-methoxy-2-methyaryl)acrylate

Yield 88%; mp 66.8°C; $^1$H-NMR $\delta$ 8.5 (s, 1H, CH=), 8.4-6.7 (m, 3H, Ph), 4.3 (t, 2H, OCH$_2$), 3.9 (s, 3H, PhOCH$_3$), 2.5 (s, 3H, PhCH$_3$), 1.8 (m, 2H, OCH$_2$CH$_2$), 1.0 (t, 3H, OCH$_2$CH$_2$CH$_2$CH$_3$); $^{13}$C-NMR $\delta$ 163 (C=O), 152 (HC=), 143, 131, 123, 112 (Ph), 115 (CN), 100 (C=), 68 (OCH$_2$), 56 (PhOCH$_3$), 22 (OCH$_2$CH$_2$), 21 (PhCH$_3$), 10 (OCH$_2$CH$_2$CH$_3$); IR (cm$^{-1}$): 3054-2818 (m, C-H), 2218 (m, CN), 1745 (s, C=O), 1597 (s,
C=C), 1246 (s, C-O-C), 828, 794 (s, C-H out of plane). Anal. Calcd. for C\textsubscript{15}H\textsubscript{17}NO\textsubscript{3}: C, 69.48; H, 6.61; N, 5.40; Found: C, 69.20; H, 6.69; N, 5.57.

3.11 Isopropyl 2-cyano-3-(4-methoxy-3-methylaryl)acrylate

Yield 42%; mp 98.2\textdegree{}C, \textsuperscript{1}H-NMR \(\delta\) 8.1 (s, 1H, CH=), 7.9-6.7 (m, 3H, Ph), 4.2 (t, 2H, OCH\textsubscript{2}), 3.9 (s, 3H, PhOCH\textsubscript{3}), 2.2 (s, 3H, PhCH\textsubscript{3}), 1.8 (m, 2H, OCH\textsubscript{2}CH\textsubscript{2}), 1.0 (t, 3H, OCH\textsubscript{2}CH\textsubscript{2}CH\textsubscript{3}); \textsuperscript{13}C-NMR \(\delta\) 163 (C=O), 155 (HC=), 133, 132, 128, 124 (Ph), 116 (CN), 99 (C=), 68 (OCH\textsubscript{2}), 56 (PhOCH\textsubscript{3}), 22 (OCH\textsubscript{2}CH\textsubscript{2}), 16 (PhCH\textsubscript{3}), 10 (OCH\textsubscript{2}CH\textsubscript{2}CH\textsubscript{3}); IR (cm\textsuperscript{-1}): 3038-2767 (m, C-H), 2212 (m, CN), 1727 (s, C=O), 1660 (s, C=C), 1228 (s, C-O-C), 998, 773 (s, C-H out of plane). Anal. Calcd. for C\textsubscript{15}H\textsubscript{17}NO\textsubscript{3}: C, 69.48; H, 6.61; N, 5.40; Found: C, 69.47; H, 6.54; N, 5.40.

