

Synthesis and styrene copolymerization of novel methyl, methoxy, chloro, and fluorophenoxy ring-substituted 2-methoxyethyl phenylcyanoacrylates

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Abstract

Novel phenoxy ring-substituted 2-methoxyethyl phenylcyanoacrylates, $RPhCH=C(CN)CO_2CH_2CH_2OCH_3$ (where R is 3-phenoxy, 3-(4-chlorophenoxy), 4-(4-chlorophenoxy), 2-(4-fluorophenoxy), 4-(4-fluorophenoxy), 2-(3-methoxyphenoxy), 2-(4-methoxyphenoxy), 3-(4-methoxyphenoxy), 4-(4-methoxyphenoxy), 3-(4-methylphenoxy), 4-(4-methylphenoxy), 3-(3,5-dichlorophenoxy), 4-(2,4-dichlorophenoxy), 3-(3-trifluoromethyl)phenoxy) were prepared and copolymerized with styrene. The acrylates were synthesized by the piperidine catalyzed Knoevenagel condensation of ring-substituted benzaldehydes and 2-methoxyethyl cyanoacetate, and characterized by CHN analysis, IR,

^1H and ^{13}C NMR. All the ethylenes were copolymerized with styrene in solution with radical initiation (ABCN) at 70°C . The compositions of the copolymers were calculated from nitrogen analysis.

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Keywords: ring-substituted phenylcyanoacrylates, Knoevenagel condensation, radical copolymerization, styrene copolymers

1. Introduction

3-Phenoxy ring-substituted ethyl phenylcyanoacrylate is reported in synthesis of substituted tetrazoles [1]; of unsaturated carbonyl compounds via (1) lipase-catalyzed [2, 3], and (2) over triazine-based microporous network [4], (3) Knoevenagel condensations; of imidazolium chloride immobilized SBA-15 as a heterogenized organocatalyst [5]; and catalyzed by Titanium (IV) Ethoxide [6], in pharmaceutically active pyranochromene compounds useful as antiviral agents [7]; and in $\text{N,N}'$ -dioxide-lanthanum(III)-catalyzed asymmetric cyclopropanation of 2-cyano-3-arylacrylates with 2-bromomalonates [8]. 2-Cyano-3-(3-phenoxyphenyl) ethyl ester of 2-butenic acid was involved in synthesis of pyruvic acid amides used as analgesics and antiinflammants [9] as well as in synthesis of 2-(3-phenoxyphenyl)propionic acid [10]. 2-Propenoic acid, 2-cyano-3-phenyl-, 2-[4-[4-(trifluoromethyl)phenoxy]phenoxy]propyl ester is reported in preparation of herbicidal composition [11]. 1-Ethenyl-4-(4-methylphenoxy)-benzene was involved in copper-catalyzed c-o coupling reactions of oxalohydrazide [12] and pyrazole moiety-containing ligands [13]. 1-Ethenyl-4-(4-methoxyphenoxy)-benzene was reported in synthesis of

aldehydes [14] and ether-based polymers used as photo-crosslinkable dielectrics [15]. 1-Ethenyl-4-(4-fluorophenoxy)-benzene involved in synthesis of (1-(tert-butylperoxy)-2-perfluoroalkyl)-ethylbenzene [16]; in crossover reactions to construct γ -peroxy esters and 1,4-dicarbonyl compounds [17]; in oxidative coupling of 1,3-dioxolanes with electron-deficient alkenes and vinylarenes based on a radical addition and Kornblum-DeLaMare rearrangement [18], as well as in reaction for the construction of β -ester- γ -amino ketones [19].

