Synthesis and styrene copolymerization of novel methoxy, methyl, halogen and oxy ring-disubstituted octyl phenylcyanoacrylates

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Abstract

Novel methoxy, methyl, halogen, and oxy ring-disubstituted octyl phenylcyanoacrylates, RPhCH=C(CN)$CO_2CH_2(CH_2)_6CH_3$ (where R is 4-methoxy-2-methyl, 4-methoxy-3-methyl, 3-ethoxy-4-methoxy, 4-ethoxy-3-methoxy, 3-benzyloxy-4-methoxy, 4-benzyloxy-3-methoxy, 2,3-(methylenedioxy), 3-bromo-4-methoxy, 5-bromo-2-methoxy, 2-chloro-3-methoxy, 2-chloro-6-methyl, 3-chloro-4-methyl) were prepared and copolymerized with styrene. The acrylates were synthesized by the piperidine catalyzed Knoevenagel condensation of ring-disubstituted benzaldehydes and octyl cyanoacetate, and characterized by CHN 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 compositions of the copolymers were calculated from nitrogen analysis.

1. Introduction

4-Methoxy-3-methyl ring-substituted phenylcyanoacrylate (PCA) is reported in stereoselective syntheses of (±)-1,14-herbertenediol, (±)-tochuinyl acetate, (±)-α-herbertenol, (±)-β-herbertenol and (±)-1,4-cuparenediol [1]; in synthesis of (±)-herbertene, (±)-β-herbertenol and (±)-herbertenediol [2]; in synthesis of 3β,10α,14β-trimethyl-1βH,11βH-tricyclo[9.3.0.03,7]tetradec-6-en-5-one, a tricyclic ketone related to the ophiobolins [3]. 4-Methoxy-3-methyl propyl [4], butyl [5], and isobutyl [6] PCA were synthesized and copolymerized with ethenyl benzene. 4-Hexyloxy-3-methoxy PCA is involved in preparation of ultraviolet absorbing compounds [7] as well as in preparation of heterocyclic compounds such as prostaglandin E synthase inhibitors [8]. 3-Methoxy-4-phenylmethoxy ethyl PCA is reported in solvent-free Knoevenagel condensation under microwave irradiation in the presence of antimony trichloride [9] and condensation of ethyl cyanoacetate with aldehydes [10]. 2,3-Methylenedioxy ethyl PCA is mentioned in molecular design, synthesis, enzyme inhibition, and inhibition of spheroid formation of Golgi mannosidase inhibitor [11]; in synthesis and study of antioxidant properties of novel pyrimidine-containing heterocycles [12]; in studies of antitumor activity of novel pyridine, thiophene and thiazole derivatives [13], and synthesis and studies of molluscicidal activity of some newly substituted chromene and pyrano[2,3-c]pyrazole derivatives [14]. 5-Bromo-2-methoxyphenyl ethyl PCA is reported in synthesis of thiazacridine derivatives as

anticancer agents against breast and hematopoietic neoplastic cells [15]; in synthesis of thiazolidinedione and evaluation of its modulatory effect on IFN-γ, IL-6, IL-17A, and IL-22 production in PBMCs from rheumatoid arthritis patients [16] and in synthesis and studies of anti-inflammatory activity of new arylidene-thiazolidine-2,4-diones as PPARγ ligands [17]. In this work we have prepared octyl ring-disubstituted cyanoacrylates, $RPhCH=C(CN)CO_2CH_2(CH_2)_6CH_3$, where R is 4-methoxy-2-methyl, 4-methoxy-3-methyl, 3-ethoxy-4-methoxy, 4-ethoxy-3-methoxy, 3-benzyloxy-4-methoxy, 4-benzyloxy-3-methoxy, 2,3-(methylenedioxy), 3-bromo-4-methoxy, 5-bromo-2-methoxy, 2-chloro-3-methoxy, 2-chloro-6-methyl, 3-chloro-4-methyl, 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 [18].