3.12 Isopropyl 2-cyano-3-(3-ethoxy-4-methoxylaryl)acrylate

Yield 93%; mp 86.7\textdegree{}C, \textsuperscript{1}H-NMR \(\delta\) 8.2 (s, 1H, CH=), 7.9-6.8 (m, 3H, Ph), 4.3 (t, 2H, OCH\textsubscript{2}), 4.2 (q, 2H, PhOCH\textsubscript{2}), 3.9 (s, 3H, PhOCH\textsubscript{3}), 1.8 (m, 2H, OCH\textsubscript{2}CH\textsubscript{2}), 1.5 (t, 3H, PhOCH\textsubscript{2}CH\textsubscript{3}), 1.0 (t, 3H, OCH\textsubscript{2}CH\textsubscript{2}CH\textsubscript{3}); \textsuperscript{13}C-NMR \(\delta\) 163 (C=O), 155 (HC=), 154, 149, 128, 125, 113, 111 (Ph), 116 (CN), 99 (C=), 68 (OCH\textsubscript{2}), 65 (PhOCH\textsubscript{2}), 56 (PhOCH\textsubscript{3}), 22 (OCH\textsubscript{2}CH\textsubscript{2}), 15 (PhOCH\textsubscript{2}CH\textsubscript{3}), 10 (OCH\textsubscript{2}CH\textsubscript{2}CH\textsubscript{3}); IR (cm\textsuperscript{-1}): 3054-2767 (m, C-H), 2229 (m, CN), 1722 (s, C=O), 1592 (s, C=C), 1248 (s, C-O-C), 838, 797 (s, C-H out of plane). Anal. Calcd. for C\textsubscript{16}H\textsubscript{19}NO\textsubscript{4}: C, 66.42; H, 6.62; N, 4.84; Found: C, 66.31; H, 6.57; N, 4.87.
3.13 Isopropyl 2-cyano-3-(3,4-dibenzyloxyaryl)acrylate

Yield 97%; mp 93°C, $^1$H-NMR $\delta$ 8.1 (s, 1H, CH=), 7.9-6.9 (m, 13H, Ph), 5.3 (d, 4H, OCH$_2$Ph), 4.3 (t, 2H, OCH$_2$), 1.8 (m, 2H, OCH$_2$CH$_2$), 1.0 (t, 3H, OCH$_2$CH$_2$CH$_3$); $^{13}$C-NMR $\delta$ 163 (C=O), 155 (HC=), 153, 149, 136, 129, 128, 127, 125 (Ph), 115 (CN), 100 (C=), 71 (PhCH$_2$O), 68 (OCH$_2$), 21 (OCH$_2$CH$_2$), 10 (OCH$_2$CH$_2$CH$_3$); IR (cm$^{-1}$): 3015-8265 (m, C-H), 2243 (m, CN), 1593 (s, C=C), 1726 (s, C=O), 1269 (s, C-O-C), 982, 862 (s, C-H out of plane). Anal. Calcd. for C$_{27}$H$_{25}$NO$_4$: C, 75.86; H, 5.89; N, 3.28; Found: C, 75.65; H, 5.88; N, 3.23.

3.14 Isopropyl 2-cyano-3-(3-benzyloxy-4-methoxyaryl)acrylate

Yield 68%; mp 113°C, $^1$H-NMR $\delta$ 8.1 (s, 1H, CH=), 7.9-6.9 (m, 8H, Ph), 5.2 (s, 2H, Ph OCH$_2$), 4.3 (t, 2H, OCH$_2$), 4.0 (s, 3H, PhOCH$_3$), 1.7 (m, 2H, OCH$_2$CH$_2$), 1.0 (t, 3H, OCH$_2$CH$_2$CH$_3$); $^{13}$C-NMR $\delta$ 163 (C=O), 152 (HC=), 155, 148, 136, 129, 128, 127, 125, 111 (Ph), 114 (CN), 99 (C=), 71 (PhOCH$_2$), 68 (OCH$_2$), 56 (PhOCH$_3$), 21 (OCH$_2$CH$_2$), 10 (OCH$_2$CH$_2$CH$_3$); IR (cm$^{-1}$): 3042-2878 (m, C-H), 2241 (m, CN), 1729 (s, C=O), 1592 (s, C=C), 1276 (s, C-O-C), 829, 745 (s, C-H out of plane). Anal. Calcd. for C$_{21}$H$_{21}$NO$_4$: C, 71.78; H, 6.02; N, 3.99; Found: C, 72.09; H, 6.11; N, 4.14.

