Synthesis and styrene copolymerization of novel ring-substituted isopropyl and isobutyl phenylcyanoacrylates

Christopher R. Savittieri, Alessandra Cimino, Ashley M. Johnson, Christopher M. Myslicki, Molly R. Nealon, Derek J. O'Neill, Aisha Patel, Kayla F. Quebral, Alec S. Seng, Kat N. Shishido, Jennifer N. Stamos, Atharva A. Shinde, Sara M Rocus, William S. Schjerven, and Gregory B. Kharas

DePaul University, Chemistry and Biochemistry Department, 1110 West Belden Avenue, Chicago, IL 60614-3214

Abstract

Novel ring-substituted isopropyl phenylcyanoacrylates, RPhCH=C(CN)$CO_2CH(CH_3)_2$ (where R is 2-chloro-4-fluoro, 2-chloro-6-fluoro, 3-chloro-2-fluoro, 3-chloro-4-fluoro, 4-chloro-3-fluoro) and isobutyl phenylcyanoacrylates, RPhCH=C(CN)$CO_2CH_2CH(CH_3)_2$ (where R is 2-methoxy, 3-methoxy, 4-methoxy, 2-ethoxy, 3-ethoxy, 4-ethoxy, 4-propoxy, 4-butoxy, 4-hexyloxy) 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.

Keywords: Phenyl cyanoacrylates, Knoevenagel condensation, radical copolymerization, styrene copolymers

* CONTACT: Gregory B. Kharas, Chemistry and Biochemistry Department, DePaul University, Chicago, IL 60614-3214. E-mail: gkharas@depaul.edu

1. Introduction

Alkyl cyanoacrylates is family of vinyl monomers renowned for their high reactivity, instant adhesive properties, and wide-ranging applications [1–3]. Trisubstituted ethylenes (TSE), ring–functionalized (R^1) alkyl (R^2) phenylcyanoacrylates, $R^1PhCH = C(CN)CO_2R^2$ (PCA) continue to attract attention as compounds with variety of applications [4-11]. Thus, 2-methoxy ring-substituted methyl PCA was used in pyrrolizinone synthesis through functionalized C-alkylpyrroles [4], as well as in molecular design for enhanced second-order nonlinear optical response [5, 6]. 3-Methoxy ring-substituted methyl PCA was employed in diastereoselective syntheses of polysubstituted cyclohexanes and cyclopentenes via chemoselective phosphine-catalyzed cascade annulations [7] and in enhancement of the hyperpolarizability of styrene [8]. Propyl PCA with 4-methoxy ring-substitution was reported in metal-free synthesis of cyanoacrylates via cyanuric chloride-mediated reactions

[9] and in technology related to antenna dyes [10]. 4-Propoxy propyl PCA was used in MgO-based catalyzed Knoevenagel reaction [11].

In regards to polymerization reactivity, previous studies showed that PCAs as all TSE monomers containing substituents larger than fluorine have very low reactivity in radical homopolymerization due to polar and steric reasons [12]. Although steric difficulties preclude homopolymerization of such monomers, their copolymerization with a monosubstituted alkenes makes it possible to overcome these steric problems. Thus, copolymerization of electrophylic TSE monomers having double bonds substituted with halo, cyano, and carbonyl groups and electron-rich monosubstituted ethylenes such as styrene, N-vinylcarbazole, and vinyl acetate [13-15] show a tendency toward the formation of alternating copolymers - thus suggesting a way of functionalization of commercial polymers via introduction of isolated monomer units in copolymers. Earlier we have reported synthesis and styrene copolymerization a number of alkoxy ring-substituted PCAs, such esters as methyl [16], ethyl [17], propyl [18], isopropyl [19], and butyl [20].
Our objectives in exploration of novel isopropyl and isobutyl phenylcyanoacrylates (IPCA) were twofold: (1) to utilize aldol condensation for synthesis of IPCA compounds with a variety of potentially reactive functional groups; (2) to employ conventional radical copolymerization with a commercial monomer styrene. Thus, in continuation of our investigation of novel TSE compounds we have prepared isopropyl phenylcyanoacrylates, $RPhCH=C(CN)CO_2CH(CH_3)_2$ where R is 2-chloro-4-fluoro, 2-chloro-6-fluoro, 3-chloro-2-fluoro, 3-chloro-4-fluoro, 4-chloro-3-fluoro, as well as isobutyl phenylcyanoacrylates, $RPhCH=C(CN)CO_2CH_2CH(CH_3)_2$, where R is 2-methoxy, 3-methoxy, 4-methoxy, 2-

ethoxy, 3-ethoxy, 4-ethoxy, 4-propoxy, 4-butoxy, 4-hexyloxy, and explore the feasibility of their copolymerization with styrene. To the best of our knowledge, there have been no reports on either synthesis of these phenylcyanoacrylates, nor their copolymerization with styrene.