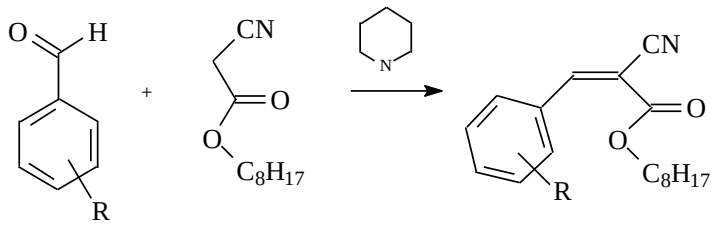
2. Experimental

4-Methoxy-2-methyl, 4-methoxy-3-methyl, 3-ethoxy-4-methoxy, 4-ethoxy-3-methoxy, 3-benzyloxy-4-methoxy, 4-benzyloxy-3-methoxy, 2,3-(methylenedioxy), 3-bromo-4-methoxy, 5-bromo-2-methoxy, 2-chloro-3-methoxy, 2-chloro-6-methyl, 3-chloro-4-methyl benzaldehydes, octyl cyanoacetate (≥98.0%), piperidine (99%), styrene (≥99%), 1,1'-azobis(cyclohexanecarbonitrile) (98%), (ABCN), and toluene (98%) supplied from Sigma-Aldrich Co., were used as received. Instrumentation details are reported in [19].

3. Results and discussion

3.1. Synthesis and characterization of octyl phenylcyanoacrylates

All octyl phenylcyanoacrylates (OPCA) compounds were synthesized by Knoevenagel condensation [20] of appropriate benzaldehydes with octyl cyanoacetate, catalyzed by base, piperidine (Scheme 1).



Scheme 1. Synthesis of octyl phenylcyanoacrylates where R is 4-methoxy-2-methyl, 4-methoxy-3-methyl, 3-ethoxy-4-methoxy, 4-ethoxy-3-methoxy, 3-benzyloxy-4-methoxy, 4-benzyloxy-3-methoxy, 2,3-(methylenedioxy), 3-bromo-4-methoxy, 5-bromo-2-methoxy, 2-chloro-3-methoxy, 2-chloro-6-methyl, 3-chloro-4-methyl.

The preparation procedure was essentially the same for all the monomers. In a typical synthesis, equimolar amounts of octyl 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. The compounds were characterized by IR, ^{1}H and ^{13}C NMR spectroscopies. No stereochemical analysis of the novel oxy ring-substituted OPCA was performed since no stereoisomers (*E* or/and *Z*) of known configuration were available.

3.1.1. ***Octyl 4-methoxy-2-methylphenylcyanoacrylate***

Yield 83%; mp 58.7°C; ^{1}H NMR δ 8.5 (s, 1H, CH=), 8.4-6.8 (m, 3H, Ph), 4.3 (t, 2H, CO_2CH_2), 3.9 (s, 3H, $PhOCH_3$), 2.5 (s, 3H, $PhCH_3$), 2.3-1.8 (q, 2H, $OCH_2C\underline{H}_2$), 1.6-1.5 (m, 6H, $OCH_2CH_2(C\underline{H}_2)_3$), 1.4-1.2 (m, 4H, $O(CH_2)_5(C\underline{H}_2)_2$), 0.9 (t, 3H, CH_3); ^{13}C NMR δ 163 (C=O), 152 (HC=), 143, 132, 124, 118, 112 (Ph), 116 (CN), 101 (C=), 68 (OCH_2), 56 ($PhOCH_3$), 32 ($O(CH_2)_5\,\underline{C}H_2$), 29 ($O(CH_2)_3(\underline{C}H_2)_2$), 28 ($OCH_2\underline{C}H_2$), 26 ($O(CH_2)_2\underline{C}H_2$), 23 ($\underline{C}H_2CH_3$), 20 ($PhCH_3$), 14 ($CH_3$); IR ($cm^{-1}$): 2928 (m, C-H), 2220 (m, CN), 1725 (s, C=O), 1584 (s, C=C), 1249 (s, C-O-CH_3), 762 (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, 71.48; H, 8.25; N, 4.52.

3.1.2. ***Octyl 4-methoxy-3-methylphenylcyanoacrylate***.

