Synthesis and styrene copolymerization of novel phenoxy and benzyloxy ring-substituted octyl phenylcyanoacrylates


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Abstract

Novel ring-substituted octyl phenylcyanoacrylates, RPhCH=C(CN)CO$_2$CH$_2$(CH$_2$)$_n$CH$_3$ (where R is 3-phenoxy, 4-phenoxy, 4-(4-bromophenoxy), 3-(4-chlorophenoxy), 2-(4-fluorophenoxy), 3-(4-methylphenoxy), 4-(4-methylphenoxy), 4-(4-nitrophenoxy), 3-[3-( trifluoromethyl)phenoxy], 2-benzyloxy, 3-benzyloxy, 4-benzyloxy) were prepared and copolymerized with styrene. The acrylates were synthesized by the piperidine catalyzed Knoevenagel condensation of ring-substituted benzaldehydes and octyl cyanoacetate, and characterized by CHN analysis, IR, $^1$H and $^{13}$C NMR. 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

3-Phenoxy ring-substituted ethyl phenylcyanoacrylate (PCA) is reported in synthesis of tetrazoles [1]; in the process for preparation of unsaturated carbonyl compounds via lipase-catalyzed [2, 3] and via triazine-based microporous network Knoevenagel condensations [4]; in imidazolium chloride immobilized SBA-15 catalyzed condensation [5]; in synthesis of pharmaceutically active pyranochromene compounds useful as antiviral agents [6]. 3-Phenoxy ring-substituted ethyl PCA is involved in DBU-mediated [4 + 2] annulations of donor-acceptor cyclopropanes with 3-aryl-2-cyanoacrylates for the synthesis of fully substituted anilines [7]; in studies on quinolin-2(1H)-one derivatives in synthesis of pyrano[3,2-c] quinoline and 3-substituted quinoline derivatives [8]; in radical copolymerization with styrene [9]; in synergistic NaBH₄ reduction/cyclization of 2-aroylcyclopropane-1-carboxylates leading to synthesis of 3-oxabicyclo[3.1.0]hexane derivatives [10]; in synthesis of azaindazoles as Btk kinase modulators [11]. Methyl, isopropyl, and butyl PCA were prepared and copolymerized with styrene [12-14]. 3-(Trifluoromethyl)phenoxy ethyl PCA is reported in preparation of amino(phenyl)alkanoic acid derivatives, addition salts thereof, and sphingosine-1-phosphate (S1P) receptor modulators [15]; in preparation of diaryl ether derivatives as immunosuppressants [16]. 4-Benzyl ethyl PCA is involved in synthesis, biological evaluation and molecular modeling studies of arylidene-thiazolidinediones with potential hypoglycemic and hypolipidemic
activities [17]; in multi-step synthesis of analytically pure α,β-unsaturated compounds in miniaturized flow reactors [18]; in synthesis of 1,3,5-trisubstituted-2-thioxoimidazolidinones [19]; in preparation of (alkoxybenzyl)pyrrolidinone derivatives as nootropics [20].

We have prepared octyl ring-substituted cyanoacrylates,

\[ \text{RPhCH}=\text{C(CN)CO}_2\text{CH}_2\text{(CH}_2)_6\text{CH}_3, \text{ where R is 3-phenoxy, 4-phenoxy, 4-(4-bromophenoxy), 3-(4-chlorophenoxy), 2-(4-fluorophenoxy), 3-(4-methylphenoxy), 4-(4-methylphenoxy), 4-(4-nitrophenoxy), 3-[3-( trifluoromethyl)phenoxy], 2-benzyloxy, 3-benzyloxy, 4-benzyloxy, and explored the feasibility of their copolymerization with styrene.} \]

To the best of our knowledge there have been no reports on either synthesis of these compounds, nor their copolymerization with styrene [21].

2. Experimental

3-Phenoxy, 4-phenoxy, 4-(4-bromophenoxy), 3-(4-chlorophenoxy), 2-(4-fluorophenoxy), 3-(4-methylphenoxy), 4-(4-methylphenoxy), 4-(4-nitrophenoxy), 3-[3-( trifluoromethyl)phenoxy], 2-benzyloxy, 3-benzyloxy, 4-benzyloxybenzaldehydes, 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 is reported in [22].

