Synthesis and styrene copolymerization of fluoro, iodo, phenoxy, methoxy, and methyl ring-disubstituted 2-methoxyethyl phenylcyanoacrylates

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Abstract

Novel ring-disubstituted 2-methoxyethyl phenylcyanoacrylates, $RPhCH=C(CN)CO_2CH_2CH_2OCH_3$ (where R is 2-fluoro-3-methoxy, 2-fluoro-4-methoxy, 2-fluoro-5-methoxy, 2-fluoro-6-methoxy, 3-fluoro-4-methoxy, 4-fluoro-3-methoxy, 2-fluoro-5-methyl, 2-fluoro-6-methyl, 3-fluoro-4-methyl, 4-fluoro-2-methyl, 4-fluoro-3-methyl, 4-fluoro-3-phenoxy, 5-iodo-2-methoxy) were prepared and copolymerized with styrene. The acrylates were synthesized by the piperidine catalyzed Knoevenagel condensation of ring-disubstituted benzaldehydes and 2-methoxyethyl 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.

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

1. Introduction

3-(4-Fluoro-3-methoxyphenyl) ethyl propenoate is reported in S,O-ligand-promoted Pd-catalyzed C-H olefination of anisole derivatives [1]; in ^{19}F- and ^{18}F-arene deoxyfluorination via organic photoredox-catalysed polarity-reversed nucleophilic aromatic substitution [2]; in studies of inhibition of benzylideneacetone derivatives of osteoclastogenesis and osteoblastogenesis based on specific structure-activity relationship [3]; synthesis of benzylideneacetone derivatives [4] and deoxyfluorination of phenols [5]; in preparation of 1,3-diphenyl-2,2-difluoro-2,3-dihydro-1H-imidazole derivative as a fluorinating agent for fluorination of hydroxy aromatic organic compounds [6], in preparation of thiophene derivatives as STAT6 inhibitors for treatment of allergic disease [7] and tricyclic sulfonamide derivatives as sodium channel inhibitors for treatment of pain [8]. 3-(4-Fluoro-3-methylphenyl) ethyl propenoate is involved in preparation of bromoalcohol compounds in presence of quinine-based derivatives [9]; in preparation of β-amino acid derivatives useful as IFNβ modulators [10]; in studies of 2,5-disubstituted tetrahydrofurans as selective serotonin re-uptake inhibitors [11]; in preparation of tetrahydrofuran derivatives as dual

inhibitors of serotonin reuptake and phosphodiesterase 4 enzyme activity for treating central nervous system disorders [12]; in preparation of 3-(2,3-Dihydro-1H-inden-5-yl)propanoic acid derivatives as NRF2 regulators [13]; in synthesis of highly substituted arenes via cyclohexadiene-alkene c-h cross coupling and aromatization [14], as well as aryl- and heteroarylalkanoic acid derivatives as NRF2 regulators [15]. 3-(3-Iodo-4-methoxyphenyl) methyl 2-propenoate is reported in Cu, Ni, and Pd mediated Ullmann homocoupling reactions in biaryl syntheses [16], and in study of Lythrum alkaloids [17].

In this work we have prepared ring-disubstituted 2-methoxyethyl phenylcyanoacrylates, $RPhCH=C(CN)CO_2CH_2CH_2OCH_3$, where R is 2-fluoro-3-methoxy, 2-fluoro-4-methoxy, 2-fluoro-5-methoxy, 2-fluoro-6-methoxy, 3-fluoro-4-methoxy, 4-fluoro-3-methoxy, 2-fluoro-5-methyl, 2-fluoro-6-methyl, 3-fluoro-4-methyl, 4-fluoro-2-methyl, 4-fluoro-3-methyl, 4-fluoro-3-phenoxy, 5-iodo-2-methoxy), 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