Yield 84%; mp 69.4°C; ^{1}H NMR δ 8.1 (s, 1H, CH=), 7.9-6.9 (m, 3H, Ph), 4.3 (t, 2H, CO_2CH_2), 3.9 (s, 3H, $PhOCH_3$), 2.3 (s, 6H, $PhCH_3$), 1.8-1.7 (q, 2H, $OCH_2C\underline{H}_2$), 1.6-1.5 (m, 6H, $OCH_2CH_2(C\underline{H}_2)_3$), 1.4-1.2 (m, 4H, $O(CH_2)_5(C\underline{H}_2)_2$), 0.9 (t, 3H, CH_3); ^{13}C NMR δ 163 (C=O), 152 (HC=), 143, 132, 124, 117, 113 (Ph), 116, (CN), 101 (C=), 68 (OCH_2), 56 ($PhOCH_3$), 32 ($O(CH_2)_5\,\underline{C}H_2$), 29 ($O(CH_2)_3(\underline{C}H_2)_2$), 28 ($OCH_2\underline{C}H_2$), 26 ($O(CH_2)_2\underline{C}H_2$), 23 ($\underline{C}H_2CH_3$), 20 ($PhCH_3$), 14 ($CH_3$); IR ($cm^{-1}$): 2930 (m, C-H), 2218 (m, CN), 1717 (s, C=O), 1601 (C=C), 1264 (s, C-O-CH_3), 828 (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, 70.51; H, 8.25; N, 4.06.

3.1.3. ***Octyl 3-ethoxy-4-methoxyphenylcyanoacrylate***.

Yield 87%; mp 70.6°C; ^{1}H NMR δ 8.1 (s, 1H, CH=), 7.8-6.9 (m, 3H, Ph), 4.3 (t, 2H, CO_2CH_2), 4.2 (q, 2H, $PhOCH_2$), 4.0 (s, 3H, $PhOCH_3$), 1.9-1.7 (q, 2H, $OCH_2C\underline{H}_2$), 1.5-1.3

(m, 6H, $OCH_2CH_2(C\underline{H}_2)_3$), 1.4-1.2 (m, 4H, $O(CH_2)_5(C\underline{H}_2)_2$), 1.3 (t, 2H, $PhOCH_2C\underline{H}_3$), 0.9 (t, 3H, CH_3); ^{13}C NMR δ163 (C=O), 153 (HC=), 153, 149-128 (Ph), 117 (CN), 100 (C=), 67 (OCH_2), 64 ($PhOCH_2$), 57 ($PhOCH_3$), 32 ($O(CH_2)_5\,\underline{C}H_2$), 29 ($O(CH_2)_3(\underline{C}H_2)_2$), 28 ($OCH_2\underline{C}H_2$), 26 ($O(CH_2)_2\underline{C}H_2$), 23 ($\underline{C}H_2CH_3$), 14 ($PhOCH_2CH_3$), 13 ($CH_3$); IR (cm^{-1}): 2927 (m, C-H), 2217 (m, CN), 1714 (s, C=O), 1615 (C=C), 1267 (s, C-O-CH_3), 824 (s, C-H out of plane). Anal. Calcd. for $C_{21}H_{29}NO_4$: C, 70.17; H, 8.13; N, 3.90; Found: C, 70.87; H, 8.47; N, 4.18.

3.1.4. ***Octyl 4-ethoxy-3-methoxyphenylcyanoacrylate***.

Yield 64%; mp 92.6°C; ^{1}H NMR δ8.1 (s, 1H, CH=), 7.9-6.9 (m, 3H, Ph), 4.3 (t, 2H, CO_2CH_2), 4.2 (q, 2H, $PhOCH_2$), 4.0 (s, 3H, $PhOCH_3$), 1.9-1.7 (q, 2H, $OCH_2C\underline{H}_2$), 1.5-1.3 (m, 6H, $OCH_2CH_2(C\underline{H}_2)_3$), 1.4-1.2 (m, 4H, $O(CH_2)_5(C\underline{H}_2)_2$), 1.3 (t, 2H, $PhOCH_2C\underline{H}_3$), 0.9 (t, 3H, CH_3); ^{13}C NMR δ163 (C=O), 154 (HC=), 150, 129, 122 (Ph), 117 (CN), 99 (C=), 68 (OCH_2), 65 ($PhOCH_2$), 57 ($PhOCH_3$), 32 ($O(CH_2)_5\,\underline{C}H_2$), 29 ($O(CH_2)_3(\underline{C}H_2)_2$), 28 ($OCH_2\underline{C}H_2$), 26 ($O(CH_2)_2\underline{C}H_2$), 23 ($\underline{C}H_2CH_3$), 14 ($PhOCH_2CH_3$), 13 ($CH_3$); IR (cm^{-1}): 2923 (m, C-H), 2220 (m, CN), 1720 (s, C=O), 1525 (C=C), 1262 (s, C-O-CH_3), 821 (s, C-H out of plane). Anal. Calcd. for $C_{21}H_{29}NO_4$: C, 70.17; H, 8.13; N, 3.90; Found: C, 70.26; H, 8.62; N, 4.09.

