Synthesis and copolymerization of novel oxy ring-substituted 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-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, $R^1PhCH = C(CN)CO_2R^2$ 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 cyclopropanes [6], in synergistic $NaBH_4$ 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].

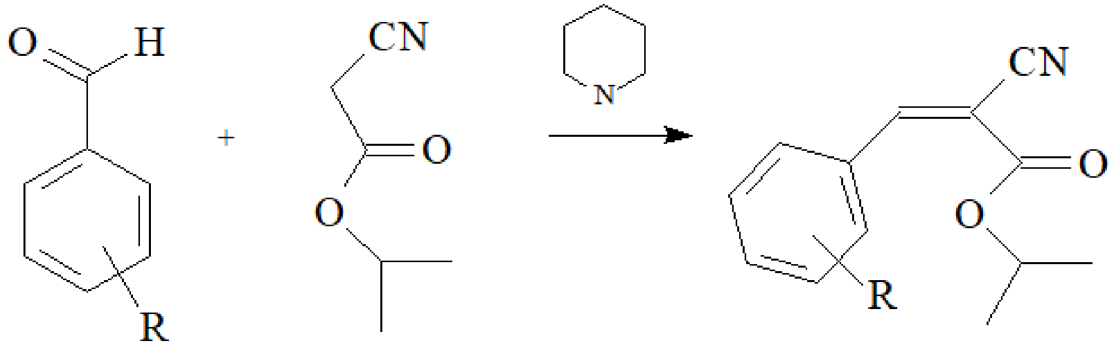
We have reported earlier synthesis and styrene copolymerization of oxy ring-substituted methyl [19-24], ethyl [25-27], propyl [28-31], butyl [32-34], isobutyl [35-37], methoxyethyl [38,39], and octyl [40-42] cyanoarylacrylates. In continuation of our exploration of novel trisubstituted ethylene compounds we have prepared isopropyl oxy ring-substituted cyanoarylacrylates, ICAA, $RPhCH=C(CN)CO_2CH(CH_3)_2$, 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, 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-benzyloxy, 3-benzyloxy, 4-benzyloxy, 4-acetoxy, 3-acetyl, 4-acetyl (90%), 4-acetamido (97%), 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-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 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-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.

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: δ 8.2 (s, 1H, CH=), 8.0-7.1 (m, 9H, Ph), 5.2 (m, 1H, C$\underline{\text{H}}$), 1.4 (d, 6H, CH_3); ^{13}C-NMR: δ 167 (C=O), 154 (HC=), 158, 157, 132, 130, 127, 123, 118, 114 (Ph), 116 (CN), 104 (C=), 68 (O$\underline{\text{C}}$H), 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: δ 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: δ 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 δ 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 δ 167 (C=O), 152 (HC=), 137, 131, 130, 129, 128, 127, 122, 112 (Ph), 116 (CN), 111 (C=), 71 (OCH_2), 68 (OCH), 22 ($\underline{C}H_3$); 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 δ 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, $C\underline{H}_3$); ^{13}C-NMR δ 166 (C=O), 154 (HC=), 159, 137, 133, 130, 129, 128, 127, 114 (Ph), 116 (CN), 104 (C=), 70 (CH_2), 68 ($\underline{C}H$), 22 ($\underline{C}H_3$); 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 δ 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 δ 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 δ 8.2 (s, 1H, CH=), 8.1-7.0 (d, 4H, Ph), 5.2 (m, 1H, CH), 2.4 (s, 3H, CH_3CO_2), 1.3 (d, 6H, $OCHC\underline{H}_3$); ^{13}C-NMR δ 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-$OCO\underline{C}H_3$); 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 $C_{15}H_{15}NO_4$: 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 δ 8.5 (s, 1H, CH=), 8.4-7.0 (m, 4H, Ph), 5.2 (m, 1H, CH), 2.7 (s, 3H, CH_3CO), 1.2 (d, 2H, CH_3); ^{13}C-NMR δ 197 (O=CCH_3) 166 (C=O), 154 (HC=), 137, 134, 129, 125 (Ph), 116 (CN), 104 (C=), 68 (CH), 26 (CH_3CO), 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 $C_{15}H_{15}NO_3$: 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 δ 8.3 (s, 1H, CH=), 8.1 (s, 4H, Ph), 5.3 (m, 1H, CH), 2.7 (s, 3H, CH_3CO), 1.4 (d, 6H, CH_3); ^{13}C-NMR δ 197 ($O{=}CCH_3$) 166 (C=O), 154 (HC=), 142, 131, 129, 125 (Ph), 116 (CN), 104 (C=), 68 (OCH), 26 ($\underline{C}H_3CO$), 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 δ 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_3CO), 1.3 (d, 6H, CH_3); ^{13}C-NMR δ 169 (NHC=O), 166 (C=O), 154 (HC=), 151, 134, 121, 119 (Ph), 116 (CN), 96 (C=), 68 (CH), 24 (CH_3CO), 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 $C_{15}H_{16}N_2O_3$: 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-methylaryl)acrylate

