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Synthesis and styrene copolymerization of novel methoxy and methyl ring-trisubstituted isopropyl cyanophenylacrylates

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Abstract
Novel methoxy and methyl ring-trisubstituted isopropyl 3-phenyl-2-cyanoacrylates, RPhCH=C (CN) CO_2 CH $(CH_3)_2$ (where R is 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,
4-hydoxy-3, 5-dimethyl) were prepared and copolymerized with styrene. The acrylates were synthesized by the piperidine catalyzed Knoevenagel condensation of ring-disubstituted benzaldehydes and isopropyl cyanoacetate and characterized by CHN elemental analysis, IR, ^{1}H- 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 IR, ^{1}H and ^{13}C-NMR, GPC, DSC, and TGA.

Keywords: phenyl cyanoacrylates, knoevenagel condensation, radical copolymerization, styrene copolymers

1. Introduction
Ring–functionalized cyanoacrylates (PCA), R^1PhCH=C (CN) CO_2R^2 continue to attract attention as compounds with interesting properties, organic intermediates, and as comonomers for modification of polymers. Earlier we have prepared and copolymerized methoxy and methyl ring-trisubstituted methyl (1, 2), propyl (3), and butyl (4) cyanoacrylates. Recently we have reported synthesis and styrene copolymerization of a number of novel alkyl (5), alkoxy (6), mono ring-substituted as well as dimethyl and dimethoxy (7) ring-disubstituted isopropyl phenyl cyanoacrylates. With the objective to design novel structures, that could serve as a spring board for further development of novel materials with new properties and applications, we have prepared novel methoxy and methyl ring-trisubstituted isopropyl phenylcyanoacrylates, $RPhCH=C(CN)CO_2CH(CH_3)_2$ where R is 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, 4-hydoxy-3,5-dimethyl, and explore the feasibility of their copolymerization with styrene. To the best of our knowledge (8), there have been no reports on either synthesis of these isopropyl 3-phenyl-2-cyanoacrylates, nor their copolymerization with styrene.

2. Experimental
2.1. Materials
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, 4-hydoxy-3,5-dimethylbenzaldehydes, isopropyl cyanoacetate, piperidine, styrene, 1,1'-azobiscyclohexanecarbonitrile, (ABCN), and toluene supplied from Sigma-Aldrich Co., were used as received.

2.2. Instrumentation
Infrared spectra of the TSE monomers and polymers (NaCl plates) were determined with an ABB FTLA 2000 FT-IR spectrometer. The melting points of the monomers, the glass transition temperatures (T_g), of the copolymers were measured with TA (Thermal Analysis, Inc.) Model Q10 differential scanning calorimeter (DSC). The thermal scans were performed in a 25 to 200ºC range 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. 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 detector. ^{1}H- and ^{13}C-NMR spectra were obtained on 10-25% (w/v) monomer or polymer solutions in $CDCl_3$ at ambient temperature using Avance 300 MHz spectrometer. Elemental analyses were performed by Midwest Microlab, LLC (IN).

2.3. Synthesis of methoxy and methyl ring-trisubstituted isopropyl phenylcyanoacrylates
The methoxy and methyl ring-trisubstituted isopropyl phenylcyanoacrylates (IPCA) were synthesized by Knoevenagel condensation (9) of a ring-trisubstituted benzaldehyde with isopropyl cyanoacetate, catalyzed by base, piperidine.

$RPhCHO + NCCH_2CO_2CH(CH_3)_2 \rightarrow RPhCH = C(CN)CO_2CH(CH_3)_2$

Where R is 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, 4-hydoxy-3, 5-dimethyl. The preparation procedure was essentially the same for all the monomers. In a typical synthesis, equimolar amounts of isopropyl cyanoacetate and an appropriate ring-trisubstituted benzaldehyde were mixed in equimolar ratio in a 20 mL vial. A few drops of piperidine were added with stirring.

The product of the reaction was isolated by filtration and purified by crystallization from 2-propanol. The condensation reaction proceeded smoothly, yielding products, which were purified by conventional techniques.

2.3.1. Isopropyl 3-(2, 3-dimethyl-4-methoxyphenyl)-2-cyanoacrylate

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_3O) 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.

2.3.2. Isopropyl 3-(2, 5-dimethyl-4-methoxyphenyl)-2-cyanoacrylate

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_3O) 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.

2.3.3. Isopropyl 3-(2, 4-dimethoxy-3-methylphenyl)-2-cyanoacrylate

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.

2.3.4. Isopropyl 3-(2, 4-dimethoxy-6-methylphenyl)-2-cyanoacrylate

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.