3.1.5. ***Octyl 3-benzyloxy-4-methoxyphenylcyanoacrylate***.

Yield 91%; mp 110.7°C; ^{1}H NMR δ8.1 (s, 1H, CH=), 7.9-6.9 (m, 8H, Ph), 5.2 (s, 2H, $PhCH_2$), 4.3 (t, 2H, CO_2CH_2), 4.0 (s, 3H, $PhOCH_3$), 1.8-1.7 (q, 2H, $OCH_2C\underline{H}_2$), 1.5-1.4 (m, 6H, $OCH_2CH_2(C\underline{H}_2)_3$), 1.4-1.2 (m, 4H, $O(CH_2)_5(C\underline{H}_2)_2$), 0.9 (t, 3H, CH_3); ^{13}C NMR δ

163 (C=O), 154 (HC=), 153, 148-112 (Ph), 117 (CN), 102 (C=), 71 ($PhCH_2O$), 67 (OCH_2), 56 ($PhOCH_3$), 32 ($O(CH_2)_5\underline{C}H_2$), 29.3 ($O(CH_2)_3(\underline{C}H_2)_2$), 28.5 ($OCH_2\underline{C}H_2$), 26 ($O(CH_2)_2\underline{C}H_2$), 23 ($\underline{C}H_2CH_3$), 14 ($CH_3$); IR ($cm^{-1}$): 2932 (m, C-H), 2220 (m, CN), 1720 (s, C=O), 1620 (s, C=C), 1256 (s, C-O-CH_3), 854 (s, C-H out of plane). Anal. Calcd. for $C_{26}H_{31}NO_4$: C, 74.08; H, 7.41; N, 3.32; Found: C, 73.81; H, 6.06; N, 4.11.

3.1.6. ***Octyl 4-benzyloxy-3-methoxyphenylcyanoacrylate***.

Yield 81%; mp 75.0°C; ^{1}H NMR δ 8.1 (s, 1H, CH=), 7.9-6.9 (m, 8H, Ph), 5.3 (s, 2H, $PhCH_2$), 4.3 (t, 2H, CO_2CH_2), 4.0 (s, 3H, $PhOCH_3$), 2.1-1.7 (q, 2H, $OCH_2C\underline{H}_2$), 1.5-1.4 (m, 6H, $OCH_2CH_2(C\underline{H}_2)_3$), 1.4-1.2 (m, 4H, $O(CH_2)_5(C\underline{H}_2)_2$), 0.9 (t, 3H, CH_3); ^{13}C NMR δ 163 (C=O), 154 (HC=), 153, 148-112 (Ph), 117 (CN), 100 (C=), 71 ($PhCH_2O$), 67 (OCH_2), 57 ($PhOCH_3$), 33 ($O(CH_2)_5\underline{C}H_2$), 29.3 ($O(CH_2)_3(\underline{C}H_2)_2$), 28.5 ($OCH_2\underline{C}H_2$), 26 ($O(CH_2)_2\underline{C}H_2$), 23 ($\underline{C}H_2CH_3$), 14 ($CH_3$); IR ($cm^{-1}$): 2921 (m, C-H), 2214 (m, CN), 1714 (s, C=O), 1622 (s, C=C), 1259 (s, C-O-CH_3), 940 (s, C-H out of plane). Anal. Calcd. for $C_{26}H_{31}NO_4$: C, 74.08; H, 7.41; N, 3.32; Found: C, 73.03; H, 7.40; N, 3.34.