Yield 88%; mp 66.8°C, ^{1}H-NMR δ 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, $OCH_2C\underline{H}_2$), 1.0 (t, 3H, $OCH_2CH_2CH_2C\underline{H}_3$); ^{13}C-NMR δ 163 (C=O), 152 (HC=), 143, 131, 123, 112 (Ph), 115 (CN), 100 (C=), 68 ($O\underline{C}H_2$), 56 ($PhOCH_3$), 22 ($OCH_2\underline{C}H_2$), 21 ($PhCH_3$), 10 ($OCH_2CH_2\underline{C}H_3$); 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 $C_{15}H_{17}NO_3$: 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°C, ^{1}H-NMR δ 8.1 (s, 1H, CH=), 7.9-6.7 (m, 3H, Ph), 4.2 (t, 2H, OCH_2), 3.9 (s, 3H, $PhOCH_3$), 2.2 (s, 3H, $PhCH_3$), 1.8 (m, 2H, $OCH_2C\underline{H}_2$), 1.0 (t, 3H, $OCH_2CH_2C\underline{H}_3$); ^{13}C-NMR δ 163 (C=O), 155 (HC=), 133, 132, 128, 124 (Ph), 116 (CN), 99 (C=), 68 ($O\underline{C}H_2$), 56 ($PhOCH_3$), 22 ($OCH_2\underline{C}H_2$), 16 ($PhCH_3$), 10 ($OCH_2CH_2\underline{C}H_3$); IR (cm^{-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 $C_{15}H_{17}NO_3$: 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°C, ^{1}H-NMR δ 8.2 (s, 1H, CH=), 7.9-6.8 (m, 3H, Ph), 4.3 (t, 2H, OCH_2), 4.2 (q, 2H, $PhOC\underline{H}_2$), 3.9 (s, 3H, $PhOCH_3$), 1.8 (m, 2H, $OCH_2C\underline{H}_2$), 1.5 (t, 3H, $PhOCH_2C\underline{H}_3$), 1.0 (t, 3H, $OCH_2CH_2C\underline{H}_3$); ^{13}C-NMR δ 163 (C=O), 155 (HC=), 154, 149, 128, 125, 113, 111 (Ph), 116 (CN), 99 (C=), 68 (OCH_2), 65 ($PhO\underline{C}H_2$), 56 ($PhOCH_3$), 22 ($OCH_2\underline{C}H_2$), 15 ($PhOCH_2\underline{C}H_3$), 10 ($OCH_2CH_2\underline{C}H_3$); IR (cm^{-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 $C_{16}H_{19}NO_4$: C, 66.42; H, 6.62; N, 4.84; Found: C, 66.31; H, 6.57; N, 4.87.