2.3.4. Isopropyl 3-(3, 5-dimethoxy-4-hydroxyphenyl)-2-cyanoacrylate

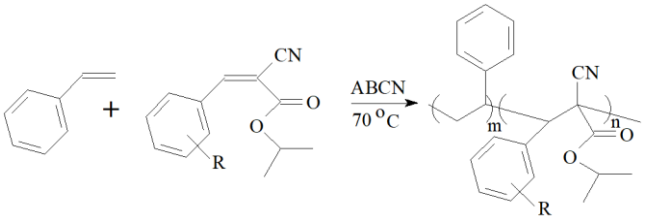
Yield 83%; mp 156.0°C, ^{1}H-NMR δ 8.1 (s, 1H, CH=), 7.3 (s, 2H, Ph), 5.1 (m, 1H, OCH), 3.8 (s, 6H, OCH_3), 1.3 (d, 6H, CH_3); ^{13}C-NMR δ 163 (C=O), 151 (HC=), 143, 135, 128 (Ph), 115 (CN), 100 (C=), 87 (OCH), 57 (CH_3O), 21 (CH_3); IR (cm^{-1}): 3012-2822 (m, C-H), 2232 (m, CN), 1716 (s, C=O), 1575 (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.

2.3.5. Isopropyl 3-(4-hydroxy-3, 5-dimethyl-4-hydroxyphenyl)-2-cyanoacrylate

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.

2.4. Copolymerization

Copolymers of the ST and the IPCA monomers were prepared in 25-mL glass screw cap vials at ST/ IPCA = 3 (mol) the monomer feed using 0.12 mol/L of ABCN at an overall monomer concentration 2.44 mol/L in 10 mL of toluene. The copolymerization was conducted at 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 copolymers' yield was kept low to minimize copolymer compositional drift at given conversion.



Scheme 1: ST-IPCA copolymer synthesis, R = 2-chloro-4-fluoro, 2-chloro-6-fluoro, 3-chloro-2-fluoro, 3-chloro-4-fluoro, 4-chloro-3-fluoro.

2.4.1. ST- Isopropyl 3-(2,3-dimethyl-4-methoxyphenyl)-2-cyanoacrylate Copolymer

Yield 12.2%; ^{1}H-NMR δ 7.6-6.7 (Ph), 5.4-4.8 (OCH), 3.9-3.7 (OCH_3), 2.4-2.0 ($PhCH_3$), 3.7-2.8 (CHPh), 2.5-2.1 (CH, IPCA), 1.8-1.4 (CH_2), 1.2-1.0 (CH_3); ^{13}C-NMR δ 166-160 (C=O), 159-124 (Ph), 117-116 (CN), 78-73 (OCH), 55-53 (CH_3O), 48-33 (CH_2), 45-38 (CHPh, ST), 35-30 (CH, IPCA), 23-21 (CH_3), 17-15 ($PhCH_3$); IR (cm^{-1}): 3250-2550 (m, C-H), 2247 (m, CN), 1751 (s, C=O), 1264 (s, C-O-C), 752, 672 (s, C-H out of plane). Anal. for N (wt%) 3.30.

2.4.2. ST- Isopropyl 3-(2,5-dimethyl-4-methoxyphenyl)-2-cyanoacrylate Copolymer

Yield 15.2%; ^{1}H-NMR δ 7.5-6.3 (Ph), 5.3-4.8 (OCH), 3.8-3.6 (OCH_3), 2.3-2.0 ($PhCH_3$), 3.6-2.9 (CHPh), 2.6-2.2 (CH, IPCA), 1.8-1.5 (CH_2), 1.2-1.0 (CH_3); ^{13}C-NMR δ 167-162 (C=O), 160-123 (Ph), 117-116 (CN), 78-74 (OCH), 56-54 (CH_3O), 48-36 (CH_2), 44-38 (CHPh, ST), 36-32 (CH, IPCA), 23-21 (CH_3), 16-15 ($PhCH_3$); IR (cm^{-1}): 3255-2551 (m, C-H), 2246 (m, CN), 1750 (s, C=O), 1253 (s, C-O-C), 756, 674 (s, C-H out of plane). Anal. for N (wt%) 3.49.

2.4.3. ST- Isopropyl 3-(2,4-dimethoxy-3-methyphenyl)-2-cyanoacrylate Copolymer

Yield 17.1%; ^{1}H-NMR δ 7.8-6.7 (Ph), 5.5-4.8 (OCH), 3.9-3.6 (OCH_3), 2.4-2.1 ($PhCH_3$), 3.8-2.7 (CHPh), 2.4-2.2 (CH, IPCA), 1.8-1.5 (CH_2), 1.3-1.0 (CH_3); ^{13}C-NMR δ 165-161 (C=O), 157-120 (Ph), 117-116 (CN), 77-73 (OCH), 56-51

(CH_3O), 48-34 (CH_2), 45-37 (CHPh, ST), 35-31 (CH, IPCA), 24-22 (CH_3), 18-15 ($PhCH_3$); IR (cm^{-1}): 3251-2542 (m, C-H), 2242 (m, CN), 1749 (s, C=O), 1258(s, C-O-C), 746 (s, C-H out of plane). Anal. for N (wt%) 2.62.