3.1.7. ***Octyl 2,3-(methylenedioxy)phenylcyanoacrylate.***

Yield 83%; mp 53.5°C; ^{1}H NMR δ 8.4 (s, 1H, CH=), 7.9-6.1 (m, 3H, Ph), 6.1 (s, OCH_2O), 4.3 (t, 2H, CO_2CH_2), 1.8-1.7 (q, 2H, $OCH_2C\underline{H}_2$), 1.5-1.4 (m, 6H, $OCH_2CH_2(C\underline{H}_2)_3$), 1.4-1.2 (m, 4H, $O(CH_2)_5(C\underline{H}_2)_2$), 0.9 (t, 3H, CH_3); ^{13}C NMR δ 163 (C=O), 153 (HC=), 152, 150, 137- 112 (Ph), 117 (CN), 100 (C=), 72 (OCH_2O), 67 (OCH_2), 32 ($O(CH_2)_5\,\underline{C}H_2$), 29.3 ($O(CH_2)_3(\underline{C}H_2)_2$), 28.5 ($OCH_2\underline{C}H_2$), 26 ($O(CH_2)_2\underline{C}H_2$), 23 ($\underline{C}H_2CH_3$), 13 ($CH_3$); IR ($cm^{-1}$): 2927 (m, C-H), 2224 (m, CN), 1729 (s, C=O), 1610

(s, C=C), 1260 (s, C-O-CH_3), 856 (s, C-H out of plane). Anal. Calcd. for $C_{19}H_{23}NO_4$: C, 69.28; H, 7.04; N, 4.25; Found: C, 67.72; H, 6.08; N, 4.19.

3.1.8. ***Octyl 3-bromo-4-methoxyphenylcyanoacrylate***.

Yield 91%; mp 92.5°C; ^{1}H NMR δ 8.2 (s, 1H, CH=), 8.1, 7.0 (m, 3H, Ph), 4.3 (t, 2H, CO_2CH_2), 4.0 (s, 3H, $PhOCH_3$), 1.8-1.7 (m, 2H, $OCH_2C\underline{H}_2$), 1.6-1.4 (m, 6H, $OCH_2CH_2(C\underline{H}_2)_3$), 1.4-1.2 (m, 4H, $O(CH_2)_5(C\underline{H}_2)_2$), 0.9 (t, 3H, CH_3); ^{13}C NMR δ 163 (C=O), 150 (HC=), 150, 137-118 (Ph), 117 (CN), 100 (C=), 68 (OCH_2), 57 ($PhOCH_3$), 32 ($O(CH_2)_5\,\underline{C}H_2$), 29.3 ($O(CH_2)_3(\underline{C}H_2)_2$), 28.5 ($OCH_2\underline{C}H_2$), 26 ($O(CH_2)_2\underline{C}H_2$), 22.8 ($O(CH_2)_6\underline{C}H_2$), 14 ($CH_3$); IR (cm^{-1}): 2920 (m, C-H), 2222 (m, CN), 1717 (s, C=O), 1568 (s, C=C), 1281 (s, C-O-CH_3), 752 (s, C-H out of plane). Anal. Calcd. for $C_{19}H_{24}NO_3$: C, 57.88; H, 6.13; N, 3.55; Found: C, 58.09; H, 6.31; N, 3.74.

3.1.9. ***Octyl 5-bromo-2-methoxyphenylcyanoacrylate***.

Yield 76%; mp 63.9°C; ^{1}H NMR δ 8.6 (s, 1H, CH=), 8.3, 7.7, 6.9 (m, 3H, Ph), 4.3 (t, 2H, CO_2CH_2), 3.9 (s, 3H, $PhOCH_3$), 1.8-1.7 (m, 2H, $OCH_2C\underline{H}_2$), 1.6-1.4 (m, 6H, $OCH_2CH_2(C\underline{H}_2)_3$), 1.4-1.2 (m, 4H, $O(CH_2)_5(C\underline{H}_2)_2$), 0.9 (t, 3H, CH_3); ^{13}C NMR δ 163 (C=O), 150 (HC=), 150, 148-118 (Ph), 116 (CN), 103 (C=), 68 (OCH_2), 57 ($PhOCH_3$), 32 ($O(CH_2)_5\,\underline{C}H_2$), 29.3 ($O(CH_2)_3(\underline{C}H_2)_2$), 28.5 ($OCH_2\underline{C}H_2$), 26 ($O(CH_2)_2\underline{C}H_2$), 22.8 ($O(CH_2)_6\underline{C}H_2$), 14 ($CH_3$); IR (cm^{-1}): 2928 (m, C-H), 2224 (m, CN), 1728 (s, C=O), 1582 (s, C=C), 1321 (s, C-O-CH_3), 842 (s, C-H out of plane). Anal. Calcd. for $C_{19}H_{24}NO_3$: C, 57.88; H, 6.13; N, 3.55; Found: C, 59.87; H, 6.72; N, 3.87.

3.1.10. ***Octyl 2-chloro-3-methoxyphenylcyanoacrylate***.

