Synthesis and styrene copolymerization of 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 4-methoxy-2-methyl, 4-methoxy-3-methyl, 3-ethoxy-4-methoxy, 4-ethoxy-3-methoxy, 3,4-dibenzyloxy, 3-benzyloxy-4-methoxy, 4-benzyloxy-3-methoxy, 2-bromo-5-methoxy, 3-bromo-4-methoxy, 5-bromo-2-methoxy, 2-chloro-3-methoxy, 3-chloro-4-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-substituted 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.

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1. Introduction

4-Methoxy-3-methyl ring-disubstituted ethyl phenylcyanoacrylate (PCA) was involved in the discovery of potent, orally bioavailable pyrimidine-5-carbonitrile-6-alkyl CXCR2 receptor antagonists [1], and in synthesis of methoxytolylsuccinic acids [2]. 3-Ethoxy-4-(2-hydroxyethoxy) ring-disubstituted ethyl PCA is reported in syntheses of 4-benzyl-2-imidazolidinones from N-[(1-cyano-2-phenyl)ethyl] carbamates [3], whereas 3,4-diethoxy PCA in synthesis of 3-hydroxypyridines via condensation of aromatic aldehydes with ethyl cyanoacetate [4]. 3,4-Dibenzyloxy ring-disubstituted ethyl PCA was part of synthesis and studies of *in vitro* anticancer activity of new 2-thioxo-oxazolidin-4-one derivatives [5]. 4-Benzyloxy-3-methoxyphenyl ethyl PCA was part of solvent-free antimony trichloride catalyzed Knoevenagel condensation reaction under microwave irradiation [6, 7]. 3-Bromo-4-methoxyphenyl ethyl PCA is reported in synthesis of thiazacridine derivatives as anticancer agents against breast and hematopoietic neoplastic cells [8]; in biochemical evaluation of virtual screening methods related to cell-active inhibitor of the cancer-promoting phosphatases of regenerating liver [9]; in synthesis, mass spectra investigation and study of biological activity of pyrimidine derivatives [10]; in synthesis, in study of vitro anticancer activity and in silico study of new disubstituted thiazolidinedione derivatives

[11]; in preparation of thiazacridines as anticancer agents [12]; in synthesis and study of in vitro anticancer activity of novel thiazacridine derivatives [13]; in synthesis and study of anti-inflammatory activity of new arylidene-thiazolidine-2,4-diones as PPARγ ligands [14]; in preparation of 2,4-thiazolidinedione derivatives having hypoglycemic activity [15], and in synthesis and study of anti-inflammatory activity of new thiazolidine-2,4-diones, 4-thioxothiazolidinones and 2-thioxoimidazolidinones [16].

In this work we have prepared ring-disubstituted 2-methoxyethyl phenylcyanoacrylates, (MEPA), $RPhCH=C(CN)CO_2CH_2CH_2OCH_3$, where R is 4-methoxy-2-methyl, 4-methoxy-3-methyl, 3-ethoxy-4-methoxy, 4-ethoxy-3-methoxy, 3,4-dibenzyloxy, 3-benzyloxy-4-methoxy, 4-benzyloxy-3-methoxy, 2-bromo-5-methoxy, 3-bromo-4-methoxy, 5-bromo-2-methoxy, 2-chloro-3-methoxy, 3-chloro-4-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 [17].

2. Experimental

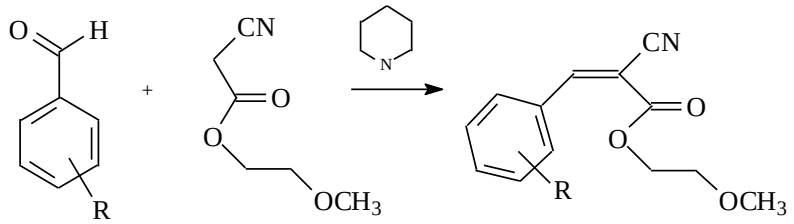
4-Methoxy-2-methyl, 4-methoxy-3-methyl, 3-ethoxy-4-methoxy, 4-ethoxy-3-methoxy, 3,4-dibenzyloxy, 3-benzyloxy-4-methoxy, 4-benzyloxy-3-methoxy, 2-bromo-5-methoxy, 3-bromo-4-methoxy, 5-bromo-2-methoxy, 2-chloro-3-methoxy, 3-chloro-4-methoxy, 2-chloro-6-methyl, 3-chloro-4-methyl-substituted benzaldehydes, 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 reported in [18].