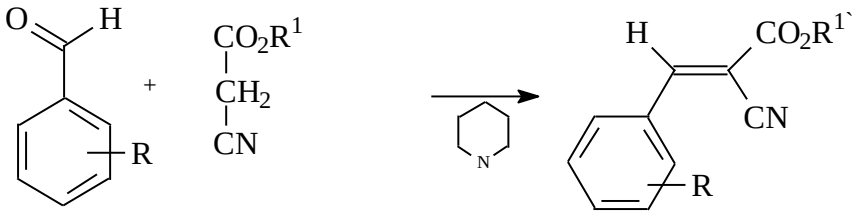
2. Experimental

2.1. 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).

2.2. Synthesis of phenylcyanoacrylates

The ring-disubstituted isopropyl and isobutyl phenylcyanoacrylates (IPCA) were synthesized by Knoevenagel condensation [21] of a ring-substituted benzaldehyde with isopropyl or isobutyl cyanoacetate, catalyzed by base, piperidine.



Scheme 1. Synthesis of R-phenylcyanoacrylates, where R^1 is isopropyl or isobutyl.

The preparation procedure was essentially the same for all the compounds. In a typical synthesis, equimolar amounts of the cyanoacetate and an appropriate ring-substituted 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.

2.2. Synthesis of isopropyl phenylcyanoacrylates

2.2.1. Isopropyl 3-(2-chloro-4-fluorophenyl)-2-cyanoacrylate

Yield 84%; mp 91.4°C, ^{1}H-NMR δ8.3 (s, 1H, CH=), 7.6-6.9 (m, 3H, Ph), 5.1 (m, 1H, OCH), 1.3 (d, 6H, CH_3); ^{13}C-NMR δ 166 (C=O), 150 (HC=), 166, 135, 131, 117, 114 (Ph), 116 (CN), 132 (C=), 68 (OCH), 22 (CH_3); IR (cm^{-1}): 3102-2834 (m, C-H), 2236 (m, CN), 1725 (s, C=O), 1585 (s, C=C), 1278 (s, C-O-C), 892, 775 (s, C-H out of

plane). Anal. Calcd. for $C_{13}H_{11}ClFNO_2$: C, 58.33; H, 4.14; N, 5.23; Found: C, 58.14; H, 4.33; N, 5.27.

2.2.2. Isopropyl 3-(2-chloro-6-fluorophenyl)-2-cyanoacrylate

Yield 92%; mp 121.2°C, ^{1}H-NMR δ8.4 (s, 1H, CH=), 7.6-7.0 (m, 3H, Ph), 5.1 (m, 1H, OCH), 1.3 (d, 6H, CH_3); ^{13}C-NMR δ 166 (C=O), 152 (HC=), 162, 135, 133, 126, 119, 116 (Ph), 115 (CN), 92 (C=), 68 (OCH), 22 (CH_3); IR (cm^{-1}): 3220-2805 (m, C-H), 2237 (m, CN), 1738 (s, C=O), 1577 (s, C=C), 1278 (s, C-O-C), 892, 752 (s, C-H out of plane). Anal. Calcd. for $C_{13}H_{11}ClFNO_2$: C, 58.33; H, 4.14; N, 5.23; Found: C, 52.17; H, 4.39; N, 5.00.

2.2.3. Isopropyl 3-(3-chloro-2-fluorophenyl)-2-cyanoacrylate

Yield 90%; mp 102.5°C, ^{1}H-NMR δ8.3 (s, 1H, CH=), 7.8.-7.1 (m, 3H, Ph), 5.1 (m, 1H, OCH), 1.3 (d, 6H, CH_3); ^{13}C-NMR δ 166 (C=O), 146 (HC=), 162, 129, 121, 120 (Ph), 116 (CN), 105 (C=), 68 (OCH), 22 (CH_3); IR (cm^{-1}): 3212-2826 (m, C-H), 2232 (m, CN), 1718 (s, C=O), 1587 (s, C=C), 1272 (s, C-O-C), 898, 781 (s, C-H out of plane). Anal. Calcd. for $C_{13}H_{11}ClFNO_2$: C, 58.33; H, 4.14; N, 5.23; Found: C, 57.75; H, 4.20; N, 5.19.