3. Results and discussion

3.1. Synthesis and characterization of octyl phenylcyanoacyrlates
All octyl phenylcyanoacrylates (OPCA) compounds were synthesized by Knoevenagel condensation [23] of appropriate benzaldehydes with octyl cyanoacetate, catalyzed by base, piperidine (Scheme 1).

\[
\begin{align*}
O & \quad H \\
\text{R} & \quad \text{CN} \\
\text{CN} & \quad \text{O} \\
\text{C}_8\text{H}_{17} & \quad \text{R} \\
\text{CN} & \quad \text{O} \\
\text{C}_8\text{H}_{17} & \\
\end{align*}
\]

Scheme 1. Synthesis of octyl phenylcyanoacrylates where R is 3-phenoxy, 4-phenoxy, 4-(4-bromophenoxy), 3-(4-chlorophenoxy), 2-(4-fluorophenoxy), 3-(4-methylphenoxy), 4-(4-methylphenoxy), 4-(4-nitrophenoxy), 3-[3-(trifluoromethyl)phenoxy], 2-benzyl, 3-benzyl, 4-benzyl.

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 3-phenoxyphenylcyanoacrylate
Yield 82%; $^1$H NMR $\delta$ 8.2 (s, 1H, CH=), 7.8-6.9 (m, 9H, Ph), 4.3 (t, 2H, CO$_2$CH$_2$), 1.7-1.8 (q, 2H, OCH$_2$CH$_2$), 1.6-1.5 (m, 6H, OCH$_2$CH$_2$(CH$_2$)$_3$), 1.4-1.2 (m, 4H, O(CH$_2$)$_5$(CH$_2$)$_2$), 0.9 (t, 3H, CH$_3$); $^{13}$C NMR $\delta$ 164 (C=O), 154 (HC=), 159, 158, 133, 130, 125, 124, 123, 120, 119 (Ph), 115 (CN), 104 (C=), 67 (OCH$_2$), 32 (O(CH$_2$)$_5$CH$_2$), 29 (O(CH$_2$)$_3$(CH$_2$)$_2$), 28 (OCH$_2$CH$_2$), 26 (O(CH$_2$)$_2$CH$_2$), 23 (CH$_2$CH$_3$), 14 (CH$_3$); IR (cm$^{-1}$): 2957 (m, C-H), 2226 (m, CN), 1732 (s, C=O), 1237 (s, C-O-CH$_3$), 781 (s, C-H out of plane). Anal. Calcd. for C$_{24}$H$_{27}$NO$_3$: C, 76.36; H, 7.21; N, 3.71; Found: C, 74.93; H, 7.45; N, 3.60.

3.1.2. Octyl 4-phenoxyphenylcyanoacrylate.

Yield 72%; $^1$H NMR $\delta$ 8.2 (s, 1H, CH=), 8.1-6.8 (m, 9H, Ph), 4.3 (t, 2H, CO$_2$CH$_2$), 1.8-1.7 (q, 2H, OCH$_2$CH$_2$), 1.6-1.5 (m, 6H, OCH$_2$CH$_2$(CH$_2$)$_3$), 1.4-1.2 (m, 4H, O(CH$_2$)$_5$(CH$_2$)$_2$), 0.9 (t, 3H, CH$_3$); $^{13}$C NMR $\delta$ 163 (C=O), 153 (HC=), 162, 156, 134, 132, 130, 126, 125, 121, 118 (Ph), 116 (CN), 101 (C=), 67 (OCH$_2$), 32 (O(CH$_2$)$_5$CH$_2$), 29 (O(CH$_2$)$_3$(CH$_2$)$_2$), 28 (OCH$_2$CH$_2$), 26 (O(CH$_2$)$_2$CH$_2$), 23 (CH$_2$CH$_3$), 14 (CH$_3$); IR (cm$^{-1}$): 3100-2800 (m, C-H), 2222 (m, CN), 1724 (s, C=O), 1598 (C=C), 1198 (s, C-O-CH$_3$), 874 (s, C-H out of plane). Anal. Calcd. for C$_{24}$H$_{27}$NO$_3$: C, 76.36; H, 7.21; N, 3.71; Found: C, 74.63; H, 7.10; N, 3.90.