3. Results and discussion

3.1. Synthesis and characterization of 2-methoxyethyl phenylcyanoacrylates

All MEPA compounds were synthesized by Knoevenagel condensation [19] of appropriate benzaldehydes with 2-methoxyethyl cyanoacetate, catalyzed by base, piperidine (Scheme 1).



Scheme 1. Synthesis of 2-methoxyethyl phenylcyanoacrylates where R is 4-methoxy-2-methyl, 4-methoxy-3-methyl, 3-ethoxy-4-methoxy, 4-ethoxy-3-methoxy, 3,4-dibenzyloxy, 3-benzyloxy-4-methoxy, 4-benzyloxy-3-methoxy, 2-bromo-5-methoxy, 3-bromo-4-methoxy, 5-bromo-2-methoxy, 2-chloro-3-methoxy, 3-chloro-4-methoxy, 2-chloro-6-methyl, 3-chloro-4-methyl.

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 4-methoxy-2-methylphenylcyanoacrylate*

Yield: 74%; ^{1}H NMR: δ 8.5 (s, 1H, CH=), 8.3-6.7 (m, 3H, Ph), 4.5 (t, 2H, $OCOCH_2$), 3.9 (s, 3H, $PhOCH_3$), 3.6 (t, 2H, OCH_2), 3.4 (s, 3H, OCH_3), 2.3 (s, 3H, $PhCH_3$); ^{13}C NMR: δ 164 (C=O), 152 (HC=), 143, 135, 131, 128, 124, 112 (Ph), 116 (CN), 100 (C=), 74 (OCH_2), 66 ($OCOCH_2$), 59 (OCH_3), 56 ($PhOCH_3$), 20 (CH_3); IR: (cm^{-1}) 2932 (m, C-H), 2220 (m, CN), 1751 (s, C=O), 1567 (s, C=C), 1292 (s, C-O-CH_3), 804, 779 (s, C-H out of plane). Anal. calcd. for $C_{15}H_{17}NO_4$: C, 65.44; H, 6.22; N, 5.09; Found: C, 62.98; H, 6.19; N, 4.93.

3.1.2. *2-Methoxyethyl 4-methoxy-3-methylphenylcyanoacrylate*

Yield: 83%; ^{1}H NMR: δ 8.1 (s, 1H, CH=), 8.0-6.8 (m, 3H, Ph), 4.5 (t, 2H, $OCOCH_2$), 3.9 (s, 3H, $PhOCH_3$), 3.6 (t, 2H, OCH_2), 3.4 (s, 3H, OCH_3), 2.3 (s, 3H, $PhCH_3$); ^{13}C NMR: δ 163 (C=O), 155 (HC=), 143, 134, 129, 128, 124, 110 (Ph), 116 (CN), 99 (C=), 74 (OCH_2), 66 ($OCOCH_2$), 59 (OCH_3), 56 ($PhOCH_3$), 20 (CH_3); IR: (cm^{-1}) 2930 (m, C-H), 2222 (m, CN), 1763 (s, C=O), 1599 (s, C=C), 1267 (s, C-O-CH_3), 818, 762 (s, C-H out of plane). Anal. calcd. for $C_{15}H_{17}NO_4$: C, 65.44; H, 6.22; N, 5.09; Found: C, 63.87; H, 6.11; N, 4.80.

3.1.3. ***2-Methoxyethyl 3-ethoxy-4-methoxyphenylcyanoacrylate***

Yield 83%; ^{1}H NMR δ8.1 (s, 1H, CH=), 8.0-6.8 (m, 3H, Ph), 4.5 (t, 2H, $OCOCH_2$), 4.4 (q. 2H, $PhOCH_2$), 3.9 (s, 3H, $PhOCH_3$), 3.7 (t, 2H, OCH_2), 3.4 (s, 3H, OCH_3), 1.5 (t, 3H, CH_2CH_3); ^{13}C NMR: δ164 (C=O), 156 (HC=), 153, 148, 126, 112 (Ph), 116 (CN), 99 (C=), 70 ($OCOCH_2$), 65 ($PhOCH_2$), 59 (OCH_3), 56 ($PhOCH_3$), 15 ($PhCH_2\underline{C}H_3$); IR: (cm^{-1}) 2928 (m, C-H), 2220 (m, CN), 1749 (s, C=O), 1587 (s, C=C), 1265 (s, C-O-CH_3), 860, 812, 762 (s, C-H out of plane). Anal. calcd. for $C_{16}H_{19}NO_5$: C, 62.94; H, 6.27; N, 4.59; Found: C, 61.47; H, 6.02; N, 4.32.

