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Synthesis and copolymerization of novel oxy ring-substituted isopropyl cyanoarylacrylates

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Abstract
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-acetoxy, 3-acetyl, 4-acetyl, 4-acetamido) 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, ^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 200-500ºC 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 trisubstituted ethylenes, esters of 2-cyano-3-arylacrylic acid, $R^1PhCH = C(CN)CO_2R^2$ have found various applications as functional compounds in organic and polymer synthesis. Thus phenoxy (R^1) ring substituted ethyl (R^2) ester of 2-cyano-3-arylacrylic acid (ECAA) was used in synthesis of tetrazoles compounds that possessed a rich variety of binding and bridging modes [1]. This ECAA was a product of Knoevenagel 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]. 4-Phenoxy ECAA was employed in DBU-mediated [4 + 2] annulations of donor-acceptor cyclopropanes for the synthesis of fully substituted anilines [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, biological evaluation and molecular modeling studies 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]. Alkyl 2-cyanoacrylates are a family of vinyl monomers renowned for their high reactivity, instant adhesive properties, and wide-ranging applications [15]. Thus isopropyl cyanoacrylate was involved in the polymer synthesis of semipermeable membrane microcapsules [16] and in a fundamental study of fissure sealant in dental application [17].

With the objective to design unique structures, that could serve as a spring board for further development of novel compounds and materials with new properties and applications we have reported synthesis and styrene copolymerization of oxy ring-substituted methyl [18-21], ethyl [22, 23], propyl [24, 25], and butyl [26, 27] cyanoarylacrylates. 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, $RPh\ CH=C(CN)CO_2CH(CH_3)_2$, where R is 3-phenoxy, 4-phenoxy, 2-benzyloxy, 3-benzyloxy, 4-benzyloxy, 4-acetoxy, 3-acetyl, 4-acetyl, 4-acetamido, 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-Phenoxy (≥99%), 4-phenoxy (≥96.5%), 2-benzyloxy (97%), 3-benzyloxy (97%), 4-benzyloxy (97%), 4-acetoxy (95%), 3-acetyl (≥98%), 4-acetyl (90%), 4-acetamido (97%) benzaldehydes, isopropyl cyanoacetate (≥98.0%), piperidine (99%), styrene (≥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 150ºC range on second heat at heating rate of 10ºC/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 800ºC at 20ºC/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 5µ Linear column at 25ºC and Viscotek 302 RI detector. ^{1}H and ^{13}C-NMR spectra were obtained on 10-25% (w/v) ICAA or polymer solutions in $CDCl_3$ 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 [28] of appropriate benzaldehydes with isopropyl cyanoacetate, catalyzed by base, piperidine (fig 1).

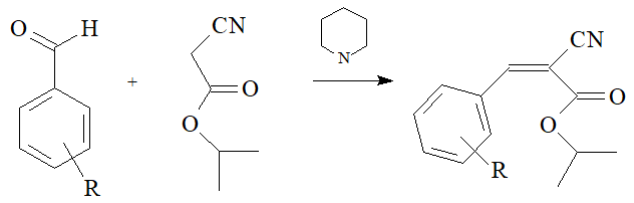

Fig 1: Synthesis of isopropyl 2-cyano-3-(R-aryl) acrylates where R is 3-phenoxy, 4-phenoxy, 2-benzyloxy, 3-benzyloxy, 4-benzyloxy, 4-acetoxy, 3-acetyl, 4-acetyl, 4-acetamido.

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}H and ^{13}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-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<u>H</u>), 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<u>C</u>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.

3.1.2 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.

3.1.3 Isopropyl 2-cyano-3-(2-henylmethoxyaryl) 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 (<u>C</u>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.

3.1.4 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<u>H</u>$_3$); ^{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 (<u>C</u>H), 22 (<u>C</u>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.

3.1.5 Isopropyl 2-cyano-3-(4-henylmethoxyaryl) 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.

3.1.6 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<u>H</u>$_3$); ^{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<u>C</u>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.