2.4.4. ST- Isopropyl 3-(2,4-dimethoxy-6-methylphenyl)-2-cyanoacrylate Copolymer

Yield 13.2%; ^{1}H-NMR δ 7.6-6.7 (Ph), 5.4-4.8 (OCH), 3.9-3.7 (OCH_3), 2.4-2.0 ($PhCH_3$), 3.7-2.8 (CHPh), 2.5-2.1 (CH, IPCA), 1.8-1.4 (CH_2), 1.2-1.0 (CH_3); ^{13}C-NMR δ 165-160 (C=O), 157-124 (Ph), 117-116 (CN), 78-74 (OCH), 55-52 (CH_3O), 49-33 (CH_2), 45-38 (CHPh, ST), 34-31 (CH, IPCA), 23-20 (CH_3), 17-15 ($PhCH_3$); IR (cm^{-1}): 3111-2609 (m, C-H), 2245 (m, CN), 1759 (s, C=O), 1282 (s, C-O-C), 782, 658 (s, C-H out of plane). Anal. for N (wt%) 3.23.

2.4.5. ST- Isopropyl 3-(3,5-dimethoxy-4-hydroxyphenyl)-2-cyanoacrylate Copolymer

Yield 10.6%; ^{1}H-NMR δ 7.7-6.6 (Ph), 5.4-4.7 (OCH), 3.8-3.5 (OCH_3), 3.7-2.6 (CHPh), 2.4-2.2 (CH, IPCA), 1.7-1.5 (CH_2), 1.3-1.0 (CH_3); ^{13}C-NMR δ 167-164 (C=O), 153-118 (Ph), 117-116 (CN), 78-74 (OCH), 55-51 (CH_3O), 48-34 (CH_2), 46-37 (CHPh, ST), 36-32 (CH, IPCA), 24-21 (CH_3); IR (cm^{-1}): 3091-2600 (m, C-H), 2232 (m, CN), 1745 (s, C=O), 1263(s, C-O-C), 823, 748 (s, C-H out of plane). Anal. for N (wt%) 2.55.

2.4.6. ST- Isopropyl 3-(4-hydroxy-3,5-dimethyphenyl)-2-cyanoacrylate Copolymer

Yield 14.1%; ^{1}H-NMR δ 7.7-6.5 (Ph), 5.4-4.7 (OCH), 3.8-2.7 (CHPh), 2.4-2.1 ($PhCH_3$, CH, IPCA), 1.7-1.5 (CH_2), 1.3-1.0 (CH_3); ^{13}C-NMR δ 164-162 (C=O), 155-120 (Ph), 117-116 (CN), 77-74 (OCH), 48-34 (CH_2, CHPh, ST), 35-31 (CH, IPCA), 24-22 (CH_3), 18-16 ($PhCH_3$); IR (cm^{-1}): 3151-2802 (m, C-H), 2241 (m, CN), 1747 (s, C=O), 1245 (s, C-O-C), 752, 674 (s, C-H out of plane). Anal. for N (wt%) 2.54.

Copolymerization (Sch. 1) of methoxy and methyl ring-trisubstituted IPCA with ST resulted in formation of copolymers (Table 1) with weight-average molecular masses 62.4 to 73.7 kD. According to elemental analysis, between 29.0 and 31.3 mol% of IPCA monomer is present in the copolymers prepared at ST/ IPCA = 3 (mol), which is indicative of relatively high reactivity of the monomers towards ST. The copolymers prepared in the present work are all soluble in ethyl acetate, THF, DMF and $CHCl_3$ and insoluble in methanol, ethyl ether, and petroleum ether.

Table 1: Copolymerization of methoxy and methyl ring-trisubstituted isopropyl phenyl cyanoacrylates with styrene.

						TGA			
R	**Yield[a] (Wt %)**	**N (Wt %)**	**M2 in copol. (Mol %)**	**Mw (kD)**	**T_g (ºC)**	**Onset of decomp. (ºC)**	**10 wt% loss (ºC)**	**50 wt% loss (ºC)**	**Residue wt%**
2,3-Dimethyl-4-methoxy	12.2	3.3	40.7	53.2	109.2	145	234	332	2.0
2,5-Dimethyl-4-methoxy	15.2	3.49	44.8	62.7	112.1	172	247	338	4.1
2,4-Dimethoxy-3-methyl	17.1	2.62	29.8	64.2	113.7	165	277	345	3.4
2,4-Dimethoxy-6-methyl	13.2	3.23	41.9	63.2	104.0	156	248	335	1.6
3,5-Dimethoxy-4-hydroxy	10.6	2.55	28.7	55.4	132.3	233	268	330	6.8
4-Hydoxy-3,5-dimethyl	14.4	2.54	40.7	52.3	109.9	199	252	339	5.7

[a]Polymerization time was 8 h.

The ST- IPCA copolymers are amorphous and show no crystalline DSC endotherm. Results of thermal analysis of ST- IPCA copolymers are presented in Table 1. Information on the degradation of the copolymers was obtained from thermogravimetric analysis. Decomposition of the copolymers in nitrogen occurred in two steps, first in the 200-500ºC range with residue (5.2-6.1% wt.), which then decomposed in the 500-800ºC range.

4. Conclusions

Novel isopropyl chloro and fluoro ring-substituted cyanophenylacrylates were prepared and copolymerized with styrene. The compositions of novel 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 200-500°C range with a residue, which then decomposed in the 500-800ºC range.

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