3.1.4. ***2-Methoxyethyl 4-ethoxy-3-methoxyphenylcyanoacrylate***

Yield 85%; mp 87.6°C; ^{1}H NMR δ8.2 (s, 1H, CH=), 7.9-6.9 (m, 3H, Ph), 4.5 (t, 2H, $OCOCH_2$), 4.2 (q. 2H, $PhOCH_2$), 3.9 (s, 3H, $PhOCH_3$), 3.7 (t, 2H, OCH_2), 3.4 (s, 3H, OCH_3), 1.5 (t, 3H, CH_2CH_3); ^{13}C NMR: δ164 (C=O), 154 (HC=), 153, 148, 126, 112 (Ph), 116 (CN), 99 (C=), 70 ($OCOCH_2$), 65 ($PhOCH_2$), 59 (OCH_3), 56 ($PhOCH_3$), 15 ($PhCH_2\underline{C}H_3$); IR: (cm^{-1}) 2943 (m, C-H), 2220 (m, CN), 1722 (s, C=O), 1580 (s, C=C), 1263 (s, C-O-CH_3), 852, 797 (s, C-H out of plane). Anal. calcd. for $C_{16}H_{19}NO_5$: C, 62.94; H, 6.27; N, 4.59; Found: C, 62.84; H, 6.20; N, 4.45.

3.1.5. ***2-Methoxyethyl 3,4-dibenzyloxyphenylcyanoacrylate***

Yield 89%; mp 105.5°C; ^{1}H NMR δ8.1 (s, 1H, CH=), 7.9-7.2 (m, 3H, Ph), 5.2 (s, 2H, $PhCH_2$), 4.4 (t, 2H, $OCOCH_2$), 3.7 (t, 2H, OCH_2), 3.4 (s, 3H, OCH_3); ^{13}C NMR: δ164 (C=O), 156 (HC=), 153, 149, 137, 129, 128, 127, 112 (Ph), 116 (CN), 101 (C=), 71 ($PhCH_2$), 66 ($OCOCH_2$), 59 (OCH_3); IR: (cm^{-1}) 2932 (m, C-H), 2216 (m, CN), 1724 (s,

C=O), 1589 (s, C=C), 1259 (s, C-O-CH_3), 852, 737, 696 (s, C-H out of plane). Anal. calcd. for $C_{27}H_{25}NO_5$: C, 73.12; H, 5.68; N, 3.16; Found: C, 73.58; H, 5.39; N, 3.43.

3.1.6. ***2-Methoxyethyl 3-benzyloxy-4-methoxylphenylcyanoacrylate***

Yield 74%; ^{1}H NMR δ8.2 (s, 1H, CH=), 7.6-6.9 (m, 3H, Ph), 5.2 (s, 2H, $PhCH_2$), 4.3 (t, 2H, $OCOCH_2$), 3.9 (s, 3H, $PhOCH_3$), 3.6 (t, 2H, OCH_2), 3.4 (s, 3H, OCH_3); ^{13}C NMR: δ 163 (C=O), 155 (HC=), 153. 139, 137, 132, 129, 128, 127, 112 (Ph), 116 (CN), 99 (C=), 71 ($PhCH_2$), 70 (OCH_2), 61 ($OCOCH_2$), 59 (OCH_3), 56 ($PhOCH_3$); IR: (cm^{-1}) 2934 (m, C-H), 2220 (m, CN), 1749 (s, C=O), 1595 (s, C=C), 1273 (s, C-O-CH_3), 862, 814, 741 (s, C-H out of plane). Anal. calcd. for $C_{21}H_{21}NO_5$: C, 68.65; H, 5.76; N, 3.81; Found: C, 67.45; H, 6.00; N, 3.80.