In this work we have prepared alkoxy ring-substituted 2-methoxyethyl phenylcyanoacrylates, $RPhCH=C(CN)CO_2CH_2CH_2OCH_3$, where R is 3-phenoxy, 3-(4-chlorophenoxy), 4-(4-chlorophenoxy), 2-(4-fluorophenoxy), 4-(4-fluorophenoxy), 2-(3-methoxyphenoxy), 2-(4-methoxyphenoxy), 3-(4-methoxyphenoxy), 4-(4-methoxyphenoxy), 3-(4-methylphenoxy), 4-(4-methylphenoxy), 3-(3,5-dichlorophenoxy), 4-(2,4-dichlorophenoxy), 3-(3-trifluoromethyl)phenoxy, 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 [20].

2. Experimental

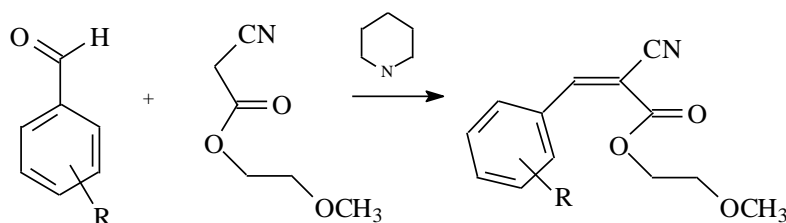
3-Phenoxy, 3-(4-chlorophenoxy), 4-(4-chlorophenoxy), 2-(4-fluorophenoxy), 4-(4-fluorophenoxy), 2-(3-methoxyphenoxy), 2-(4-methoxyphenoxy), 3-(4-methoxyphenoxy), 4-(4-methoxyphenoxy), 3-(4-methylphenoxy), 4-(4-methylphenoxy), 3-(3,5-dichlorophenoxy), 4-(2,4-dichlorophenoxy), 3-(3-trifluoromethyl)phenoxy substituted benzaldehydes, 2-methoxyethyl cyanoacetate ($\geq 98.0\%$), piperidine (99%), styrene ($\geq 99\%$),

1,1'-azobis(cyclohexanecarbonitrile) (98%), (ABCN), and toluene (98%) supplied from Sigma-Aldrich Co., were used as received. Instrumentation is reported in [21].

3. Results and discussion

3.1. Synthesis and characterization of 2-methoxyethyl phenylcyanoacrylates

All MEPA compounds were synthesized by Knoevenagel condensation [22] of appropriate benzaldehydes with 2-methoxyethyl cyanoacetate, catalyzed by base, piperidine (Scheme 1).



Scheme 1. Synthesis of 2-methoxyethyl phenylcyanoacrylates where R is 3-phenoxy, 3-(4-chlorophenoxy), 4-(4-chlorophenoxy), 2-(4-fluorophenoxy), 4-(4-fluorophenoxy), 2-(3-methoxyphenoxy), 2-(4-methoxyphenoxy), 3-(4-methoxyphenoxy), 4-(4-methoxyphenoxy), 3-(4-methylphenoxy), 4-(4-methylphenoxy), 3-(3,5-dichlorophenoxy), 4-(2,4-dichlorophenoxy), 3-(3-trifluoromethyl)phenoxy.

The preparation procedure was essentially the same for all the MEPA compounds. In a typical synthesis, equimolar amounts of 2-methoxyethyl 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, ^1H and ^{13}C NMR spectroscopies. No stereochemical analysis of the novel alkoxy ring-substituted MEPA was performed since no stereoisomers (*E* or/and *Z*) of known configuration were available.

3.1.1. 2-Methoxyethyl 3-phenoxyphenylcyanoacrylate

Yield: 82%; ^1H NMR: δ 8.3 (s, 1H, CH=), 8.1-6.7 (m, 9H, Ph), 4.5 (t, 2H, OCOCH₂), 3.7 (t, 2H, OCH₂), 3.4 (s, 3H, OCH₃); ^{13}C NMR: δ 163 (C=O), 154 (HC=), 135, 133, 131, 129, 128, 125, 123, 122, 121 (Ph), 116 (CN), 104 (C=), 74 (OCH₂), 66 (OCOCH₂); IR: (cm⁻¹) 2931 (m, C-H), 2215 (m, CN), 1732 (s, C=O), 1607 (s, C=C), 1273 (s, C-O-CH₃), 762 (s, C-H out of plane). Anal. calcd. for C₁₉H₁₇NO₄: C, 70.58; H, 5.30; N, 4.33; Found: C, 68.47; H, 5.62; N, 4.65.