2.2.4. Isopropyl 3-(3-chloro-4-fluorophenyl)-2-cyanoacrylate

Yield 71%; mp 82.8°C, ^{1}H-NMR δ8.5 (s, 1H, CH=), 8.1-7.2 (m, 3H, Ph), 5.1 (m, 1H, OCH), 1.3 (d, 6H, CH_3); ^{13}C-NMR δ 166 (C=O), 152 (HC=), 160. 132, 130, 129, 129, 116 (Ph), 115 (CN), 103 (C=), 68 (OCH), 22 (CH_3); IR (cm^{-1}): 3232-2822 (m, C-H), 2233 (m, CN), 1720 (s, C=O), 1592 (s, C=C), 1262 (s, C-O-C), 891, 779 (s, C-H out of

plane). Anal. Calcd. for $C_{13}H_{11}ClFNO_2$: C, 58.33; H, 4.14; N, 5.23; Found: C, 55.96; H, 4.13; N, 5.16.

2.2.5. Isopropyl 3-(4-chloro-3-fluorophenyl)-2-cyanoacrylate

Yield 87%; mp 101.2°C, ^{1}H-NMR δ8.6 (s, 1H, CH=), 7.9-7.2 (m, 3H, Ph), 5.1 (m, 1H, OCH), 1.3 (d, 6H, CH_3); ^{13}C-NMR δ 166 (C=O), 153 (HC=), 159, 133, 130 (Ph), 116 (CN), 104 (C=), 68 (OCH), 22 (CH_3); IR (cm^{-1}): 3301-2845 (m, C-H), 2232 (m, CN), 1737 (s, C=O), 1581 (s, C=C), 1266 (s, C-O-C), 987, 843 (s, C-H out of plane). Anal. Calcd. for $C_{13}H_{11}ClFNO_2$: C, 58.33; H, 4.14; N, 5.23; Found: C, 58.47; H, 4.29; N, 5.9.

2.3. Synthesis of isobutyl phenylcyanoacrylates

2.3.1. ***Isobutyl 2-methoxyphenylcyanoacrylate***

Yield: 73.6%; mp 74.5°C; ^{1}H NMR: δ8.8 (s, 1H, CH=), 8.3-6.9 (m, 4H, Ph), 4.2 (d, 2H, CH_2), 3.9 (s, 3H, CH_3O), 2.1 (m, 1H, CH), 1.0 (d, 6H, CH_3); ^{13}C NMR: δ 163 (C=O), 155 (HC=), 134, 131, 130, 122 (Ph), 115 (CN), 111 (C=), 73 (CH_2), 63 (OCH_3), 28 (CH), 20 (CH_3); FTIR: (cm^{-1}) 3004-2822 (m, C-H), 2218 (m, CN), 1724 (s, C=O), 1587 (s, C=C), 1288 (s, C-O-CH_3), 754, 752 (s, C-H out of plane). Anal. calcd. for $C_{15}H_{16}NO_3$: C, 69.75; H, 6.24; N, 5.42; Found: C, 68.76; H, 6.76; N, 5.63.

2.3.2. ***Isobutyl 3-methoxyphenylcyanoacrylate***

Yield 84%; ^{1}H NMR δ8.2 (s, 1H, CH=), 7.6-7.0 (m, 4H, Ph), 4.1 (d, 2H, CH_2), 3.9 (s, 3H, CH_3O), 2.1 (m, 1H, CH), 1.0 (d, 6H, CH_3); ^{13}C NMR δ 163 (C=O), 155 (HC=), 150, 138, 133, 128, 124, 120, 119 (Ph), 115 (CN), 103 (C=), 72, 69 (CH_2), 56 (OCH_3), 31, 27

(CH), 19 (CH_3); IR (cm^{-1}): 2143 (m, CN), 1740 (s, C=O), 1670, 1474 (C=C), 1223 (s, C-O-CH_3), 882, 788 (s, C-H out of plane). Anal. Calcd. for $C_{15}H_{16}NO_3$: C, 69.75; H, 6.24; N, 5.42; Found: C, 67.44; H, 6.27; N, 5.66.