3.15 Isopropyl 2-cyano-3-(4-benzyloxy-3-methoxyaryl)acrylate

Yield 68%; mp 108.9°C, $^1$H-NMR $\delta$ 8.1 (s, 1H, CH=), 7.9-6.9 (m, 8H, Ph), 5.3 (s, 2H, Ph OCH$_2$), 4.3 (t, 2H, OCH$_2$), 4.0 (s, 3H, PhOCH$_3$), 1.8 (m, 2H, OCH$_2$CH$_2$), 1.0 (t, 3H, OCH$_2$CH$_2$CH$_3$); $^{13}$C-NMR $\delta$ 163 (C=O), 153 (HC=), 155, 150, 136, 129, 128, 127, 125, 113, 112 (Ph), 114 (CN), 100 (C=), 71 (PhOCH$_2$), 68 (OCH$_2$), 56 (PhOCH$_3$), 22
(OCH₂CH₂), 10 (OCH₂CH₂CH₃); IR (cm⁻¹): 3069-2812 (m, C-H), 2234 (m, CN), 1742 (s, C=O), 1565 (s, C=C), 1246 (s, C-O-C), 845, 723 (s, C-H out of plane). Anal. Calcd. for C₂₁H₂₁NO₄: C, 71.78; H, 6.02; N, 3.99; Found: C, 71.77; H, 6.04; N, 3.99.

3.16 Isopropyl 2-cyano-3-(2,3-dimethyl-4-methoxyaryl)acrylate
Yield 72%; mp 146.1°C, ¹H-NMR δ 8.6 (s, 1H, CH=), 8.1-6.8 (m, 2H, Ph), 5.3 (m, 1H, OCH), 3.8 (s, 3H, OCH₃), 2.3, 2.0 (s, 6H, PhCH₃), 1.3 (d, 6H, CH₃); ¹³C-NMR δ 160 (C=O), 153 (HC=), 145, 138, 121, 117 (Ph), 115 (CN), 108 (C=), 69 (OCH), 55 (CH₃O) 21 (CH₃), 16 (PhCH₃); IR (cm⁻¹): 3188-2838 (m, C-H), 2234 (m, CN), 1736 (s, C=O), 1601 (s, C=C), 1266 (s, C-O-C), 768, 699 (s, C-H out of plane). Anal. Calcd. for C₁₆H₁₉NO₃: C, 70.31; H, 7.01; N, 5.12; Found: C, 69.96; H, 7.13; N, 5.18.

3.17 Isopropyl 2-cyano-3-(2,5-dimethyl-4-methoxyaryl)acrylate
Yield 83%; mp 120.7°C, ¹H-NMR δ 8.4 (s, 1H, CH=), 8.1-6.6 (m, 2H, Ph), 5.2 (m, 1H, OCH), 3.7 (s, 3H, OCH₃), 2.3, 2.0 (s, 6H, PhCH₃), 1.3 (d, 6H, CH₃); ¹³C-NMR δ 168 (C=O), 157 (HC=), 145, 133, 128, 126 (Ph), 115 (CN), 105 (C=), 71 (OCH), 59 (CH₃O) 22 (CH₃), 19 (PhCH₃); IR (cm⁻¹): 3183-2812 (m, C-H), 2236 (m, CN), 1731 (s, C=O), 1623 (s, C=C), 1265 (s, C-O-C), 776, 693 (s, C-H out of plane). Anal. Calcd. for C₁₆H₁₉NO₃: C, 70.31; H, 7.01; N, 5.12; Found: C, 69.75; H, 7.25; N, 5.18.

3.18 Isopropyl 2-cyano-3-(2,4-dimethoxy-3-methylaryl)acrylate
Yield 78%; mp 117.4°C, ¹H-NMR δ 8.5 (s, 1H, CH=), 8.2-6.7 (m, 2H, Ph), 5.1 (m, 1H, OCH), 3.8, 3.6 (s, 6H, OCH₃), 2.0 (s, 3H, PhCH₃), 1.3 (d, 6H, CH₃); ¹³C-NMR δ 163 (C=O), 150 (HC=), 161, 162, 150, 129, 120, 118 (Ph), 116 (CN), 109 (C=), 71 (OCH),
64, 57 (CH₃O) 21 (CH₃), 16 (PhCH₃); IR (cm⁻¹): 3132-2812 (m, C-H), 2218 (m, CN), 1717 (s, C=O), 1571 (s, C=C), 1278 (s, C-O-C), 781, 676 (s, C-H out of plane). Anal. Calcd. for C₁₆H₁₉NO₄: C, 66.42; H, 6.62; N, 4.84; Found: C, 66.70; H, 6.73; N, 4.87.