3.1.2. 2-Methoxyethyl 3-(4-chlorophenoxy)phenylcyanoacrylate

Yield 84%; ^1H NMR δ 8.2 (s, 1H, CH=), 7.7-6.9 (m, 8H, Ph), 4.4 (t, 2H, OCOCH₂), 3.7 (t, 2H, OCH₂), 3.4 (s, 3H, OCH₃); ^{13}C NMR: δ 163 (C=O), 154 (HC=), 155, 131, 130, 129, 128, 124, 121, 120, 119 (Ph), 116 (CN), 100 (C=), 74 (OCH₂), 66 (OCOCH₂), 59 (OCH₃); IR: (cm⁻¹) 2923 (m, C-H), 2214 (m, CN), 1734 (s, C=O), 1609 (s, C=C), 1248 (s, C-O-CH₃), 763 (s, C-H out of plane). Anal. calcd. for C₁₉H₁₆ClNO₄: C, 63.78; H, 4.51; N, 3.91; Found: C, 64.29; H, 4.85; N, 4.32.

3.1.3. 2-Methoxyethyl 4-(4-chlorophenoxy)phenylcyanoacrylate

Yield 73%; $^1\text{H NMR}$ δ 8.2 (s, 1H, CH=), 8.1-6.8 (m, 8H, Ph), 4.5 (t, 2H, OCOCH₂), 3.7 (t, 2H, OCH₂), 3.4 (s, 3H, OCH₃); $^{13}\text{C NMR}$: δ 162 (C=O), 154 (HC=), 156, 149, 131, 132, 130, 129, 119 (Ph), 116 (CN), 100 (C=), 74 (OCH₂), 66 (OCOCH₂), 59 (OCH₃); IR: (cm⁻¹) 2932 (m, C-H), 2224 (m, CN), 1728 (s, C=O), 1622 (s, C=C), 1231 (s, C-O-CH₃), 846 (s, C-H out of plane). Anal. calcd. for C₁₉H₁₆ClNO₄: C, 63.78; H, 4.51; N, 3.91; Found: C, 63.63; H, 4.91; N, 3.98.

3.1.4. 2-Methoxyethyl 2-(4-fluorophenoxy)phenylcyanoacrylate

Yield 89%; $^1\text{H NMR}$ δ 8.3 (s, 1H, CH=), 7.6-6.6 (m, 8H, Ph), 4.4 (t, 2H, OCOCH₂), 3.7 (t, 2H, OCH₂), 3.4 (s, 3H, CH₃O); $^{13}\text{C NMR}$ δ 163 (C=O), 154 (HC=), 159, 153, 131, 125, 119 (Ph), 115 (CN), 100 (C=), 70 (OCH₂), 64 (OCOCH₂), 59 (OCH₃); IR (cm⁻¹): 2932 (m, C-H), 2224 (m, CN), 1732 (s, C=O), 1599 (s, C=C), 1248 (s, C-O-CH₃), 764 (s, C-H out of plane). Anal. Calcd. for C₁₉H₁₆FNO₄: C, 66.86; H, 4.72; N, 4.10; Found: C, 67.73; H, 4.82; N, 4.54.