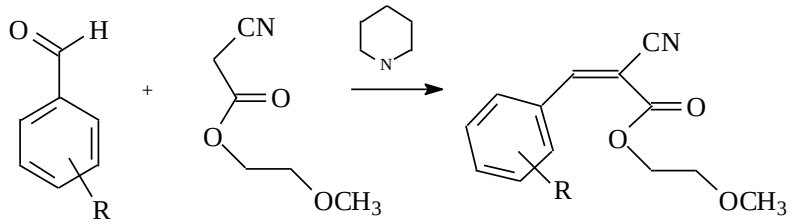
2-Fluoro-3-methoxy, 2-fluoro-4-methoxy, 2-fluoro-5-methoxy, 2-fluoro-6-methoxy, 3-fluoro-4-methoxy, 4-fluoro-3-methoxy, 2-fluoro-5-methyl, 2-fluoro-6-methyl, 3-fluoro-4-methyl, 4-fluoro-2-methyl, 4-fluoro-3-methyl, 4-fluoro-3-phenoxy, 5-iodo-2-methoxy -substituted benzaldehydes, 2-methoxyethyl cyanoacetate (≥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 described in [19].

3. Results and discussion

3.1. Synthesis and characterization of 2-methoxyethyl phenylcyanoacrylates

All MEPA compounds were synthesized by Knoevenagel condensation [20] of appropriate benzaldehydes with 2-methoxyethyl cyanoacetate, catalyzed by base, piperidine (Scheme 1).



Scheme 1. Synthesis of 2-methoxyethyl phenylcyanoacrylates where R is 2-fluoro-3-methoxy, 2-fluoro-4-methoxy, 2-fluoro-5-methoxy, 2-fluoro-6-methoxy, 3-fluoro-4-methoxy, 4-fluoro-3-methoxy, 2-fluoro-5-methyl, 2-fluoro-6-methyl, 3-fluoro-4-methyl, 4-fluoro-2-methyl, 4-fluoro-3-methyl, 4-fluoro-3-phenoxy, 5-iodo-2-methoxy.

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, ^{1}H 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 2-fluoro-3-methoxyphenylcyanoacrylate***

Yield: 74%; ^{1}H NMR: δ 8.6 (s, 1H, CH=), 8.0-7.1 (m, 3H, Ph), 4.5 (t, 2H, $OCOCH_2$), 3.9 (s, 3H, $PhOCH_3$), 3.7 (t, 2H, OCH_2), 3.4 (s, 3H, OCH_3); ^{13}C NMR: δ 164 (C=O), 154 (HC=), 143, 135, 131, 125, 112, 106 (Ph), 116 (CN), 105 (C=), 74 (OCH_2), 65 ($OCOCH_2$), 59 (OCH_3), 56 ($PhOCH_3$); IR: (cm^{-1}) 2943 (m, C-H), 2228 (m, CN), 1734 (s, C=O), 1580 (s, C=C), 1277 (s, C-O-CH_3), 784, 721 (s, C-H out of plane). Anal. calcd. for $C_{14}H_{14}FNO_4$: C, 60.21; H, 5.05; N, 5.02; Found: C, 54.74; H, 4.61; N, 4.87.

3.1.2. ***2-Methoxyethyl 2-fluoro-4-methoxyphenylcyanoacrylate***

Yield: 83%; ^{1}H NMR: δ 8.5 (s, 1H, CH=), 7.9-6.6 (m, 3H, Ph), 4.5, 4.4 (t, 2H, $OCOCH_2$), 3.9 (s, 3H, $PhOCH_3$), 3.7, 3.6 (t, 2H, OCH_2), 3.4 (s, 3H, OCH_3); ^{13}C NMR: δ 168-163 (C=O), 146 (HC=), 130, 118, 114-111 (Ph), 116 (CN), 102 (C=), 74, 70 (OCH_2), 66 ($OCOCH_2$), 62, 59 (OCH_3), 56 ($PhOCH_3$); IR: (cm^{-1}) 2935 (m, C-H), 2222 (m, CN), 1749 (s, C=O), 1620 (s, C=C), 1275 (s, C-O-CH_3), 843, 814 (s, C-H out of plane). Anal. calcd. for $C_{14}H_{14}FNO_4$: C, 60.21; H, 5.05; N, 5.02; Found: C, 58.74; H, 4.87; N, 4.89.