3.1.3. Octyl 4-(4-bromophenoxy)phenylcyanoacrylate.

Yield 87%; mp 77.0°C; $^1$H NMR $\delta$ 8.2 (s, 1H, CH=), 8.1-6.9 (m, 8H, Ph), 4.3 (t, 2H, CO$_2$CH$_2$), 1.9-1.7 (q, 2H, OCH$_2$CH$_2$), 1.5-1.3 (m, 6H, OCH$_2$CH$_2$(CH$_2$)$_3$), 1.4-1.2 (m, 4H, O(CH$_2$)$_5$(CH$_2$)$_2$), 0.9 (t, 3H, CH$_3$); $^{13}$C NMR $\delta$ 163 (C=O), 154 (HC=), 162, 154, 134,
134, 126, 122, 118 (Ph), 116 (CN), 101 (C=), 67 (OCH₂), 32 (O(CH₂)₃CH₂), 29
(O(CH₂)₃(CH₂)₂), 28 (OCH₂CH₂), 26 (O(CH₂)₂CH₂), 23 (CH₂CH₃), 14 (CH₃); IR (cm⁻¹):
2922 (m, C-H), 2222 (m, CN), 1713 (s, C=O), 1578 (C=C), 1283 (s, C-O-CH₃), 870 (s,
C-H out of plane). Anal. Calcd. for C₂₄H₂₆BrNO₃: C, 63.16; H, 5.74; N, 3.07; Found: C,
62.39; H, 5.30; N, 3.08.

3.1.4. Octyl 3-(4-chlorophenoxy)phenylcyanoacrylate.

Yield 73%; mp 85.7°C; ¹H NMR δ 8.2 (s, 1H, CH=), 7.8-6.9 (m, 8H, Ph), 4.3 (t, 2H,
CO₂CH₂), 1.8-1.7 (q, 2H, OCH₂CH₂), 1.5-1.4 (m, 6H, OCH₂CH₂(CH₂)₃), 1.4-1.2 (m, 4H,
O(CH₂)₅(CH₂)₂), 0.9 (t, 3H, CH₃); ¹³C NMR δ 162 (C=O), 154 (HC=), 158, 155, 133,
131, 130, 129, 126, 123, 121, 120 (Ph), 115 (CN), 104 (C=), 67 (OCH₂), 32 (O(CH₂)₅
CH₂), 29.3 (O(CH₂)₃(CH₂)₂), 28.6 (OCH₂CH₂), 25.8 (O(CH₂)₂CH₂), 23 (CH₂CH₃), 14.1
(CH₃); IR (cm⁻¹): 2924 (m, C-H), 2226 (m, CN), 1718 (s, C=O), 1612, 15.74 (s, C=C),
1231 (s, C-O-CH₃), 858 (s, C-H out of plane). Anal. Calcd. for C₂₄H₂₆ClNO₃: C, 69.98;
H, 6.36; N, 3.40; Found: C, 68.64; H, 6.50; N, 3.43.

3.1.5. Octyl 2-(4-fluorophenoxy)phenylcyanoacrylate.

Yield 81%; ¹H NMR δ 8.8 (s, 1H, CH=), 8.5-6.8 (m, 8H, Ph), 4.3 (t, 2H, CO₂CH₂), 1.8-
1.7 (q, 2H, OCH₂CH₂), 1.5-1.4 (m, 6H, OCH₂CH₂(CH₂)₃), 1.4-1.2 (m, 4H,
O(CH₂)₅(CH₂)₂), 0.9 (t, 3H, CH₃); ¹³C NMR δ 163 (C=O), 149 (HC=), 161, 158, 135,
130, 124, 123, 121, 117 (Ph), 116 (CN), 104 (C=), 67 (OCH₂), 32 (O(CH₂)₅CH₂), 29.3
(O(CH₂)₃(CH₂)₂), 28.5 (OCH₂CH₂), 26 (O(CH₂)₂CH₂), 23 (CH₂CH₃), 14 (CH₃); IR (cm⁻¹):
2924 (m, C-H), 2226 (m, CN), 1718 (s, C=O), 1612, 1547 (s, C=C), 1262 (s, C-O-
CH₃, 858 (s, C-H out of plane). Anal. Calcd. for C₂₄H₂₆FNO₃: C, 72.89; H, 6.63; N, 3.54; Found: C, 72.66; H, 6.66; N, 3.62.