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

Yield 92%; $^1\text{H NMR}$ δ 8.2 (s, 1H, CH=), 8.0 – 6.7 (m, 8H, Ph), 4.3 (t, 2H, OCOCH₂), 3.6 (t, 2H, OCH₂), 3.4 (s, 3H, CH₃O); $^{13}\text{C NMR}$ δ 164 (C=O), 148 (HC=), 158, 154, 131, 118, 116 (Ph), 115 (CN), 100 (C=), 70 (OCH₂), 63 (OCOCH₂), 59 (OCH₃); IR (cm⁻¹): 2944 (m, C-H), 2219 (m, CN), 1732 (s, C=O), 1567 (s, C=C), 1221 (s, C-O-CH₃), 835 (s, C-H out of plane). Anal. Calcd. for C₁₉H₁₆FNO₄: C, 66.86; H, 4.72; N, 4.10; Found: C, 64.47; H, 4.89; N, 4.91.

3.1.6. 2-Methoxyethyl 2-(3-methoxyphenoxy)phenylcyanoacrylate

Yield 92%; $^1\text{H NMR}$ δ 8.8 (s, 1H, CH=), 8.4-6.4 (m, 8H, Ph), 4.4 (t, 2H, OCOCH₂), 3.8 (s, 3H, PhOCH₃), 3.7 (t, 2H, OCH₂), 3.4 (s, 3H, CH₃O); $^{13}\text{C NMR}$ δ 162 (C=O), 154 (HC=), 158, 157, 145, 133, 131, 130, 128, 128, 114 (Ph), 116 (CN), 103 (C=), 70 (OCH₂), 64 (OCOCH₂), 59 (OCH₃), 56 (PhOCH₃); IR (cm⁻¹): 2993 (m, C-H), 2222 (m, CN), 1732 (s, C=O), 1601 (s, C=C), 1263 (s, C-O-CH₃), 762 (s, C-H out of plane). Anal. Calcd. for C₂₀H₁₉NO₅: C, 67.98; H, 5.42; N, 3.96; Found: C, 68.40; H, 5.75; N, 4.19.

3.1.7. 2-Methoxyethyl 2-(4-methoxyphenoxy)phenylcyanoacrylate

Yield 79%; mp 75°C; $^1\text{H NMR}$ δ 8.8 (s, 1H, CH=), 8.5-6.7 (m, 8H, Ph), 4.4 (t, 2H, OCOCH₂), 3.8 (s, 3H, PhOCH₃), 3.7 (t, 2H, OCH₂), 3.4 (s, 3H, CH₃O); $^{13}\text{C NMR}$ δ 163 (C=O), 153 (HC=), 158, 156, 145, 133, 131, 130, 128, 125, 114 (Ph), 116 (CN), 103 (C=), 70 (OCH₂), 64 (OCOCH₂), 59 (OCH₃), 56 (PhOCH₃); IR (cm⁻¹): 2976 (m, C-H), 2220 (m, CN), 1732 (s, C=O), 1599 (s, C=C), 1237 (s, C-O-CH₃), 834 (s, C-H out of plane). Anal. Calcd. for C₂₀H₁₉NO₅: C, 67.98; H, 5.42; N, 3.96; Found: C, 66.44; H, 5.90; N, 4.42.

3.1.8. 2-Methoxyethyl 3-(4-methoxyphenoxy)phenylcyanoacrylates

Yield 93%; $^1\text{H NMR}$ δ 8.2 (s, 1H, CH=), 7.8-6.5 (m, 8H, Ph), 4.4 (t, 2H, OCOCH₂), 3.8 (s, 3H, PhOCH₃), 3.5 (t, 2H, OCH₂), 3.4 (s, 3H, CH₃O); $^{13}\text{C NMR}$ δ 162 (C=O), 155 (HC=), 159, 157, 150, 145, 138, 135, 131, 125, 123, 113 (Ph), 116 (CN), 104 (C=), 70 (OCH₂), 66 (OCOCH₂), 59 (OCH₃), 56 (PhOCH₃); IR (cm⁻¹): 2943 (m, C-H), 2219 (m, CN), 1728 (s, C=O), 1589 (s, C=C), 1250 (s, C-O-CH₃), 787 (s, C-H out of plane). Anal. Calcd. for C₂₀H₁₉NO₅: C, 67.98; H, 5.42; N, 3.96; Found: C, 68.10; H, 5.90; N, 4.06.