3.1.7. ***2-Methoxyethyl 4-benzyloxy-3-methoxyphenylcyanoacrylate***

Yield 74%; ^{1}H NMR δ8.2 (s, 1H, CH=), 7.8-6.9 (m, 3H, Ph), 5.2 (s, 2H, $PhCH_2$), 4.3 (t, 2H, $OCOCH_2$), 3.9 (s, 3H, $PhOCH_3$), 3.6 (t, 2H, OCH_2), 3.4 (s, 3H, OCH_3); ^{13}C NMR: δ 163 (C=O), 154 (HC=), 150. 138, 137, 133, 129, 128, 127, 114 (Ph), 116 (CN), 99 (C=), 74 ($PhCH_2$), 71 (OCH_2), 64 ($OCOCH_2$), 59 (OCH_3), 56 ($PhOCH_3$); IR: (cm^{-1}) 2934 (m, C-H), 2220 (m, CN), 1767 (s, C=O), 1597 (s, C=C), 1287 (s, C-O-CH_3), 858, 810, 735 (s, C-H out of plane). Anal. calcd. for $C_{21}H_{21}NO_5$: C, 68.65; H, 5.76; N, 3.81; Found: C, 68.76; H, 5.21; N, 3.28.

3.1.8. ***2-Methoxyethyl 2-bromo-5-methoxyphenylcyanoacrylates***

Yield 89%; mp 49.1°C; ^{1}H NMR δ8.7 (s, 1H, CH=), 7.8-6.8 (m, 3H, Ph), 4.5 (t, 2H, $OCOCH_2$), 3.9 (s, 3H, $PhOCH_3$), 3.7 (t, 2H, OCH_2), 3.3 (s, 3H, CH_3O); ^{13}C NMR δ162

(C=O), 154 (HC=), 131, 126, 125, 114, 112 (Ph), 116 (CN), 105 (C=), 70 (OCH_2), 65 ($OCOCH_2$), 59 (OCH_3), 56 ($PhOCH_3$); IR (cm^{-1}): 2945 (m, C-H), 2224 (m, CN), 1749 (s, C=O), 1583 (s, C=C), 1263 (s, C-O-CH_3), 822, 760 (s, C-H out of plane). Anal. Calcd. for $C_{14}H_{14}BrNO_4$: C, 49.43; H, 4.15; N, 4.12; Found: C, 49.11; H, 4.10; N, 4.12.

3.1.9. ***2-Methoxyethyl 3-bromo-4-methoxyphenylcyanoacrylate***

Yield 78%; ^{1}H NMR δ 8.6 (s, 1H, CH=), 7.9-6.7 (m, 3H, Ph), 4.5 (t, 2H, $OCOCH_2$), 3.9 (s, 3H, $PhOCH_3$), 3.7 (t, 2H, OCH_2), 3.3 (s, 3H, CH_3O); ^{13}C NMR δ 163 (C=O), 150 (HC=), 132, 126, 125, 114, 112 (Ph), 116 (CN), 100 (C=), 70 (OCH_2), 64 ($OCOCH_2$), 59 (OCH_3), 56 ($PhOCH_3$); IR (cm^{-1}): 2943 (m, C-H), 2224 (m, CN), 1749 (s, C=O), 1576 (s, C=C), 1268 (s, C-O-CH_3), 816, 745 (s, C-H out of plane). Anal. Calcd. for $C_{14}H_{14}NO_4$: C, 49.43; H, 4.15; N, 4.12; Found: C, 47.71; H, 3.98; N, 3.92.

3.1.10. ***2-Methoxyethyl 5-bromo-2-methoxyphenylcyanoacrylates***

Yield 92%; mp 109.3°C; ^{1}H NMR δ 8.6 (s, 1H, CH=), 8.4-6.8 (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, CH_3O); ^{13}C NMR δ 163 (C=O), 156 (HC=), 138, 137, 132, 131, 114, 112 (Ph), 116 (CN), 105 (C=), 70 (OCH_2), 65 ($OCOCH_2$), 59 (OCH_3), 57 ($PhOCH_3$); IR (cm^{-1}): 2937 (m, C-H), 2218 (m, CN), 1753 (s, C=O), 1591 (s, C=C), 1203 (s, C-O-CH_3), 824 (s, C-H out of plane). Anal. Calcd. for $C_{14}H_{14}BrNO_4$: C, 49.43; H, 4.15; N, 4.12; Found: C, 48.91; H, 3.92; N, 4.22.