Yield 93%; mp 78.6°C; ^{1}H NMR δ8.7 (s, 1H, CH=), 7.9-7.1 (m, 3H, Ph), 4.3 (t, 2H, CO_2CH_2), 3.9 (s, 3H, $PhOCH_3$), 1.7-1.8 (q, 2H, $OCH_2C\underline{H}_2$), 1.6-1.5 (m, 6H, $OCH_2CH_2(C\underline{H}_2)_3$), 1.4-1.2 (m, 4H, $O(CH_2)_5(C\underline{H}_2)_2$), 0.9 (t, 3H, CH_3); ^{13}C NMR δ162 (C=O), 152 (HC=), 153, 132, 128, 122, 118 (Ph), 117 (CN), 107 (C=), 68 (OCH_2), 57 ($PhOCH_3$), 32 ($O(CH_2)_5\,\underline{C}H_2$), 29 ($O(CH_2)_3(\underline{C}H_2)_2$), 28 ($OCH_2\underline{C}H_2$), 26 ($O(CH_2)_2\underline{C}H_2$), 23 ($\underline{C}H_2CH_3$), 14 ($CH_3$); IR (cm^{-1}): 2963 (m, C-H), 2232 (m, CN), 1730 (s, C=O), 1612 (s, C=C), 1283 (s, C-O-CH_3), 865 (s, C-H out of plane). Anal. Calcd. for $C_{19}H_{24}ClNO_3$: C, 65.23; H, 6.91; N, 4.00; Found: C, 64.25; H, 6.62; N, 4.23.

3.1.11. ***Octyl 2-chloro-6-methylphenylcyanoacrylate***.

Yield 81%; ^{1}H NMR δ8.4 (s, 1H, CH=), 7.6-7.2 (m, 3H, Ph), 4.3 (t, 2H, CO_2CH_2), 2.3 (s, 3H, $PhCH_3$), 1.8-1.7 (q, 2H, $OCH_2C\underline{H}_2$), 1.6-1.5 (m, 6H, $OCH_2CH_2(C\underline{H}_2)_3$), 1.4-1.2 (m, 4H, $O(CH_2)_5(C\underline{H}_2)_2$), 0.9 (t, 3H, CH_3); ^{13}C NMR δ162 (C=O), 154 (HC=), 139, 132, 131, 130, 129 (Ph), 116 (CN), 114 (C=), 68 (OCH_2), 32 ($O(CH_2)_5\,\underline{C}H_2$), 29 ($O(CH_2)_3(\underline{C}H_2)_2$), 28 ($OCH_2\underline{C}H_2$), 26 ($O(CH_2)_2\underline{C}H_2$), 23 ($\underline{C}H_2CH_3$), 21 ($PhCH_3$), 14 ($CH_3$); IR (cm^{-1}): 2928 (m, C-H), 2232 (m, CN), 1708 (s, C=O), 1652 (s, C=C), 1271 (s, C-O-CH_3), 852 (s, C-H out of plane). Anal. Calcd. for $C_{19}H_{24}ClNO_2$: C, 68.36; H, 7.25; N, 4.20; Found: C, 69.58; H, 7.55; N, 4.45.

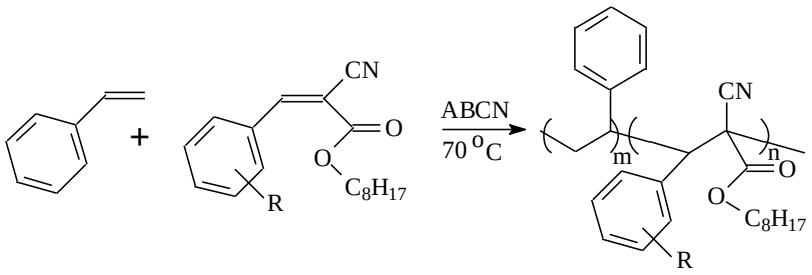
3.1.12. ***Octyl 3-chloro-4-methylphenylcyanoacrylate***.