3.19 Isopropyl 2-cyano-3-(2,4-dimethoxy-6-methylaryl)acrylate

Yield 91%; mp 102.3°C; ¹H-NMR δ 8.3 (s, 1H, CH=), 7.3 (m, 2H, Ph), 5.1 (m, 1H, OCH), 3.8, 3.7 (s, 6H, OCH₃), 2.3 (s, 3H, PhCH₃), 1.3 (d, 6H, CH₃O); ¹³C-NMR δ 161 (C=O), 151 (HC=), 160, 150, 141, 120, 118 (Ph), 116 (CN), 96 (C=), 70 (OCH), 55, 54 (CH₃O) 21 (CH₃), 19 (PhCH₃); IR (cm⁻¹): 3122-2811 (m, C-H), 2227 (m, CN), 1700 (s, C=O), 1565 (s, C=C), 1291 (s, C-O-C), 786, 687 (s, C-H out of plane). Anal. Calcd. for C₁₆H₁₉NO₄: C, 66.42; H, 6.62; N, 4.84; Found: C, 65.74; H, 6.91; N, 4.81.

3.20 Isopropyl 2-cyano-3-(3,5-dimethoxy-4-hydroxyaryl)acrylate

Yield 83%; mp 156.0°C; ¹H-NMR δ 8.1 (s, 1H, CH=), 7.3 (s, 2H, Ph), 5.1 (m, 1H, OCH), 3.8 (s, 6H, OCH₃), 1.3 (d, 6H, CH₃); ¹³C-NMR δ 163 (C=O), 151 (HC=), 143, 135, 128 (Ph), 115 (CN), 100 (C=), 87 (OCH), 57 (CH₃O), 21 (CH₃); IR (cm⁻¹): 3012-2822 (m, C-H), 2232 (m, CN), 1716 (s, C=O), 1575 (s, C=C), 1267 (s, C-O-C), 789, 689 (s, C-H out of plane). Anal. Calcd. for C₁₅H₁₇NO₅: C, 61.85; H, 5.88; N, 4.81; Found: C, 62.04; H, 6.17; N, 4.81.

3.21 Isopropyl 2-cyano-3-(4-hydroxy-3,5-dimethyl-4-hydroxyaryl)acrylate

Yield 74%; mp 201.6°C; ¹H-NMR δ 8.2 (s, 1H, CH=), 7.3 (s, 2H, Ph), 5.1 (m, 1H, OCH), 2.2 (s, 6H, CH₃), 1.3 (d, 6H, CH₃); ¹³C-NMR δ 166 (C=O), 153 (HC=), 161, 126, 125, 123 (Ph), 115 (CN), 100 (C=), 67 (OCH), 22 (CH₃), 16 (PhCH₃); IR (cm⁻¹): 3022-2834
(m, C-H), 2236 (m, CN), 1721 (s, C=O), 1585 (s, C=C), 1256 (s, C-O-C), 792, 676 (s, C-H out of plane). Anal. Calcd. for C_{15}H_{17}NO_{3}: C, 69.48; H, 6.61; N, 5.40; Found: C, 69.63; H, 6.89; N, 5.50.

4. Copolymerization

Copolymers of the styrene (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 conversion of the copolymers was kept between 10 and 20% to minimize compositional drift (Table 1). Since ICAA monomers do not homopolymerize, the most likely structure of the copolymers would be short styrene 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-phenoxy, 4-phenoxy, 2-benzylxoy, 3-benzylxoy, 4-benzylxoy, 4-acetyl xoy, 3-acetyl, 4-acetyl, 4-acetamino, 4-methoxy-2-methyl, 4-methoxy-3-methyl, 3-
ethoxy-4-methoxy, 3,4-dibenzyloxy, 3-benzyloxy-4-methoxy, 4-benzyloxy-3-methoxy, 2,3-dimethyl-4-methoxy, 2,5-dimethyl-4-methoxy, 2,4-dimethoxy-3-methyl, 2,4-dimethoxy-6-methyl, 3,5-dimethoxy-4-hydroxy.