3.1.3. ***2-Methoxyethyl 2-fluoro-5-methoxyphenylcyanoacrylate***

Yield 91%; ^{1}H NMR: δ 8.5 (s, 1H, CH=), 7.9-7.0 (m, 3H, Ph), 4.5, 4.4 (t, 2H, $OCOCH_2$), 3.9, 3.8 (s, 3H, $PhOCH_3$), 3.7, 3.6 (t, 2H, OCH_2), 3.4 (s, 3H, OCH_3); ^{13}C NMR: δ 166, 164 (C=O), 158, 156 (HC=), 146, 124, 123, 120, 115, 110 (Ph), 117 (CN), 104 (C=), 74

(OCH_2), 70, 66 ($OCOCH_2$), 59 (OCH_3), 56 ($PhOCH_3$); IR: (cm^{-1}) 2943 (m, C-H), 2228 (m, CN), 1734 (s, C=O), 1580 (s, C=C), 1277 (s, C-O-CH_3), 784, 721 (s, C-H out of plane). Anal. calcd. for $C_{14}H_{14}FNO_4$: C, 60.21; H, 5.05; N, 5.02; Found: C, 54.74; H, 4.61; N, 4.87.

3.1.4. ***2-Methoxyethyl 2-fluoro-6-methoxyphenylcyanoacrylate***

Yield 85%; ^1H NMR: δ8.3, 8.4 (s, 1H, CH=), 7.6-6.7 (m, 3H, Ph), 4.5 (t, 2H, $OCOCH_2$), 3.9 (s, 3H, $PhOCH_3$), 3.7 (t, 2H, OCH_2), 3.4 (s, 3H, OCH_3); ^{13}C NMR: δ165, 163, 162 (C=O), 160 (HC=), 146, 136, 134, 125, 110, 109, 108 (Ph), 115. 114 (CN), 107 (C=), 74, 70 (OCH_2), 66 ($OCOCH_2$), 59 (OCH_3), 56 ($PhOCH_3$); IR: (cm^{-1}) 2943 (m, C-H), 2230 (m, CN), 1732 (s, C=O), 1616 (s, C=C), 1261 (s, C-O-CH_3), 785, 756 (s, C-H out of plane). Anal. calcd. for $C_{14}H_{14}FNO_4$: C, 60.21; H, 5.05; N, 5.02; Found: C, 57.97; H, 4.82; N, 4.88.

3.1.5. ***2-Methoxyethyl 3-fluoro-4-methoxyphenylcyanoacrylate***

Yield 74%; ^1H NMR: δ8.1 (s, 1H, CH=), 8.0-7.0 (m, 3H, Ph), 4.5 (t, 2H, $OCOCH_2$), 4.0 (s, 3H, $PhOCH_3$), 3.7 (t, 2H, OCH_2), 3.4 (s, 3H, OCH_3); ^{13}C NMR: δ166, 163 (C=O), 154, 153 (HC=), 130, 129, 125, 118, 1115 (Ph), 116 (CN), 101 (C=), 74, 70 (OCH_2), 66 ($OCOCH_2$), 62, 59 (OCH_3), 56 ($PhOCH_3$); IR: (cm^{-1}) 2938 (m, C-H), 2222 (m, CN), 1749 (s, C=O), 1609 (s, C=C), 1283 (s, C-O-CH_3), 874, 818, 744 (s, C-H out of plane). Anal. calcd. for $C_{14}H_{14}FNO_4$: C, 60.21; H, 5.05; N, 5.02; Found: C, 57.75; H, 4.72; N, 4.91.