Yield 94%; mp 96.5°C; ^{1}H NMR δ8.1 (s, 1H, CH=), 8.0-7.4 (m, 3H, Ph), 4.3 (t, 2H, CO_2CH_2), 2.5 (s, 3H, $PhCH_3$), 1.8-1.7 (q, 2H, $OCH_2C\underline{H}_2$), 1.6-1.5 (m, 6H, $OCH_2CH_2(C\underline{H}_2)_3$), 1.4-1.2 (m, 4H, $O(CH_2)_5(C\underline{H}_2)_2$), 0.9 (t, 3H, CH_3); ^{13}C NMR δ162

(C=O), 154 (HC=), 143, 136, 132, 131, 130, 129 (Ph), 117 (CN), 103 (C=), 68 (OCH_2), 32 ($O(CH_2)_5\underline{C}H_2$), 29 ($O(CH_2)_3(\underline{C}H_2)_2$), 28 ($OCH_2\underline{C}H_2$), 26 ($O(CH_2)_2\underline{C}H_2$), 23 ($\underline{C}H_2CH_3$), 21 ($PhCH_3$), 14 ($CH_3$); IR ($cm^{-1}$): 2933 (m, C-H), 2223 (m, CN), 1716 (s, C=O), 1625 (s, C=C), 1245 (s, C-O-CH_3), 859 (s, C-H out of plane). Anal. Calcd. for $C_{19}H_{24}ClNO_2$: C, 68.36; H, 7.25; N, 4.20; Found: C, 69.09; H, 7.79; N, 4.34.

3.2. ***Synthesis and characterization of styrene – OPCA copolymers***

Copolymers of the ST and the OPCA compounds, P(ST-co-OPCA) were prepared in 25-mL glass screw cap vials at ST/ OPCA = 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 OPCA). The novel synthesized OPCA 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 between 10 and 20% to minimize compositional drift (Table 1).



Scheme 2. Copolymerization of ST and the octyl phenylcyanoacrylates, where R is 4-methoxy-2-methyl, 4-methoxy-3-methyl, 3-ethoxy-4-methoxy, 4-ethoxy-3-methoxy, 3-benzyloxy-4-methoxy, 4-benzyloxy-3-methoxy, 2,3-(methylenedioxy), 3-bromo-4-methoxy, 5-bromo-2-methoxy, 2-chloro-3-methoxy, 2-chloro-6-methyl, 3-chloro-4-methyl.

Table 1. Copolymerization of styrene and octyl phenylcyanoacrylates.

R	Yield[a] (wt%)	N (wt%)	ST in copol. (mol%)	OPCA in copol. (mol%)
4-methoxy-2-methyl	11.2	1.84	80.6	19.4
4-methoxy-3-methyl	13.1	2.00	78.1	21.9
3-Ethoxy-4-methoxy	12.4	2.12	74.3	25.7
4-Ethoxy-3-methoxy	16.5	2.31	70.3	29.7
3-Benzyloxy-4-methoxy	12.1	2.21	67.0	33.0
4-Benzyloxy-3-methoxy	15.6	2.2	67.3	32.7
2,3-(Methylenedioxy)	12.2	2.51	68.7	31.3
3-Bromo-4-methoxy	14.5	2.34	66.3	33.7
5-Bromo-2-methoxy	13.6	2.45	63.0	37.0
2-Chloro-3-methoxy	18.7	3.01	52.5	47.5
2-Chloro-6-methyl	12.9	2.22	74.0	26.0
3-Chloro-4-methyl	1.8	2.24	73.7	26.3

Nitrogen elemental analysis showed that between 19.4 and 47.5 mol% of OPCA is present in the copolymers prepared at ST/ OPCA = 3 (mol), which is indicative of relatively high reactivity of the OPCA monomers towards ST radical which is typical of ring-substituted PCA. Since OPCA monomers do not homopolymerize, the most likely structure of the copolymers would be isolated OPCA monomer units alternating with short ST sequences (Scheme 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.

4 Conclusions

Novel trisubstituted ethylenes, methyl, halogen, and oxy ring-disubstituted octyl phenylcyanoacrylates, $RPhCH=C(CN)CO_2CH_2(CH_2)_6CH_3$ (where R is 4-methoxy-2-methyl, 4-methoxy-3-methyl, 3-ethoxy-4-methoxy, 4-ethoxy-3-methoxy, 3-benzyloxy-4-methoxy, 4-benzyloxy-3-methoxy, 2,3-(methylenedioxy), 3-bromo-4-methoxy, 5-bromo-2-methoxy, 2-chloro-3-methoxy, 2-chloro-6-methyl, 3-chloro-4-methyl) were prepared and copolymerized with styrene.

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