3.1.6. Octyl 3-(4-methylphenoxy)phenylcyanoacrylate.

Yield 92%; mp 73.4°C; ¹H NMR δ 8.16 (s, 1H, CH=), 7.8-6.9 (m, 8H, Ph), 4.3 (t, 2H, CO₂CH₂), 2.4 (s, 3H, PhCH₃), 1.8-1.7 (q, 2H, OCH₂CH₂), 1.5-1.4 (m, 6H, OCH₂CH₂(CH₂)₃), 1.4-1.2 (m, 4H, O(CH₂)₃(CH₂)₂), 0.9 (t, 3H, CH₃); ¹³C NMR δ 162 (C=O), 154 (HC=), 159, 134, 133, 131, 125, 123, 120 (Ph), 115 (CN), 104 (C=), 67 (OCH₂), 32 (O(CH₂)₅CH₂), 29.3 (O(CH₂)₃(CH₂)₂), 28.5 (OCH₂CH₂), 26 (O(CH₂)₂CH₂), 23 (CH₂CH₃), 21 (PhCH₃), 14 (CH₃); IR (cm⁻¹): 2922 (m, C-H), 2266 (m, CN), 1717 (s, C=O), 1610 (s, C=C), 1250 (s, C-O-CH₃), 816 (s, C-H out of plane). Anal. Calcd. for C₂₅H₂₉NO₃: C, 76.70; H, 7.47; N, 3.58; Found: C, 75.02; H, 7.43; N, 3.67.

3.1.7. Octyl 4-(4-methylphenoxy)phenylcyanoacrylate.

Yield 65%; mp 56.4°C; ¹H NMR δ 8.2 (s, 1H, CH=), 8.0-6.9 (m, 8H, Ph), 4.3 (t, 2H, CO₂CH₂), 2.4 (s, 3H, PhCH₃), 1.8-1.7 (q, 2H, OCH₂CH₂), 1.5-1.4 (m, 6H, OCH₂CH₂(CH₂)₃), 1.4-1.2 (m, 4H, O(CH₂)₃(CH₂)₂), 0.9 (t, 3H, CH₃); ¹³C NMR δ 163 (C=O), 154 (HC=), 152, 135, 134, 131, 126, 121, 118 (Ph), 116 (CN), 101 (C=), 67 (OCH₂), 32 (O(CH₂)₅CH₂), 29.3 (O(CH₂)₃(CH₂)₂), 28.5 (OCH₂CH₂), 26 (O(CH₂)₂CH₂), 23 (CH₂CH₃), 21 (PhCH₃), 14 (CH₃); IR (cm⁻¹): 2922 (m, C-H), 2220 (m, CN), 1724 (s, C=O), 1589 (s, C=C), 1250 (s, C-O-CH₃), 837 (s, C-H out of plane). Anal. Calcd. for C₂₅H₂₉NO₃: C, 76.70; H, 7.47; N, 3.58; Found: C, 75.66; H, 7.40; N, 3.78.