3.1.6. ***2-Methoxyethyl 4-fluoro-3-methoxyphenylcyanoacrylate***

Yield 79%; ^{1}H NMR: δ8.2 (s, 1H, CH=), 7.9-7.1 (m, 3H, Ph), 4.5, 4.4 (t, 2H, $OCOCH_2$), 4.0 (s, 3H, $PhOCH_3$), 3.8, 3.7 (t, 2H, OCH_2), 3.4 (s, 3H, OCH_3); ^{13}C NMR: δ165, 164 (C=O), 158, 157, 154 (HC=), 149, 134, 128, 126, 125, 114 (Ph), 117 (CN), 103, 102 (C=), 74, 70 (OCH_2), 65, 62 ($OCOCH_2$), 59 (OCH_3), 56 ($PhOCH_3$); IR: (cm^{-1}) 2941 (m, C-H), 2224 (m, CN), 1751 (s, C=O), 1595 (s, C=C), 1265 (s, C-O-CH_3), 858, 783, 762 (s, C-H out of plane). Anal. calcd. for $C_{14}H_{14}FNO_4$: C, 60.21; H, 5.05; N, 5.02; Found: C, 57.44; H, 4.85; N, 4.91.

3.1.7. ***2-Methoxyethyl 2-fluoro-5-methylphenylcyanoacrylate***

Yield 79%; ^{1}H NMR δ8.5 (s, 1H, CH=), 7.7-7.0 (m, 3H, Ph), 5.2 (s, 2H, $PhCH_2$), 4.5, 4.3 (t, 2H, $OCOCH_2$), 3.6 (t, 2H, OCH_2), 3.4 (s, 3H, OCH_3), 2.4 (s, 3H, $PhCH_3$); ^{13}C NMR: δ163 (C=O), 158 (HC=), 148, 137, 136, 130, 124, 120 (Ph), 116 (CN), 104 (C=), 74, 70 (OCH_2), 66 ($OCOCH_2$), 59 (OCH_3), 20 ($PhCH_3$); IR: (cm^{-1}) 2932 (m, C-H), 2226 (m, CN), 1734 (s, C=O), 1609 (s, C=C), 1236 (s, C-O-CH_3), 824, 764, 714 (s, C-H out of plane). Anal. calcd. for $C_{14}H_{14}FNO_3$: C, 63.87; H, 5.36; N, 5.32; Found: C, 59.80; H, 5.16; N, 4.90.

3.1.8. ***2-Methoxyethyl 2-fluoro-6-methylphenylcyanoacrylates***

Yield 89%; ^{1}H NMR δ8.3 (s, 1H, CH=), 7.5-6.9 (m, 3H, Ph), 4.5 (t, 2H, $OCOCH_2$), 3.7 (t, 2H, OCH_2), 3.4 (s, 3H, OCH_3), 2.4 (s, 3H, $PhCH_3$); ^{13}C NMR: δ165 (C=O), 150 (HC=), 143, 140, 135, 133, 126, 123 (Ph), 116 (CN), 104 (C=), 74, 70 (OCH_2), 66 ($OCOCH_2$), 59 (OCH_3), 21 ($PhCH_3$); IR: (cm^{-1}) 2934 (m, C-H), 2233 (m, CN), 1750 (s,

C=O), 1614 (s, C=C), 1256 (s, C-O-CH_3), 862, 827, 787 (s, C-H out of plane). Anal. calcd. for $C_{14}H_{14}FNO_3$: C, 63.87; H, 5.36; N, 5.32; Found: C, 60.80; H, 5.19; N, 5.28.

3.1.9. ***2-Methoxyethyl 3-fluoro-4-methylphenylcyanoacrylate***

Yield 83%; ^{1}H NMR δ 8.2 (s, 1H, CH=), 7.8-7.3 (m, 3H, Ph), 4.5 (t, 2H, $OCOCH_2$), 3.6 (t, 2H, OCH_2), 3.4 (s, 3H, OCH_3), 2.4 (s, 3H, $PhCH_3$); ^{13}C NMR: δ 166 (C=O), 154 (HC=), 136, 134, 133, 127, 126, 115 (Ph), 117 (CN), 104 (C=), 70 (OCH_2), 66 ($OCOCH_2$), 59 (OCH_3), 25 ($PhCH_3$); IR: (cm^{-1}) 2932 (m, C-H), 2224 (m, CN), 1754 (s, C=O), 1607 (s, C=C), 1277 (s, C-O-CH_3), 874, 824, 781 (s, C-H out of plane). Anal. calcd. for $C_{14}H_{14}FNO_3$: C, 63.87; H, 5.36; N, 5.32; Found: C, 66.76; H, 5.44; N, 5.78.