3.13 Isoropyl 2-cyano-3-(3,4-dibenzyloxyaryl)acrylate

Yield 97%; mp 93°C, ^{1}H-NMR δ 8.1 (s, 1H, CH=), 7.9-6.9 (m, 13H, Ph), 5.3 (d, 4H, OCH_2Ph), 4.3 (t, 2H, OCH_2), 1.8 (m, 2H, $OCH_2C\underline{H}_2$), 1.0 (t, 3H, $OCH_2CH_2C\underline{H}_3$); ^{13}C-NMR δ 163 (C=O), 155 (HC=), 153, 149, 136, 129, 128, 127, 125 (Ph), 115 (CN), 100 (C=), 71 ($PhCH_2O$), 68 (OCH_2), 21 ($OCH_2\underline{C}H_2$), 10 ($OCH_2CH_2\underline{C}H_3$); 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 δ 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, $OCH_2C\underline{H}_2$), 1.0 (t, 3H, $OCH_2CH_2C\underline{H}_3$); ^{13}C-NMR δ 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 ($OCH_2\underline{C}H_2$), 10 ($OCH_2CH_2\underline{C}H_3$); 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 δ 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, $OCH_2C\underline{H}_2$), 1.0 (t, 3H, $OCH_2CH_2C\underline{H}_3$); ^{13}C-NMR δ 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

(OCH$_2\underline{C}H_2$), 10 (OCH$_2$CH$_2\underline{C}H_3$); 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 $C_{21}H_{21}NO_4$: 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, ^{1}H-NMR δ 8.6 (s, 1H, CH=), 8.1-6.8 (m, 2H, Ph), 5.3 (m, 1H, OCH), 3.8 (s, 3H, OCH$_3$), 2.3, 2.0 (s, 6H, PhCH$_3$), 1.3 (d, 6H, CH$_3$); ^{13}C-NMR δ 160 (C=O), 153 (HC=), 145, 138, 121, 117 (Ph), 115 (CN), 108 (C=), 69 (OCH), 55 (CH$_3$O) 21 (CH$_3$), 16 (PhCH$_3$); 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 $C_{16}H_{19}NO_3$: 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, ^{1}H-NMR δ 8.4 (s, 1H, CH=), 8.1-6.6 (m, 2H, Ph), 5.2 (m, 1H, OCH), 3.7 (s, 3H, OCH$_3$), 2.3, 2.0 (s, 6H, PhCH$_3$), 1.3 (d, 6H, CH$_3$); ^{13}C-NMR δ 168 (C=O), 157 (HC=), 145, 133, 128, 126 (Ph), 115 (CN), 105 (C=), 71 (OCH), 59 (CH$_3$O) 22 (CH$_3$), 19 (PhCH$_3$); 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 $C_{16}H_{19}NO_3$: 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, ^{1}H-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, OCH$_3$), 2.0 (s, 3H, PhCH$_3$), 1.3 (d, 6H, CH$_3$); ^{13}C-NMR δ 163 (C=O), 150 (HC=), 161, 162, 150, 129, 120, 118 (Ph), 116 (CN), 109 (C=), 71 (OCH), 64, 57 (CH_3O) 21 (CH_3), 16 ($PhCH_3$); 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 $C_{16}H_{19}NO_4$: 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, ^{1}H-NMR δ 8.3 (s, 1H, CH=), 7.3 (m, 2H, Ph), 5.1 (m, 1H, OCH), 3.8, 3.7 (s, 6H, OCH_3), 2.3 (s, 3H, $PhCH_3$), 1.3 (d, 6H, CH_3); ^{13}C-NMR δ 161 (C=O), 151 (HC=), 160, 150, 141, 120, 118 (Ph), 116 (CN), 96 (C=), 70 (OCH), 55, 54 (CH_3O) 21 (CH_3), 19 ($PhCH_3$); 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 $C_{16}H_{19}NO_4$: 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