3.1.7 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.

3.1.8 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.

3.1.9 Propyl 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.

3.2. 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 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 compounds were characterized by nitrogen elemental analysis, FTIR, ^{1}H and ^{13}C-NMR spectroscopies.

3.2.1 Styrene – isopropy l2 – cyano – 3 -(3- phenoxyaryl) acrylate copolymer

Yield 12%; ^{1}H-NMR: δ 7.4-6.8 (Ph), 5.2-5.0 (OCH), 3.5-0.2 (CH), 1.6-1.5 (CH_2), 1.3-1.2 (CH_3); ^{13}C-NMR: δ 173-168 (C=O), 158-117 (Ph), 118-116 (CN), 72-70 (OCH), 60-34 (CH), 37-32 (CH_2), 25-19 (CH_3); IR: (cm^{-1}) 3150-2800 (m, C-H), 2236 (m, CN), 1754 (s, C=O), 1256 (s, C-O-CH_3), 753 (s, C-H out of plane). Anal. for N, 2.39.

3.2.2 Styrene - isopropyl 2-cyano-3-(4-phenoxyaryl) acrylate copolymer

Yield: 14%; ^{1}H-NMR: δ 7.5-6.7 (Ph), 5.2-4.9 (OCH), 3.6-0.4 (CH), 1.3-1.1 (CH_3); ^{13}C-NMR: δ 173-168 (C=O), 158-117 (Ph), 118-116 (CN), 72-70 (OCH), 60-34 (CH), 37-32 (CH_2), 25-19 (CH_3); FTIR: (cm^{-1}) 3152-2825 (m, C-H), 2231 (m, CN), 1734 (s, C=O), 1267 (s, C-O-CH_3), 754, 698 (s, C-H out of plane). Anal. calcd. for N, 2.48.

3.2.3 Styrene – isopropyl 2-cyano-3-(2-phenylmethoxyaryl) acrylate copolymer

Yield 11%; ^{1}H-NMR δ 7.8-6.8 (Ph), 5.3-4.8 (OCH, OCH_2), 3.6-0.3 (CH), 1.3-1.1 (CH_3); ^{13}C-NMR: δ 172-166 (C=O), 159-118 (Ph), 118-116 (CN), 74-64 (OCH, OCH_2), 61-35 (CH), 38-33 (CH_2), 26-18 (CH_3); FTIR (cm^{-1}): 3105-2851 (m, C-H), 2244 (m, CN), 1738 (s, C=O), 1265 (s, C-O-CH_3), 754, 698 (s, C-H out of plane). Anal. Calcd. for N, 2.27.

3.2.4 Styrene - isopropyl 2 – cyano – 3 - (3 - phenylmethoxyaryl) acrylate copolymer

Yield 12%; ^{1}H-NMR δ 7.7-6.7 (Ph), 5.2-4.6 (OCH, OCH_2), 3.5-0.2 (CH), 1.3-1.1 (CH_3); ^{13}C-NMR: δ 172-166 (C=O), 159-118 (Ph), 118-116 (CN), 74-64 (OCH, OCH_2), 61-35 (CH), 38-33 (CH_2), 26-18 (CH_3); FTIR (cm^{-1}): 3200-2800 (m, C-H), 2240 (m, CN), 1736 (s, C=O), 1261 (s, C-O-CH_3), 735, 698 (s, C-H out of plane). Anal. Calcd. for N, 2.44.

3.2.5 Styrene - isopropyl 2 – cyano – 3 - (4-phenylmethoxyaryl) acrylate copolymer

Yield 16%; ^{1}H-NMR δ 7.9-6.5 (Ph), 5.3-4.8 (OCH, OCH_2), 3.6-0.3 (CH); ^{13}C-NMR: δ 173-165 (C=O), 156-119 (Ph), 118-116 (CN), 73-62 (OCH, OCH_2), 59-34 (CH), 38-32 (CH_2), 27-19 (CH_3); FTIR (cm^{-1}): 3172-2822 (m, C-H), 2231 (m, CN), 1732 (s, C=O), 1265 (s, C-O-CH_3), 737, 698 (s, C-H out of plane). Anal. Calcd. for N, 2.19.