3.1.9. 2-Methoxyethyl 4-(4-methoxyphenoxy)phenylcyanoacrylate

Yield 87%; $^1\text{H NMR}$ δ 8.2 (s, 1H, CH=), 8.1-6.7 (m, 8H, Ph), 4.5 (t, 2H, OCOCH₂), 3.9 (s, 3H, PhOCH₃), 3.7 (t, 2H, OCH₂), 3.4 (s, 3H, CH₃O); $^{13}\text{C NMR}$ δ 163 (C=O), 155 (HC=), 157, 155, 150, 148, 134, 132, 131, 127, 125, 114 (Ph), 116 (CN), 100 (C=), 70 (OCH₂), 65 (OCOCH₂), 62 (OCH₃), 56 (PhOCH₃); IR (cm⁻¹): 2946 (m, C-H), 2222 (m, CN), 1728 (s, C=O), 1541 (s, C=C), 1276 (s, C-O-CH₃), 832 (s, C-H out of plane). Anal. Calcd. for C₂₀H₁₉NO₅: C, 67.98; H, 5.42; N, 3.96; Found: C, 67.17; H, 5.62; N, 4.11.

3.1.10. 2-Methoxyethyl 3-(4-methylphenoxy)phenylcyanoacrylates

Yield 91%; $^1\text{H NMR}$ δ 8.2 (s, 1H, CH=), 7.8-6.7 (m, 8H, Ph), 4.4 (t, 2H, OCOCH₂), 3.5 (t, 2H, OCH₂), 3.4 (s, 3H, CH₃O) 2.4 (s, 3H, PhCH₃); $^{13}\text{C NMR}$ δ 163 (C=O), 154 (HC=), 155, 133, 131, 130, 120 (Ph), 116 (CN), 100 (C=), 70 (OCH₂), 64 (OCOCH₂), 59 (OCH₃), 21 (PhCH₃); IR (cm⁻¹): 2921 (m, C-H), 2219 (m, CN), 1729 (s, C=O), 1589 (s, C=C), 1222 (s, C-O-CH₃), 809 (s, C-H out of plane). Anal. Calcd. for C₂₀H₁₉NO₄: C, 71.20; H, 5.68; N, 4.15; Found: C, 71.22; H, 5.80; N, 4.46.

3.1.11. 2-Methoxyethyl 4-(4-methylphenoxy)phenylcyanoacrylates

Yield 85%; $^1\text{H NMR}$ δ 8.2 (s, 1H, CH=), 8.1-6.8 (m, 8H, Ph), 4.4 (t, 2H, OCOCH₂), 3.5 (t, 2H, OCH₂), 3.4 (s, 3H, CH₃O) 2.4 (s, 3H, PhCH₃); $^{13}\text{C NMR}$ δ 163 (C=O), 157 (HC=), 154, 153, 135, 134, 132, 131, 129, 118, 117 (Ph), 116 (CN), 100 (C=), 70 (OCH₂), 66 (OCOCH₂), 59 (OCH₃), 21 (PhCH₃); IR (cm⁻¹): 2911 (m, C-H), 2219 (m, CN), 1728 (s, C=O), 1587 (s, C=C), 1200 (s, C-O-CH₃), 823 (s, C-H out of plane). Anal. Calcd. for C₂₀H₁₉NO₄: C, 71.20; H, 5.68; N, 4.15; Found: C, 70.68; H, 6.06; N, 4.22.