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<th>R</th>
<th>Yield&lt;sup&gt;a&lt;/sup&gt; wt%</th>
<th>N wt%</th>
<th>ICAA in pol., mol%</th>
<th>M&lt;sub&gt;W&lt;/sub&gt; kD</th>
<th>T&lt;sub&gt;g&lt;/sub&gt; ºC</th>
<th>Onset of decomp. 10% wt loss, ºC</th>
<th>50% wt loss, ºC</th>
<th>Residue at 500ºC, wt%</th>
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</table>

*a*Conditions: ST/ICAA: 3 (mol) / Toluene / 70°C / 5 hrs.*
5. Structure and Thermal Properties

The structure of ST-ICAA copolymers was characterized by IR and NMR spectroscopy. A comparison of the spectra of the monomers, copolymers and polystyrene shows, that the reaction between the trisubstituted ethylenes and styrene is a copolymerization. IR spectra of the copolymers show overlapping bands in 3300-2700 cm\(^{-1}\) region corresponding to C-H stretch vibrations. The bands for the PCPP monomer unit are 2242-2227 (w, CN), 1742-1726 (s, C=O), and 1252-1227 cm\(^{-1}\) (m, C-O). Benzene rings of both monomers show ring stretching bands at 1512-1468 and 1523-1461 cm\(^{-1}\) as well as a doublet 786-671 cm\(^{-1}\), associated with C-H out of plane deformations. These bands can be readily identified in styrene copolymers with trisubstituted ethylene monomers containing cyano and carbonyl electron withdrawing groups [19-42].

The \(^1\)H-NMR spectra of the ST-ICAA copolymers show a broad double peak in a 6.0-8.0 ppm region corresponding to phenyl ring protons. A resonance at 4.3-3.8 ppm is assigned to the methoxy and methyleneoxy protons of ICAA monomer unit. A broad resonance at 3.9-2.1 ppm is assigned to the methyl and methine protons of ICAA, and methine and methylene protons of ST monomer unit close to the propenoate unit, which are more subjected to deshielding than the ones in polystyrene. The low and high field components of the signal are associated with ICAA monomer unit in head-to-tail and head-to-head structures. A broad resonance peak in 0.9-2.2 ppm range is attributed to the methine and methylene protons of styrene monomer sequences, as well as to alkyl ester and alkyl-Ph protons of ICAA. The \(^{13}\)C-NMR spectra also support the suggested skeletal structure of the copolymers. Thus, the assignment of the peaks is as follows: 164-160 ppm (C=O), 156-130
ppm (quaternary carbons of both phenyls), 143-120 ppm (phenyl carbons), 118-112 ppm (CN), 60-50 ppm (methine, quaternary carbons and alkoxy ICAA carbons), 47-45 ppm (ST methine), and 44-40 ppm (ST methylene), 36-14 ppm alkyl carbons of ICAA. 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 molecular weights were measured by GPC in THF. According to GPC analysis the copolymers had weight-average molecular masses 24.8 to 64.3 kD (Table 1).

All the copolymers were amorphous and show no crystalline DSC endotherm on repeated heating and cooling cycles. 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 was observed for all the copolymers with values 84-154°C. 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 247-500°C range with residue (2-11% 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.

**Conclusions**

Novel trisubstituted ethylenes, oxy ring-substituted isopropyl cyanoarylacylates were prepared and copolymerized with styrene. The compositions of the 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 two steps,
first in the 247-500°C range with residue (2-11%wt), which then decomposed in the 500-800°C range.

Acknowledgments

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