3.1.8. Octyl 4-(4-nitrophenoxy)phenylcyanoacrylate.
Yield 87%; mp 57.7°C; $^1$H NMR $\delta$ 8.3 (s, 1H, CH=), 8.28-7.1 (m, 8H, Ph), 4.3 (t, 2H, CO$_2$CH$_2$), 1.8-1.7 (m, 2H, OCH$_2$CH$_2$), 1.6-1.4 (m, 6H, OCH$_2$CH$_2$(CH$_2$)$_3$), 1.4-1.2 (m, 4H, O(CH$_2$)$_5$(CH$_2$)$_2$), 0.9 (t, 3H, CH$_3$); $^{13}$C NMR $\delta$ 162 (C=O), 153 (HC=), 161, 159, 144, 134, 128, 126, 120, 119 (Ph), 116 (CN), 103 (C=), 67 (OCH$_2$), 32 (O(CH$_2$)$_5$CH$_2$), 29.3 (O(CH$_2$)$_3$(CH$_2$)$_2$), 28.5 (OCH$_2$CH$_2$), 26 (O(CH$_2$)$_5$CH$_2$), 22.8 (O(CH$_2$)$_6$CH$_2$), 14.1 (CH$_3$); IR (cm$^{-1}$): 2928 (m, C-H), 2224 (m, CN), 1726 (s, C=O), 1558 (s, C=O), 1246 (s, C-O-CH$_3$), 879 (s, C-H out of plane). Anal. Calcd. for C$_{24}$H$_{26}$N$_2$O$_5$: C, 68.23; H, 6.20; N, 6.63; Found: C, 65.77; H, 6.35; N, 6.64.


Yield 77%; $^1$H NMR $\delta$ 8.2 (s, 1H, CH=), 7.8-7.1 (m, 8H, Ph), 4.3 (t, 2H, CO$_2$CH$_2$), 1.9-1.8 (m, 2H, OCH$_2$CH$_2$), 1.6-1.4 (m, 6H, OCH$_2$CH$_2$(CH$_2$)$_3$), 1.5-1.2 (m, 4H, O(CH$_2$)$_5$(CH$_2$)$_2$), 0.9 (t, 3H, CH$_3$); $^{13}$C NMR $\delta$ 162 (C=O), 154 (HC=), 157, 156, 133, 131, 126, 123, 122, 120, 116 (Ph), 115 (CN), 104 (C=), 67 (OCH$_2$), 32 (O(CH$_2$)$_5$CH$_2$), 29.3 (O(CH$_2$)$_3$(CH$_2$)$_2$), 28.7 (OCH$_2$CH$_2$), 26 (O(CH$_2$)$_5$CH$_2$), 22.8 (O(CH$_2$)$_6$CH$_2$), 14.2 (CH$_2$CH$_3$); IR (cm$^{-1}$): 2930 (m, C-H), 2226 (m, CN), 1732 (s, C=O), 1207 (s, C-O-CH$_3$), 836 (s, C-H out of plane). Anal. Calcd. for C$_{25}$H$_{28}$F$_3$NO$_3$: C, 67.40; H, 5.88; N, 3.14; Found: C, 67.61; H, 6.65; N, 3.45.

3.1.10. Octyl 2-benzyloxyphenylcyanoacrylate

Yield 78%; mp 63.5°C; $^1$H NMR $\delta$ 8.8 (s, 1H, CH=), 8.4-6.9 (m, 9H, Ph), 5.2 (s, 2H, PhCH$_2$), 4.3 (t, 2H, CO$_2$CH$_2$), 1.7-1.8 (q, 2H, OCH$_2$CH$_2$), 1.6-1.5 (m, 6H, OCH$_2$CH$_2$(CH$_2$)$_3$), 1.4-1.2 (m, 4H, O(CH$_2$)$_5$(CH$_2$)$_2$), 0.9 (t, 3H, CH$_3$); $^{13}$C NMR $\delta$ 163
(C=O), 150 (HC=), 158, 136, 135, 130, 129, 127, 121, 113 (Ph), 116 (CN), 103 (C=), 71 (PhOCH₂), 67 (OCH₂), 32 (O(CH₂)₃CH₂), 29 (O(CH₂)₃(CH₂)₂), 28 (OCH₂CH₂), 26 (O(CH₂)₂CH₂), 23 (CH₂CH₃), 14 (CH₃); IR (cm⁻¹): 2922 (m, C-H), 2222 (m, CN), 1699 (s, C=O), 1591 (s, C=C), 1248 (s, C-O-CH₃), 733 (s, C-H out of plane). Anal. Calcd. for C₂₅H₂₉NO₃: C, 76.70; H, 7.47; N, 3.58; Found: C, 74.20; H, 8.22; N, 3.86.