2.3.3. ***Isobutyl 4-methoxyphenylcyanoacrylates***

Yield 83%; mp 79.4°C; ^{1}H NMR δ8.2 (s, 1H, CH=), 8.0-7.0 (m, 4H, Ph), 4.1 (d, 2H, CH_2), 3.9 (s, 3H, CH_3O), 2.1 (m, 1H, CH), 1.0 (d, 6H, CH_3); ^{13}C NMR δ 164 (C=O), 155 (HC=), 150, 138, 134, 124, 119 (Ph), 116, 115 (CN), 99 (C=), 73 (CH_2), 56 (OCH_3), 28 (CH), 19 (CH_3); IR (cm^{-1}): 2961, 2937 (m, C-H), 2221 (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 $C_{15}H_{16}NO_3$: C, 69.75; H, 6.24; N, 5.42; Found: C, 69.11; H, 6.94; N, 5.50.

2.3.4. ***Isobutyl 2-ethoxyphenylcyanoacrylate***

Yield 81%; mp 78.3°C; ^{1}H NMR δ8.8 (s, 1H, CH=), 8.3-6.8 (m, 4H, Ph), 4.1 (m, 2H, $CH_3C\underline{H}_2O$ & 2H, OCH_2), 2.1 (m, 1H, CH), 1.5 (t, 3H, CH_3), 1.0 (d, 6H, $(CH_3)_2$); ^{13}C NMR δ 163 (C=O), 159 (HC=), 135, 129, 121, 112 (Ph), 116 (CN), 102 (C=), 73 (CH_2), 65 ($CH_3\underline{C}H_2O$), 28 (CH), 19 $(CH_3)_2$, 14 ($\underline{C}H_3CH_2O$); IR (cm^{-1}): 2918 (m, C-H), 2222 (m, CN), 1707 (s, C=O), 1593 (s, C=C), 1248 (s, C-O-CH_3), 764 (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, 70.23; H, 7.10; N, 5.29.

2.3.5. ***Isobutyl 3-ethoxyphenylcyanoacrylates***

Yield 94%; mp 67.7°C; ^{1}H NMR δ8.2 (s, 1H, CH=), 7.6-7.0 (m, 4H, Ph), 4.1 (m, 2H, $CH_3C\underline{H}_2O$ & 2H, OCH_2), 2.1 (m, 1H, CH), 1.4 (t, 3H, CH_3), 1.0 (d, 6H, $(CH_3)_2$); ^{13}C NMR δ163 (C=O), 160 (HC=), 155, 132, 130, 124, 120 (Ph), 115 (CN), 103 (C=), 73

(CH_2), 64 ($CH_3\underline{C}H_2O$), 28 (CH), 19 $(CH_3)_2$, 15 ($\underline{C}H_3CH_2O$); IR (cm^{-1}): 2928 (m, C-H), 2221 (m, CN), 1728 (s, C=O), 1609 (s, C=C), 1277 (s, C-O-CH_3), 768, 762 (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, 68.96; H, 7.46; N, 5.35.

2.3.6. ***Isobutyl 4-ethoxyphenylcyanoacrylate***

Yield 76%; mp 79.3°C; ^{1}H NMR δ8.1 (s, 1H, CH=), 7.9-6.9 (m, 4H, Ph), 4.1 (m, 2H, $CH_3C\underline{H}_2O$ & 2H, OCH_2), 2.1 (m, 1H, CH), 1.4 (t, 3H, CH_3), 1.0 (d, 6H, $(CH_3)_2$); ^{13}C NMR δ163 (C=O), 155 (HC=), 133, 124 (Ph), 116 (CN), 99 (C=), 73 (CH_2), 64 ($CH_3\underline{C}H_2O$), 28 (CH), 19 $(CH_3)_2$, 15 ($\underline{C}H_3CH_2O$); IR (cm^{-1}): 2928-2878 (m, C-H), 2222 (m, CN), 1717 (s, C=O), 1560 (s, C=C), 1271 (s, C-O-CH_3), 841 (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, 69.14; H, 7.11; N, 5.20.