3.1.12. 2-Methoxyethyl 3-(3,5-dichlorophenoxy)phenylcyanoacrylates

Yield 78%; $^1\text{H NMR}$ δ 8.2 (s, 1H, CH=), 7.9-6.5 (m, 8H, Ph), 4.4 (t, 2H, OCOCH₂), 3.5 (t, 2H, OCH₂), 3.4 (s, 3H, CH₃O); $^{13}\text{C NMR}$ δ 163 (C=O), 154 (HC=), 154, 134, 131, 128, 127, 122 (Ph), 117 (CN), 100 (C=), 70 (OCH₂), 64 (OCOCH₂), 59 (OCH₃); IR (cm⁻¹): 2934 (m, C-H), 2221 (m, CN), 1722 (s, C=O), 1576 (s, C=C), 1245 (s, C-O-CH₃), 811 (s, C-H out of plane). Anal. Calcd. for C₁₉H₁₅Cl₂NO₄: C, 58.11; H, 3.85; N, 3.57; Found: C, 58.63; H, 3.98; N, 3.86.

3.1.13. 2-Methoxyethyl 4-(2,4-dichlorophenoxy)phenylcyanoacrylates

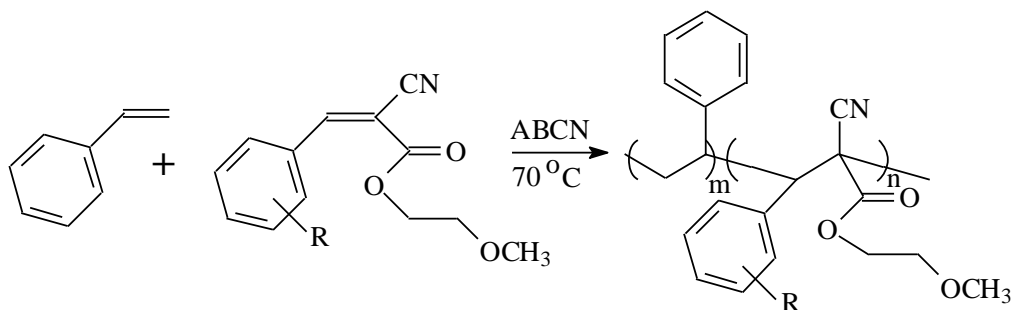
Yield 91%; $^1\text{H NMR}$ δ 8.2 (s, 1H, CH=), 7.7-6.8 (m, 8H, Ph), 4.4 (t, 2H, OCOCH₂), 3.5 (t, 2H, OCH₂), 3.4 (s, 3H, CH₃O); $^{13}\text{C NMR}$ δ 162 (C=O), 153 (HC=), 154, 133, 131, 128, 126, 125, 122, 118 (Ph), 116 (CN), 101 (C=), 70 (OCH₂), 64 (OCOCH₂), 59 (OCH₃); IR (cm⁻¹): 2928 (m, C-H), 2227 (m, CN), 1728 (s, C=O), 1596 (s, C=C), 1248 (s, C-O-CH₃), 833 (s, C-H out of plane). Anal. Calcd. for C₁₉H₁₅Cl₂NO₄: C, 58.11; H, 3.85; N, 3.57; Found: C, 56.41; H, 4.29; N, 4.11.

3.1.14. 2-Methoxyethyl 3-(3-trifluoromethyl)phenoxyphenylcyanoacrylates

Yield 78%; $^1\text{H NMR}$ δ 8.2 (s, 1H, CH=), 7.8-6.8 (m, 8H, Ph), 4.5 (t, 2H, OCOCH₂), 3.5 (t, 2H, OCH₂), 3.4 (s, 3H, CH₃O); $^{13}\text{C NMR}$ δ 163 (C=O), 154 (HC=), 157, 134, 131, 128, 127, 122 (Ph), 117 (CN), 100 (C=), 70 (OCH₂), 64 (OCOCH₂), 59 (OCH₃); IR (cm⁻¹): 2926 (m, C-H), 2223 (m, CN), 1719 (s, C=O), 1587 (s, C=C), 1249 (s, C-O-CH₃), 834 (s, C-H out of plane). Anal. Calcd. for C₂₀H₁₆F₃NO₄: C, 61.38; H, 4.12; N, 3.58; Found: C, 60.03; H, 4.59; N, 4.98.