3.1.10. ***2-Methoxyethyl 4-fluoro-2-methylphenylcyanoacrylates***

Yield 91%; ^{1}H NMR δ 8.5 (s, 1H, CH=), 8.3-6.9 (m, 3H, Ph), 4.5 (t, 2H, $OCOCH_2$), 3.7 (t, 2H, OCH_2), 3.4 (s, 3H, OCH_3), 2.5 (s, 3H, $PhCH_3$); ^{13}C NMR: δ 163 (C=O), 153 (HC=), 144, 135, 131, 127, 119, 114 (Ph), 116 (CN), 104 (C=), 70 (OCH_2), 66 ($OCOCH_2$), 59 (OCH_3), 20 ($PhCH_3$); IR: (cm^{-1}) 2932 (m, C-H), 2226 (m, CN), 1751 (s, C=O), 1591 (s, C=C), 1244 (s, C-O-CH_3), 866, 824 (s, C-H out of plane). Anal. calcd. for $C_{14}H_{14}FNO_3$: C, 63.87; H, 5.36; N, 5.32; Found: C, 60.82; H, 5.14; N, 5.54.

3.1.11. ***2-Methoxyethyl 4-fluoro-3-methylphenylcyanoacrylates***

Yield 76%;^{1}H NMR δ 8.2 (s, 1H, CH=), 7.9-7.1 (m, 3H, Ph), 4.5 (t, 2H, $OCOCH_2$), 3.7 (t, 2H, OCH_2), 3.4 (s, 3H, OCH_3), 2.3 (s, 3H, $PhCH_3$); ^{13}C NMR: δ 163 (C=O), 153 (HC=), 145, 144, 136, 131, 127, 119 (Ph), 116 (CN), 104 (C=), 70 (OCH_2), 66 ($OCOCH_2$), 59 (OCH_3), 20 ($PhCH_3$); IR: (cm^{-1}) 2932 (m, C-H), 2224 (m, CN), 1751 (s,

C=O), 1589 (s, C=C), 1250 (s, C-O-CH_3), 827 (s, C-H out of plane). Anal. calcd. for $C_{14}H_{14}FNO_3$: C, 63.87; H, 5.36; N, 5.32; Found: C, 61.80; H, 5.22; N, 5.13.

3.1.12. ***2-Methoxyethyl 4-fluoro-3-phenoxyphenylcyanoacrylates***

Yield 83%; ^{1}H NMR δ 8.1 (s, 1H, CH=), 7.7-7.0 (m, 3H, Ph), 4.4 (t, 2H, $OCOCH_2$), 3.6 (t, 2H, OCH_2), 3.4 (s, 3H, CH_3O); ^{13}C NMR δ 163 (C=O), 156 (HC=), 145, 134, 130, 127, 125, 121, 118 (Ph), 117 (CN), 101 (C=), 74 (OCH_2), 66 ($OCOCH_2$), 59 (OCH_3); IR (cm^{-1}): 2934 (m, C-H), 2224 (m, CN), 1761 (s, C=O), 1589 (s, C=C), 1254 (s, C-O-CH_3), 822, 756 (s, C-H out of plane). Anal. Calcd. for $C_{19}H_{16}FNO_4$: C, 66.86; H, 4.72; N, 4.10; Found: C, 65.54; H, 4.52; N, 4.71.

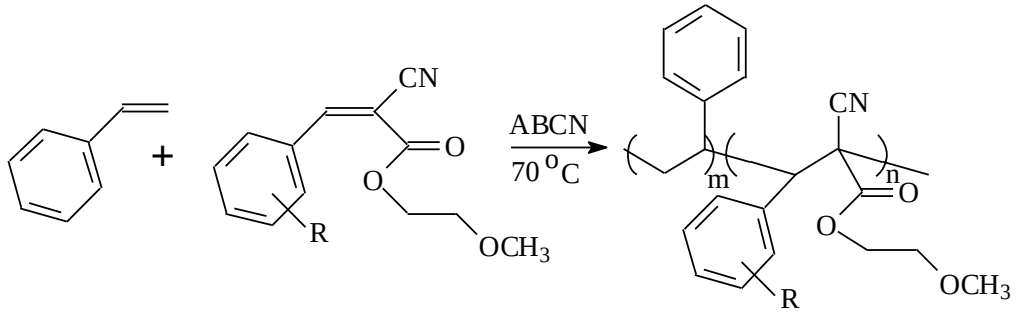
3.1.13. ***2-Methoxyethyl 5-iodo-2-methoxyphenylcyanoacrylates***