2.3.7. ***Isobutyl 4-propoxyphenylcyanoacrylate***

Yield 79%; mp 75.9°C; ^{1}H NMR δ8.2 (s, 1H, CH=), 8.1-6.9 (m, 4H, Ph), 4.1 (t, 2H, $CH_3CH_2C\underline{H}_2O$), 3.9 (d, 2H, CH_2O), 2.1 (m, 1H, CH), 1.8 (m, 2H, $CH_3C\underline{H}_2CH_2O$), 1.0 (m, 6H, $CH(C\underline{H}_3)_2$ & 3H, $C\underline{H}_3CH_2CH_2$); ^{13}C NMR δ 163 (C=O), 155 (HC=), 134, 124 (Ph), 115 (CN), 99 (C=), 73 ($CH_3CH_2\underline{C}H_2O$), 70 ($OCH_2$), 28 (CH) 23 ($CH_3\underline{C}H_2CH_2O$), 19 $(CH_3)_2$, 10 (CH_3); IR (cm^{-1}): 3035-2805 (m, C-H), 2217 (m, CN), 1717 (s, C=O), 1507 (C=C), 1271 (s, C-O-CH_3), 841 (s, C-H out of plane). Anal. Calcd. for $C_{17}H_{21}NO_3$: C, 71.06; H, 7.37; N, 4.87; Found: C, 71.08; H, 7.45; N, 4.99.

2.3.8. ***Isobutyl 4-butoxyphenylcyanoacrylates***

Yield 73; mp 56.9°C; ^{1}H NMR δ8.2 (s, 1H, CH=), 7.3, 7.0 (m, 4H, Ph), 4.1 (m, 2H, OCH_2 & 2H, $C_3H_7C\underline{H}_2O$), 2.2 (d, 1H, CH), 1.8 (m, 2H, $C_2H_5C\underline{H}_2CH_2O$), 1.5 (m, 2H, $CH_3C\underline{H}_2CH_2CH_2O$), 1.0 (d, 6H, $(CH_3)_2$ & (t, 3H, $C\underline{H}_3CH_2CH_2CH_2O$); ^{13}C NMR δ 164 (C=O), 155 (HC=), 134, 124 (Ph), 116 (CN), 99 (C=), 73 (CH), 68 ($C_3H_7\underline{C}H_2O$), 31 ($C_2H_5\underline{C}H_2CH_2O$), 19 $(CH_3)_2$, 19 ($CH_3\underline{C}H_2CH_2CH_2O$), 14 ($C\underline{H}_3CH_2CH_2CH_2O$); IR ($cm^{-1}$): 3034-2818 (m, C-H), 2222 (m, CN), 1728 (s, C=O), 1585 (C=C), 1256 (s, C-O-CH_3), 837 (s, C-H out of plane). Anal. Calcd. for $C_{18}H_{23}NO_3$: C, 71.73; H, 7.69; N, 4.65; Found: C, 70.59; H, 7.58; N, 4.75.

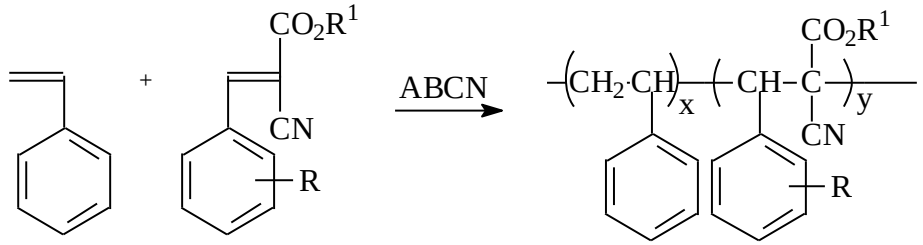
2.3.9. ***Isobutyl 4-hexyloxyphenylcyanoacrylate***

Yield 78.0%; mp 49.2°C; ^{1}H NMR δ8.2 (s, 1H, CH=), 8.0, 7.0 (m, 4H, Ph), 4.1 (m, 4H, $C_5H_{11}CH_2$ & CH_2O), 2.1 (m, 1H, CH), 1.8 (m, 2H, $C\underline{H}_2CH_2O$), 1.6 (m, 2H, $C\underline{H}_2CH_2CH_2O$), 1.3 (m, 4H, $C\underline{H}_2CH_2CH_2CH_2O$ & $C\underline{H}_2CH_2CH_2CH_2CH_2O$), 1.0 (d, 3H, CH_3 & t, 6H, $(CH_3)_2$); ^{13}C NMR δ 164 (C=O), 155 (HC=), 133, 124 (Ph), 115 (CN), 111 (C=), 73 ($C_5H_{11}CH_2O$), 69 ($\underline{C}H_2O$), 31-14 ($\underline{C}H_2CH_2CH_2CH_2O$ & $\underline{C}H_2CH_2O$ & $C\underline{H}_2CH_2CH_2O$ & ($CH_3\underline{C}H_2$) & $CH\underline{C}H_3$ & $\underline{C}H_3CH_2$ & $(CH_3)_3$; IR (cm^{-1}): 3063-2808 (m, C-H), 2222 (m, CN), 1724 (s, C=O), 1589 (C=C), 1266 (s, C-O-CH_3), 924 (s, C-H out of plane). Anal. Calcd. for $C_{20}H_{27}NO_3$: C, 72.92; H, 8.26; N, 4.25; Found: C, 71.93; H, 8.42; N, 4.30.