3.2.6 Styrene - isopropyl 2-cyano-3-(4-acetoxyaryl) acrylate copolymer

Yield 8%; ^{1}H-NMR δ 7.3-6.5 (Ph), 5.3-4.8 (OCH), 3.6-0.3 (CH, CH_2), 2.2-2.0 (CH_3O), 1.3-1.1 (CH_3); ^{13}C-NMR: δ 172-165 (C=O), 151-119 (Ph), 117-115 (CN), 72-62 (OCH), 57-32 (CH), 36-31 (CH_2), 28-17 (CH_3); FTIR (cm^{-1}): 3200-2800 (m, C-H), 2244 (m, CN), 1736 (s, C=O), 1203 (s, C-O-CH_3), 772, 698 (s, C-H out of plane). Anal. Calcd. for N, 2.15.

3.2.7 Styrene - isopropyl 2-cyano-3-(3-acetylaryl) acrylate copolymer

Yield 12%; ^{1}H-NMR δ 7.3-6.7 (Ph), 5.1-4.9 (OCH), 3.5-0.4 (CH, CH_2), 2.2 (CH_3C=O), 1.3-1.1 (CH_3); ^{13}C-NMR: δ 173-168 (C=O), 151-121 (Ph), 119-116 (CN), 72-62 (OCH), 57-34 (CH), 38-33 (CH_2), 28-17 (CH_3); FTIR (cm^{-1}): 3026-2812 (m, C-H), 2239 (m, CN), 1738 (s, C=O), 1281 (s, C-O-CH_3), 697 (s, C-H out of plane). Anal. Calcd. for N, 2.53.

3.2.8 Styrene - isopropyl 2-cyano-3-(4-acetylaryl) acrylate copolymer

Yield 13%; ^{1}H-NMR δ 7.4-6.8 (Ph), 5.2-4.7 (OCH), 3.4-0.3 (CH, CH_2), 2.2-2.0 (CH_3C=O), 1.3-1.0 (CH_3); ^{13}C-NMR: δ 172-167 (C=O), 152-120 (Ph), 118-116 (CN), 71-62 (OCH), 58-34 (CH), 36-31 (CH_2), 27-17 (CH_3); FTIR (cm^{-1}): 3175-2851 (m, C-H), 2244 (m, CN), 1734 (s, C=O), 1276 (s, C-O-CH_3), 908 (s, C-H out of plane). Anal. Calcd. for N, 2.64.

3.2.9 Styrene - isopropyl 2-cyano-3-(4-acetamidoaryl) acrylate copolymer

Yield 12%; ^{1}H-NMR δ 9.5-8.9 (NH), 7.7-7.1 (Ph), 5.2-4.9 (OCH), 3.6-0.5 (CH, CH_2), 2.2 (CH_3C=O), 1.3-1.1 (CH_3); ^{13}C-NMR: δ 173-167 (C=O), 147-120 (Ph), 118-116 (CN), 72-62 (OCH), 57-32 (CH), 37-33 (CH_2), 27-17 (CH_3); FTIR (cm^{-1}): 3062-2814 (m, C-H), 2240 (m, CN), 1735 (s, C=O), 1222 (s, C-O-CH_3), 758 (s, C-H out of plane). Anal. Calcd. for N, 3.82.

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 18.4 and 29.2 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 which is typical of oxy ring-substituted ICAA [18-27]. 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) (fig 2).