3.1.11. ***2-Methoxyethyl 2-chloro-3-methoxyphenylcyanoacrylates***

Yield 91%; ^{1}H NMR δ 8.7 (s, 1H, CH=), 8.1-7.1 (m, 3H, Ph), 4.4 (t, 2H, $OCOCH_2$), 3.9 (s, 3H, $PhOCH_3$), 3.7 (t, 2H, OCH_2), 3.4 (s, 3H, CH_3O); ^{13}C NMR δ 163 (C=O), 155

(HC=), 134, 131, 128, 127, 125, 121, 120 (Ph), 117 (CN), 106 (C=), 74 (OCH_2), 64 ($OCOCH_2$), 59 (OCH_3), 57 ($PhOCH_3$); IR (cm^{-1}): 2935 (m, C-H), 2228 (m, CN), 1753 (s, C=O), 1574 (s, C=C), 1279 (s, C-O-CH_3), 862, 785 (s, C-H out of plane). Anal. Calcd. for $C_{14}H_{14}ClNO_4$: C, 56.86; H, 4.77; N, 4.74; Found: C, 53.87; H, 4.56; N, 4.16.

3.1.12. ***2-Methoxyethyl 3-chloro-4-methoxyphenylcyanoacrylates***

Yield 83%; ^{1}H NMR δ 8.1 (s, 1H, CH=), 8.0-7.0 (m, 3H, Ph), 4.4 (t, 2H, $OCOCH_2$), 4.0 (s, 3H, $PhOCH_3$), 3.6 (t, 2H, OCH_2), 3.4 (s, 3H, CH_3O); ^{13}C NMR δ 164 (C=O), 155 (HC=), 133, 132, 131, 130, 125, 124 (Ph), 116 (CN), 101 (C=), 74 (OCH_2), 66 ($OCOCH_2$), 59 (OCH_3), 56 ($PhOCH_3$); IR (cm^{-1}): 2949 (m, C-H), 2224 (m, CN), 1749 (s, C=O), 1593 (s, C=C), 1312 (s, C-O-CH_3), 862, 770 (s, C-H out of plane). Anal. Calcd. for $C_{14}H_{14}ClNO_4$: C, 56.86; H, 4.77; N, 4.74; Found: C, 53.02; H, 4.82; N, 4.37.

3.1.13. ***2-Methoxyethyl 2-chloro-6-methylphenylcyanoacrylates***

Yield 79%; ^{1}H NMR δ 8.4 (s, 1H, CH=), 7.4-7.1 (m, 3H, Ph), 4.4 (t, 2H, $OCOCH_2$), 3.7 (t, 2H, OCH_2), 3.4 (s, 3H, CH_3O), 2.6 (s, 3H, $PhCH_3$); ^{13}C NMR δ 163 (C=O), 155 (HC=), 143, 140, 138, 135, 128 (Ph), 117 (CN), 103 (C=), 74 (OCH_2), 64 ($OCOCH_2$), 59 (OCH_3), 21 ($PhCH_3$); IR (cm^{-1}): 2932 (m, C-H), 2264 (m, CN), 1749 (s, C=O), 1591 (s, C=C), 1190 (s, C-O-CH_3), 862, 783 (s, C-H out of plane). Anal. Calcd. for $C_{14}H_{14}ClNO_3$: C, 60.11; H, 5.04; N, 5.01; Found: C, 58.87; H, 4.96; N, 4.90.