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 2. ST-IPCA copolymer synthesis, R = isopropyl or isobutyl

2.4.1. ST- Isopropyl 3-(2-chloro-4-fluorophenyl)-2-cyanoacrylate Copolymer

Yield 13.6%; ^{1}H-NMR δ 7.6-6.7 (Ph), 5.4-4.8 (OCH), 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), 48-33 (CH_2), 45-38 (CHPh, ST), 35-30 (CH, IPCA), 23-21 (CH_3); IR (cm^{-1}): 3823-2809 (m, C-H), 2244 (m, CN), 1738 (s, C=O), 1134 (s, C-O-C), 813, 747 (s, C-H out of plane). Anal. for N (wt%) 2.73.

2.4.2. ST- Isopropyl 3-(2-chloro-6-fluorophenyl)-2-cyanoacrylate Copolymer

Yield 11.2%; ^{1}H-NMR δ 7.7-6.4 (Ph), 5.1-4.7 (OCH), 3.8-2.6 (CHPh), 2.4-2.1 (CH, IPCA), 1.7-1.3 (CH_2), 1.2-1.0 (CH_3); ^{13}C-NMR δ 167-162 (C=O), 159-122 (Ph), 117-116 (CN), 75-71 (OCH), 46-33 (CH_2), 43-37 (CHPh, ST), 34-31 (CH, IPCA), 25-22

(CH_3); IR (cm^{-1}): 3500-2800 (m, C-H), 2241 (m, CN), 1739 (s, C=O), 1249 (s, C-O-C), 832, 777 (s, C-H out of plane). Anal. for N (wt%) 2.68.

2.4.3. ST- Isopropyl 3-(3-chloro-2-fluorophenyl)-2-cyanoacrylate Copolymer

Yield 13.4%; ^{1}H-NMR δ 7.9-6.6 (Ph), 5.1-4.8 (OCH), 3.8-2.6 (CHPh), 2.6-2.3 (CH, IPCA), 1.7-1.2 (CH_2), 1.5-1.2 (CH_3); ^{13}C-NMR δ 165-161 (C=O), 159-119 (Ph), 117-116 (CN), 76-72 (OCH), 47-35 (CH_2), 42-37 (CHPh, ST), 36-30 (CH, IPCA), 25-21 (CH_3); IR (cm^{-1}): 3843-2825 (m, C-H), 2245 (m, CN), 1747 (s, C=O), 1249 (s, C-O-C), 832, 749 (s, C-H out of plane). Anal. for N (wt%) 2.82.

2.4.4. ST- Isopropyl 3-(3-chloro-fluorophenyl)-2-cyanoacrylate Copolymer

Yield 11.6%; ^{1}H-NMR δ 7.9-6.3 (Ph), 5.3-4.8 (OCH), 3.7-2.7 (CHPh), 2.5-2.1 (CH, IPCA), 1.6-1.3 (CH_2), 1.3-1.1 (CH_3); ^{13}C-NMR δ 168-163 (C=O), 157-124 (Ph), 118-116 (CN), 76-71 (OCH), 47-36 (CH_2), 43-36 (CHPh, ST), 36-32 (CH, IPCA), 25-20 (CH_3); IR (cm^{-1}): 3834-2808 (m, C-H), 2243 (m, CN), 1743 (s, C=O), 1248 (s, C-O-C), 828, 748 (s, C-H out of plane). Anal. for N (wt%) 2.69.