3.1.11. Octyl 3-benzylxyphenylcyanoacrylate

Yield 91%; ¹H NMR δ 8.2 (s, 1H, CH=), 7.7-7.1 (m, 9H, Ph), 5.1 (s, 2H, PhCH₂), 4.3 (t, 2H, CO₂CH₂), 1.7-1.8 (q, 2H, OCH₂CH₂), 1.6-1.5 (m, 6H, OCH₂CH₂(CH₂)₃), 1.4-1.2 (m, 4H, O(CH₂)₃(CH₂)₂), 0.9 (t, 3H, CH₃); ¹³C NMR δ 163 (C=O), 150 (HC=), 159, 155, 136, 133, 130, 129, 128, 125, 113 (Ph), 116 (CN), 103 (C=), 71 (PhOCH₂), 67 (OCH₂), 32 (O(CH₂)₃(CH₂)₂), 28 (OCH₂CH₂), 26 (O(CH₂)₂CH₂), 23 (CH₂CH₃), 14 (CH₃); IR (cm⁻¹): 2961 (m, C-H), 2220 (m, CN), 1722 (s, C=O), 1610 (s, C=C), 1221 (s, C-O-CH₃), 852 (s, C-H out of plane). Anal. Calcd. for C₂₅H₂₉NO₃: C, 76.70; H, 7.47; N, 3.58; Found: C, 74.18; H, 7.70; N, 3.67.

3.1.12. Octyl 4-benzylxyphenylcyanoacrylate

Yield 72%; mp 83.2°C; ¹H NMR δ 8.2 (s, 1H, CH=), 8.1-7.0 (m, 9H, Ph), 5.2 (s, 2H, PhCH₂), 4.3 (t, 2H, CO₂CH₂), 1.7-1.8 (q, 2H, OCH₂CH₂), 1.6-1.5 (m, 6H, OCH₂CH₂(CH₂)₃), 1.4-1.2 (m, 4H, O(CH₂)₃(CH₂)₂), 0.9 (t, 3H, CH₃); ¹³C NMR δ 163 (C=O), 154 (HC=), 163, 136, 134, 129, 128, 125, 115 (Ph), 116 (CN), 99 (C=), 71 (PhOCH₂), 67 (OCH₂), 32 (O(CH₂)₃CH₂), 29 (O(CH₂)₃(CH₂)₂), 28 (OCH₂CH₂), 26 (O(CH₂)₂CH₂), 23 (CH₂CH₃), 14 (CH₃); IR (cm⁻¹): 2924 (m, C-H), 2222 (m, CN), 1712
(s, C=O), 1610 (s, C=C), 1236 (s, C-O-CH₃), 766 (s, C-H out of plane). Anal. Calcd. for C_{25}H_{29}NO₃: C, 76.70; H, 7.47; N, 3.58; Found: C, 75.32; H, 7.42; N, 3.55.

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 3-phenoxy, 4-phenoxy, 4-(4-bromophenoxy), 3-(4-chlorophenoxy), 2-(4-fluorophenoxy), 3-
(4-methylphenoxy), 4-(4-methylphenoxy), 4-(4-nitrophenoxy), 3-[3-(trifluoromethyl)phenoxy], 2-benzyloxy, 3-benzyloxy, 4-benzyloxy.

**Table 1.** Copolymerization of styrene and octyl phenylcyanoacrylates.

<table>
<thead>
<tr>
<th>R</th>
<th>Yield(^a) (wt%)</th>
<th>N (wt%)</th>
<th>ST in copol. (mol%)</th>
<th>OPCA in copol. (mol%)</th>
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<td>23.6</td>
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</tbody>
</table>

Nitrogen elemental analysis showed that between 20.1 and 33.1 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 oxy ring-substituted OPCA. 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, octyl phenylcyanoacrylates,
RPhCH=CH(CN)CO₂CH₂(CH₂)₆CH₃ (where R is 3-phenoxy, 4-phenoxy, 4-(4-bromophenoxy), 3-(4-chlorophenoxy), 2-(4-fluorophenoxy), 3-(4-methylphenoxy), 4-(4-methylphenoxy), 4-(4-nitrophenoxy), 3-[3-(trifluoromethyl)phenoxy], 2-benzyloxy, 3-benzyloxy, 4-benzyloxy) were prepared and copolymerized with styrene.

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