3.2. Synthesis and characterization of styrene – MEPA copolymers

Copolymers of the ST and the MEPA compounds, P(ST-co-MEPA) were prepared in 25-mL glass screw cap vials at ST/MEPA = 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 70°C. 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 MEPA monomers). The novel synthesized MEPA 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 phenoxy ring-substituted 2-methoxyethyl phenylcyanoacrylates, $R\text{PhCH} = \text{C}(\text{CN})\text{CO}_2\text{CH}_2\text{CH}_2\text{OCH}_3$. R is 3-phenoxy, 3-(4-chlorophenoxy), 4-(4-chlorophenoxy), 2-(4-fluorophenoxy), 4-(4-fluorophenoxy), 2-(3-methoxyphenoxy), 2-(4-methoxyphenoxy), 3-(4-methoxyphenoxy), 4-(4-methoxyphenoxy),

3-(4-methylphenoxy), 4-(4-methylphenoxy), 3-(3,5-dichlorophenoxy), 4-(2,4-dichlorophenoxy), 3-(3-trifluoromethyl)phenoxy.

Table 1. Copolymerization of Styrene and 2-Methoxyethyl phenylcyanoacrylates.

R	Yield ^a (wt%)	N (wt%)	ST in copol. (mol%)	MEPA in copol. (mol%)
3-Phenoxy	12.2	2.01	78.2	21.8
3-(4-Chlorophenoxy)	13.3	2.33	69.9	30.1
4-(4-Chlorophenoxy)	14.2	2.31	70.4	29.6
2-(4-Fluorophenoxy)	14.6	2.38	70.4	29.6
4-(4-Fluorophenoxy)	13.5	2.18	74.3	25.7
2-(3-Methoxyphenoxy)	12.9	2.36	69.8	30.2
2-(4-Methoxyphenoxy)	16.2	2.45	67.7	32.3
3-(4-Methoxyphenoxy)	12.8	2.40	68.9	31.1
4-(4-Methoxyphenoxy)	15.5	1.84	79.7	20.3
3-(4-Methylphenoxy)	16.9	2.09	76.2	23.8
4-(4-Methylphenoxy)	13.4	2.37	70.9	29.1
3-(3,5-Dichlorophenoxy)	15.2	1.73	80.0	20.0
4-(2,4-Dichlorophenoxy)	13.2	2.14	71.6	28.4
3-[3-(Trifluoromethyl)phenoxy]	12.4	1.71	80.4	19.6

Nitrogen elemental analysis showed that between 19.6 and 32.3 mol% of MEPA is present in the copolymers prepared at ST/MEPA = 3 (mol), which is indicative of relatively high reactivity of the MEPA monomers towards ST radical which is typical of phenoxy ring-substituted phenylcyanoacrylates. Since MEPA monomers do not homopolymerize, the most likely structure of the copolymers would be isolated MEPA 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, phenoxy ring-substituted 2-methoxyethyl phenylcyanoacrylates, $RPhCH=C(CN)CO_2CH_2CH_2OCH_3$ (where R is 3-phenoxy, 3-(4-chlorophenoxy), 4-(4-chlorophenoxy), 2-(4-fluorophenoxy), 4-(4-fluorophenoxy), 2-(3-methoxyphenoxy), 2-(4-methoxyphenoxy), 3-(4-methoxyphenoxy), 4-(4-methoxyphenoxy), 3-(4-methylphenoxy), 4-(4-methylphenoxy), 3-(3,5-dichlorophenoxy), 4-(2,4-dichlorophenoxy), 3-(3-trifluoromethyl)phenoxy) were prepared and copolymerized with styrene.

Acknowledgments

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