2.4.5. ST- Isopropyl 3-(4-chloro-3-fluorophenyl)-2-cyanoacrylate Copolymer

Yield 17.6%; ^{1}H-NMR δ 7.9-6.6 (Ph), 5.5-4.9 (OCH), 3.9-2.7 (CHPh), 2.8-2.3 (CH, IPCA), 1.8-1.3 (CH_2), 1.4-1.0 (CH_3); ^{13}C-NMR δ 169-165 (C=O), 148-120 (Ph), 118-116 (CN), 76-73 (OCH), 47-35 (CH_2), 42-32 (CHPh, ST), 37-33 (CH, IPCA), 24-22 (CH_3); IR (cm^{-1}): 3832-2848 (m, C-H), 2241 (m, CN), 1742 (s, C=O), 1276 (s, C-O-C), 821, 781 (s, C-H out of plane). Anal. for N (wt%) 2.76.

Copolymerization (Sch. 1) of ring-substituted IPCA with ST resulted in formation of copolymers (Table 1 & 2). 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 isopropyl phenylcyanoacrylates with styrene.

						TGA			
R	Yield[a] (wt%)	N (wt%)	m_2 in copol. (mol%)	M_W (kD)	T_g (ºC)	Onset of decomp. (ºC)	10 wt% loss (ºC)	50 wt% loss (ºC)	Residue wt%
2-Chloro-4-fluoro	13.6	2.73	29.8	62.4	123	158	283	349	5.2
2-Chloro-6-fluoro	11.2	2.68	29.0	73.7	132	172	288	342	6.1
3-Chloro-2-fluoro	13.4	2.82	31.3	67.9	115	174	288	346	5.7
3-Chloro-4-fluoro	11.6	2.69	29.2	72.4	127	162	278	349	4.9
4-Chloro-3-fluoro	17.6	2.76	30.3	68.5	119	168	286	339	5.7

Table 2. Copolymerization of isobutyl phenylcyanoacrylates with styrene.

R	Conversion %	Nitrogen wt%	% mole ST	% mole IPCA	M_W kD
2-CH_3O	12.1	2.06	80.2	19.8	57.2
3-CH_3O	14.2	2.74	70.9	29.1	55.1
4-CH_3O	12.8	2.09	79.8	20.2	57.2
2-C_2H_5O	12.7	1.98	80.7	19.3	55.4
3-C_2H_5O	11.2	2.20	77.7	22.3	58.5
4-C_2H_5O	13.4	2.06	79.6	20.4	55.3
4-C_3H_7O	15.1	2.03	79.5	20.5	52.5
4-C_4H_9O	14.1	1.95	80.0	20.0	52.5
4-$C_6H_{13}O$	12.7	1.86	80.3	19.7	54.3

Table 3. DSC and TGA data for isobutyl P(ST-*co*-IPCA) copolymers.

R	T_g ºC	Onset of decomp., ºC	10% wt loss, ºC	50% wt loss, ºC	Residue at 500 ºC, wt%
2-CH_3O	136	233	307	337	1.8
3-CH_3O	128	221	317	345	3.2
4-CH_3O	137	243	300	334	3.3
2-C_2H_5O	129	252	305	339	2.1
3-C_2H_5O	128	243	303	335	2.5
4-C_2H_5O	128	251	304	338	3.0
4-C_3H_7O	135	243	308	342	2.7
4-C_4H_9O	117	252	302	337	3.0
4-$C_6H_{13}O$	107	233	303	339	3.3

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 and 2. 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 (4.9-6.1% wt.), which then decomposed in the 500-800ºC range.

4. Conclusions

Novel isopropyl and isobutyl 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.

Funding

The authors are grateful to acknowledge that the project was partly supported by the Chicago Society of Coating Technology (CSCT).

References

[1] Klemarczyk, P.; Guthrie, J. Advances in anaerobic and cyanoacrylate adhesives. In Advances in Structural Adhesive Bonding, 1st ed.; Dillard, D., Ed.; Woodhead Publishing Limited: Cambridge, UK, 2010; pp. 96–131, ISBN 978-1-84569-435-7.

[2] Shantha, K.L.; Thennarasu, S.; Krishnamurti, N. Developments and applications of cyanoacrylate adhesives. J. Adhes. Sci. Technol. 1989, 3, 237–260.

[3] J.M. Korde and B. Kandasubramanian, Biocompatible alkyl cyanoacrylates and their derivatives as bio-adhesives, Biomaterials Science, 10.1039/C8BM00312B, 6, 7, (1691-1711), (2018).

[4] Unaleroglu, C.; Tasgin, D.I.; Aytac, S.; Temelli, B. An efficient synthetic route for pyrrolizinone synthesis through functionalized C-alkylpyrroles. Synthesis (2009), (19), 3243-3250.