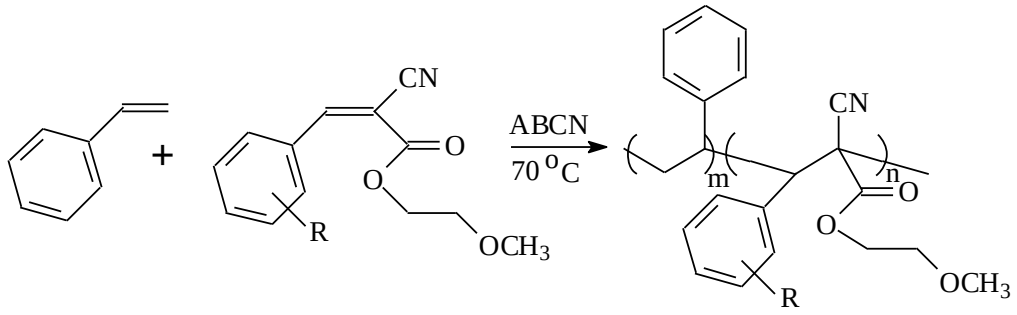
3.1.14. ***2-Methoxyethyl 3-chloro-4-methylphenylcyanoacrylates***

Yield 73%; ^{1}H NMR δ 8.2 (s, 1H, CH=), 8.0-7.3 (m, 3H, Ph), 4.5 (t, 2H, $OCOCH_2$), 36 (t, 2H, OCH_2), 3.4 (s, 3H, CH_3O), 2.5 (s, 3H, $PhCH_3$); ^{13}C NMR δ 163 (C=O), 154

(HC=), 143, 136, 132, 131, 129, 128 (Ph), 115 (CN), 103 (C=), 74 (OCH_2), 66 ($OCOCH_2$), 60 (OCH_3), 21 ($PhCH_3$); IR (cm^{-1}): 2949 (m, C-H), 2224 (m, CN), 1749 (s, C=O), 1593 (s, C=C), 1312 (s, C-O-CH_3), 862, 770 (s, C-H out of plane). Anal. Calcd. for $C_{14}H_{14}ClNO_3$: C, 60.11; H, 5.04; N, 5.01; Found: C, 58.83; H, 4.80; N, 5.00.

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 4-methoxy-2-methyl, 4-methoxy-3-methyl, 3-ethoxy-4-methoxy, 4-ethoxy-3-methoxy, 3,4-dibenzyloxy, 3-benzyloxy-4-methoxy, 4-benzyloxy-3-methoxy, 2-bromo-5-methoxy, 3-bromo-4-methoxy, 5-bromo-2-methoxy, 2-chloro-3-methoxy, 3-chloro-4-methoxy, 2-chloro-6-methyl, 3-chloro-4-methyl.

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

R	Yield[a] (wt%)	N (wt%)	ST in copol. (mol%)	MEPA in copol. (mol%)
4-Methoxy-2-methyl	10.2	1.45	86.9	13.1
4-Methoxy-3-methyl	17.5	2.11	78.9	21.1
3-Ethoxy-4-methoxy	15.7	1.88	80.9	19.1
4-Ethoxy-3-methoxy	17.4	2.04	78.6	21.4
3,4-Dibenzyloxy	12.2	1.99	71.4	28.6
3-Benzyloxy-4-methoxy	15.6	1.67	81.9	18.1
4-Benzyloxy-3-methoxy	13.7	1.31	87.1	12.9
2-Bromo-5-Methoxy	11.3	2.1	75.9	24.1
3-Bromo-4-methoxy	15.4	1.35	87.0	13.0
5-Bromo-2-methoxy	15.1	2.26	72.9	27.1
2-Chloro-3-methoxy	13.2	1.99	79.7	20.3
3-Chloro-4-methoxy	16.1	1.83	81.9	18.1
2-Chloro-6-methyl	13.2	0.81	82.6	17.4
3-Chloro-4-methyl	15.1	1.89	81.6	18.4

Nitrogen elemental analysis showed that between 12.9 and 28.6 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 ring-disubstituted 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-disubstituted 2-methoxyethyl phenylcyanoacrylates, $RPhCH=C(CN)CO_2CH_2CH_2OCH_3$ (where R is 4-methoxy-2-methyl, 4-methoxy-3-methyl, 3-ethoxy-4-methoxy, 4-ethoxy-3-methoxy, 3,4-dibenzyloxy, 3-benzyloxy-4-methoxy, 4-benzyloxy-3-methoxy, 2-bromo-5-methoxy, 3-bromo-4-methoxy, 5-bromo-2-methoxy, 2-chloro-3-methoxy, 3-chloro-4-methoxy, 2-chloro-6-methyl, 3-chloro-4-methyl) were prepared and copolymerized with styrene.

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