Yield 79%; mp 117.5°C; ^{1}H NMR δ 8.4 (s, 1H, CH=), 8.2-6.7 (m, 3H, Ph), 4.5 (t, 2H, $OCOCH_2$), 3.8 (s, 3H, $PhCH_3$), 3.7 (t, 2H, OCH_2), 3.4 (s, 3H, CH_3O), 2.6 (s, 3H, $PhCH_3$); ^{13}C NMR δ 160 (C=O), 155 (HC=), 143, 138, 123, 114 (Ph), 117 (CN), 103 (C=), 74 (OCH_2), 64 ($OCOCH_2$), 59 (OCH_3) 55 ($PhOCH_3$); IR (cm^{-1}): 2949 (m, C-H), 2214 (m, CN), 1730 (s, C=O), 1583 (s, C=C), 1246 (s, C-O-CH_3), 818, 762 (s, C-H out of plane). Anal. Calcd. for $C_{14}H_{14}INO_4$: C, 43.43; H, 3.64; N, 3.62; Found: C, 44.30; H, 3.74; N, 3.62.

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 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 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, RPhCH = $C(CN)CO_2CH_2CH_2OCH_3$. R is 2-fluoro-3-methoxy, 2-fluoro-4-methoxy, 2-fluoro-5-methoxy, 2-fluoro-6-methoxy, 3-fluoro-4-methoxy, 4-fluoro-3-methoxy, 2-fluoro-5-methyl, 2-fluoro-6-methyl, 3-fluoro-4-methyl, 4-fluoro-2-methyl, 4-fluoro-3-methyl, 4-fluoro-3-phenoxy, 5-iodo-2-methoxy.

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

R	Yield[a] (wt%)	N (wt%)	ST in copol. (mol%)	MEPA in copol. (mol%)
2-Fluoro-3-methoxy	11.5	2.36	75.1	24.9
2-Fluoro-4-methoxy	14.1	2.22	77.2	22.8
2-Fluoro-5-methoxy	13.2	2.43	74.1	25.9
2-Fluoro-6-methoxy	14.2	2.35	75.3	24.7
3-Fluoro-4-methoxy	13.0	2.28	76.3	23.7
4-Fluoro-3-methoxy	11.8	2.2	77.5	22.5
2-Fluoro-5-methyl	12.9	2.65	71.8	28.2
2-Fluoro-6-methyl	11.5	1.83	82.8	17.2
3-Fluoro-4-methyl	12.9	2.42	75.2	24.8
4-Fluoro-2-methyl	14.5	1.98	81.0	19.0
4-Fluoro-3-methyl	11.3	2.06	80.0	20.0
4-Fluoro-3-phenoxy	12.5	1.99	77.7	22.3
5-Iodo-2-methoxy	14.7	2.11	72.7	27.3

Nitrogen elemental analysis showed that between 17.2 and 28.2 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 ring-substituted 2-methoxyethyl phenylcyanoacrylates, $RPhCH=C(CN)CO_2CH_2CH_2OCH_3$ (where R is 2-fluoro-3-methoxy, 2-fluoro-4-methoxy, 2-fluoro-5-methoxy, 2-fluoro-6-methoxy, 3-fluoro-4-methoxy, 4-fluoro-3-methoxy, 2-fluoro-5-methyl, 2-fluoro-6-methyl, 3-fluoro-4-methyl, 4-fluoro-2-methyl, 4-fluoro-3-methyl, 4-fluoro-3-phenoxy, 5-iodo-2-methoxy) were prepared and copolymerized with styrene.

Acknowledgments

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