[5] Takada, M.; Wada, T.; Sasabe, H. Novel molecular design for enhanced second-order nonlinear optical response with wide transparency: cyanovinyl aromatics. Molecular

Crystals and Liquid Crystals Science and Technology, Section A: Molecular Crystals and Liquid Crystals (1994), 255, 113-120.

[6] Nakatani, H.; Hayashi, H.; Hidaka, T. Linear and nonlinear optical properties of 2-cyano-3-(2-methoxyphenyl)-2-propenoic acid methyl ester. Japanese Journal of Applied Physics, Part 1: Regular Papers, Short Notes & Review Papers (1992), 31(6A), 1802-1806.

[7] Cai, L.; Zhang, B.; Wu, G.; Song, H.; He, Z. Chemoselective phosphine-catalyzed cascade annulations between two different activated alkenes: highly diastereoselective syntheses of polysubstituted cyclohexanes and cyclopentenes. Chem. Commun. (Cambridge, UK) (2011), 47(3), 1045-1047.

[8] Morley, J.O.Unusual enhancement of the hyperpolarizability of a donor-acceptor styrene by an additional meta substituent. J. Phys. Chem. (1994), 98(46), 11818-20.

[9] Wan, J.; Jing, Y.; Liu, Y.; Sheng, S. Metal-free synthesis of cyano acrylates via cyanuric chloride-mediated three-component reactions involving a cascade consists of Knoevenagel condensation/cyano hydration/esterification. RSC Advances (2014), 4(109), 63997-64000.

[10] Anon. Technology useful in combination with antenna dyes. IP.com Journal (2002), 2(2), 124.

[11] Alvarez, L.; Hidalgo-Carrillo, J.; Marinas, A.; Marinas, J.M.; Urbano, F.J. Sustainable C-C bond formation through Knoevenagel reaction catalyzed by MgO-based catalysts. Reaction Kinetics, Mechanisms and Catalysis (2016), 118(1), 247-265.

[12] Odian, G. *Principles of Polymerization*, 4th Ed., Wiley-Interscience: New York, 2004.

[13] Hall, H. K., Jr.; Padias, A. B. *J. Polym. Sci.Part A: Polym. Chem.* **2004**, *42*, 2845-2858.

[14] Hall, H. K. Jr.; Ykman, P. *Macromolecules.* 1977, *10*, 464.

[15] Kharas, G. B. *Trisubstituted Ethylene Copolymers. In Polymeric Materials Encyclopedia*, Salamone, J.C., (Ed.) CRC Press: Boca Raton, FL, *11*, 8405, 1996.

[16] Kharas, G.B.; Eaker, J.M.; Armatys, S.A. et al. Effect of substituents on the radical copolymerization of ring-substituted methyl 2-cyano-3-phenyl-2-propenoates with styrene. J. Macromol. Sci., Pure & Appl. Chem. 1997, 34(4), 627-640.

[17] Kharas, G.B.; Delgado, A.A.; Gange, N.; Hartzell, M.C. et al. Novel copolymers of styrene. 5. Oxy ring-substituted ethyl 2-cyano-3-phenyl-2-propenoates. J. Macromol. Sci., Part A: Pure & Appl. Chem. (2013), 50(3), 271-275.

[18] Kharas, G.B.; Dos Santos, C.F.; Gao, Y. et al. Novel copolymers of styrene. 2. Oxy ring-substituted propyl 2-cyano-3-phenyl-2-propenoates. J. Macromol. Sci., Part A: Pure & Appl. Chem. (2016), 53(10), 600-604.

[19] Kharas, G.B.; Shinde, N.; Jody, J.K.; Mosher, E.K. et al. Synthesis and styrene copolymerization of novel trisubstituted ethylenes: 3. Alkoxy ring-substituted isopropyl 2-cyano-3-phenyl-2-propenoates. Designed Monomers and Polymers (2018), 21(1), 163-171.

[20] Kharas, G.B.; Feng, H.; Aranda, C.; Navarro, M.E. et al. Novel copolymers of

styrene. 2. Oxy ring-substituted butyl 2-cyano-3-phenyl-2-propenoates. J. Macromol. Sci., Part A: Pure & Appl. Chem. (2015), 52(7), 504-509.

[21] Smith, M. B.; March, J. *Addition to Carbon-Hetero Multiple Bonds*, In March's Advanced Organic Chemistry, J. Wiley & Sons: New York, Ch.16, 1225 (2001).