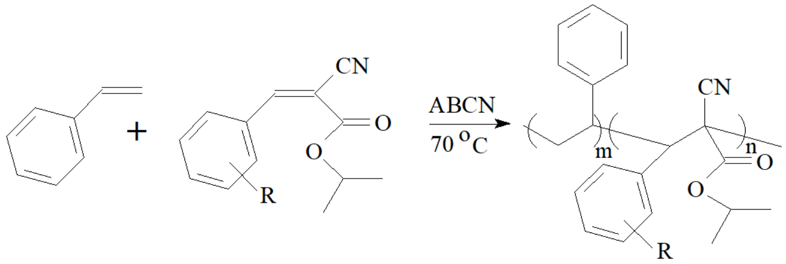
Yield 83%; mp 156.0°C, ^{1}H-NMR δ 8.1 (s, 1H, CH=), 7.3 (s, 2H, Ph), 5.1 (m, 1H, OCH), 3.8 (s, 6H, OCH_3), 1.3 (d, 6H, CH_3); ^{13}C-NMR δ 163 (C=O), 151 (HC=), 143, 135, 128 (Ph), 115 (CN), 100 (C=), 87 (OCH), 57 (CH_3O), 21 (CH_3); IR (cm^{-1}): 3012-2822 (m, C-H), 2232 (m, CN), 1716 (s, C=O), 1575 (s, C=C), 1267 (s, C-O-C), 789, 689 (s, C-H out of plane). Anal. Calcd. for $C_{15}H_{17}NO_5$: 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, ^{1}H-NMR δ 8.2 (s, 1H, CH=), 7.3 (s, 2H, Ph), 5.1 (m, 1H, OCH), 2.2 (s, 6H, CH_3), 1.3 (d, 6H, CH_3); ^{13}C-NMR δ 166 (C=O), 153 (HC=), 161, 126, 125, 123 (Ph), 115 (CN), 100 (C=), 67 (OCH), 22 (CH_3), 16 ($PhCH_3$); 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 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 (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-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.

						TGA			
R	Yield[a] wt%	N wt%	ICAA in pol., mol%	M_W kD	T_g °C	Onset of decomp. °C	10% wt loss, °C	50 % wt loss , °C	Residue at 500°C, wt%
3-C_6H_5O	14.1	2.39	27.2	41.2	116	217	285	358	3
4-C_6H_5O	10.2	2.48	28.8	38.8	154	218	268	367	2
2-$C_6H_5CH_2O$	11.3	2.27	26.0	32.1	137	219	294	342	3
3-$C_6H_5CH_2O$	15.3	2.44	29.2	41.9	123	212	291	364	3
4-$C_6H_5CH_2O$	12.3	2.19	24.6	34.9	110	240	298	377	2
4-CH_3COO	14.1	2.15	24.8	29.5	136	218	289	350	4
3-CH_3CO	10.7	2.53	26.0	59.1	136	214	285	390	4
4-CH_3CO	10.4	2.64	27.6	64.3	129	225	282	342	2
3-CH_3CONH	11.4	3.82	18.4	39.0	129	210	296	381	3
4-CH_3O-2-CH_3	14.4	2.94	32.4	24.8	110	159	247	345	3
4-CH_3O-3-CH_3	12.1	2.22	21.9	30.2	128	274	314	357	4

3-C_2H_5O-4-CH_3O	16.8	2.58	29.1	31.0	83	242	312	358	4
3,4-$(PhCH_2O)_2$	17.2	1.94	26.2	42.0	88	234	317	356	2
3-$PhCH_2O$-4-CH_3O	12.8	2.08	24.4	35.1	114	270	329	366	9
4-$PhCH_2O$-3-CH_3O	14.3	1.99	22.8	42.8	117	244	317	354	11
2,3-Dimethyl-4-methoxy	12.2	3.3	40.7	53.2	109	145	234	332	2.0
2,5-Dimethyl-4-methoxy	15.2	3.49	44.8	62.7	112	172	247	338	4.1
2,4-Dimethoxy-3-methyl	17.1	2.62	29.8	64.2	113	165	277	345	3.4
2,4-Dimethoxy-6-methyl	13.2	3.23	41.9	63.2	104	156	248	335	1.6
3,5-Dimethoxy-4-hydroxy	10.6	2.55	28.7	55.4	132	233	268	330	6.8
4-Hydoxy-3,5-dimethyl	14.4	2.54	40.7	52.3	110	199	252	339	5.7

[a] Conditions: ST/ICAA: 3 (mol) / Toluene / 70ºC / 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 $CHCl_3$ 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 84-154ºC. 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 247-500ºC range with residue (2-11% wt), which then decomposed in the 500-800ºC 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 cyanoarylacrylates 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 247-500°C range with residue (2-11%wt), which then decomposed in the 500-800ºC range.

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