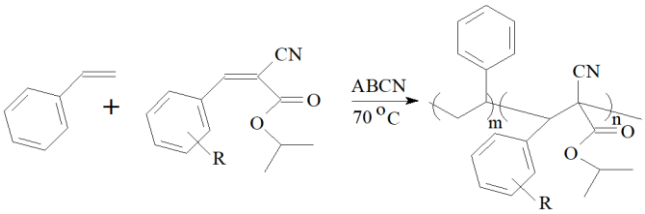

Fig 2: Copolymerization of ST and the ring-substituted isopropyl 2-cyano-3-(R-aryl) acrylates. R is 3-phenoxy, 4-phenoxy, 2-benzyloxy, 3-benzyloxy, 4-benzyloxy, 4-acetoxy, 3-acetyl, 4-acetyl, 4-acetamido.

Table 1: Molecular characteristics of P(ST-co-ICAA) copolymers[a].

R	Nitrogen wt%	% mole ST	% mole ICAA	$1/r_1$	M_W[b] kD
3-C_6H_5O	2.39	72.8	27.2	1.79	41.2
4-C_6H_5O	2.48	71.2	28.8	2.03	38.8
2-$C_6H_5CH_2O$	2.27	74.0	26.0	1.63	32.1
3-$C_6H_5CH_2O$	2.44	70.8	29.2	2.10	41.9
4-$C_6H_5CH_2O$	2.19	75.4	24.6	1.46	34.9
4-CH_3COO	2.15	75.2	24.8	1.48	29.5
3-CH_3CO	2.53	74.0	26.0	1.62	59.1
4-CH_3CO	2.64	72.4	27.6	1.84	64.3
3-CH_3CONH	3.82	81.6	18.4	0.87	39.0

[a] Conditions: ST/ICAA: 3 (mol) / Toluene / 70ºC / 5 hrs. [b]by GPC in THF

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 29.5 to 64.3 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 [29].

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

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, $r_1 = k_{ST\text{-}ST}/k_{ST\text{-}ICAA}$ and $r_2 = k_{ICAA\text{-}ICAA}/k_{ICAA\text{-}ST}$. In the absence of self-propagation of ICAA monomers ($k_{ICAA\text{-}ICAA} = 0$, $r_2 = 0$), 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 $1/r_1 = k_{ST\text{-}ICAA}/k_{ST\text{-}ST}$ 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-$C_6H_5CH_2O$ (2.10) > 4-C_6H_5O (2.03) > 4-CH_3CO (1.84) > 3-C_6H_5O (1.79) > 2-$C_6H_5CH_2O$ (1.63) > 3-CH_3CO (1.62) > 4-CH_3COO (1.48) > 4-$C_6H_5CH_2O$ (1.46) > 3-CH_3CONH (0.87). These ratios signify that most ICAA monomers are slightly more reactive than styrene in the addition to a ST-ended polymer radical. The above reactivities of isopropyl cyanoarylacrylates are slightly higher than those of propyl cyanoarylacrylates [24, 25] where the order of relative reactivity ($1/r_1$) decrease as follows: 3-CH_3CO (2.83) > 3-$C_6H_5CH_2O$ (1.59) > 4-CH_3COO (1.48) > 2-$C_6H_5CH_2O$ (1.16) > 4-$C_6H_5CH_2O$ (0.92) > 4-CH_3CONH (0.51).

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 (104ºC).

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

		TGA			
R	**T_g ºC**	**Onset of decomp., ºC**	**10% wt loss, ºC**	**50% wt loss, ºC**	**Residue at 500 ºC, wt%**
3-C_6H_5O	116	217	285	358	2.5
4-C_6H_5O	154	218	268	367	2.0
2-$C_6H_5CH_2O$	137	219	294	342	3.1
3-$C_6H_5CH_2O$	123	212	291	364	2.7
4-$C_6H_5CH_2O$	110	240	298	377	1.9
4-CH_3COO	136	218	289	350	3.5
3-CH_3CO	136	214	285	390	3.7
4-CH_3CO	129	225	282	342	2.1
3-CH_3CONH	129	210	296	381	2.9

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 250-500ºC range with residue (2-4% 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.

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 500-800ºC range.

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