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

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Abstract

Novel fluoro, methoxy, and methyl ring-disubstituted octyl phenylcyanoacrylates, $RPhCH=C(CN)CO_2CH_2(CH_2)_6CH_3$ (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) 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

2-Fluoro-3-methoxy ring-substituted 1-ethenylbenzene is reported in preparation of tetrahydropyrrole compounds as D2 receptors and DAT receptors inhibitors [1], as well as in synthesis of benzofuranyl substituted phenylalkylcarboxylic acids as Gpr120 receptor agonists [2]. 3-Fluoro-5-methoxy benzaldehyde was used in sequential Ir/Cu-mediated method for the meta-selective C-H radiofluorination of heteroarenes [3]; in synthesis and styrene copolymerization of ring-disubstituted isopropyl [4] and butyl [5] phenylcyanoacrylates. 4-Fluoro-3-methylphenyl ethyl ester of 2-propenoic acid was reported in synthesis of bromoalcohol compounds in presence of quinine-based derivatives as catalyst, and L(-)-camphorsulfonic acid as additive [6]; in synthesis of β-amino acid derivatives useful as IFNβ modulators [7]; in preparation of tetrahydrofuran derivatives as dual inhibitors of serotonin reuptake and phosphodiesterase 4 enzyme activity for treating central nervous system disorders [8]; in carboxyl group-assisted C-H acetoxylation of hydrocinnamic and phenylacetic acids [9]; in synthesis of multiple-functional diphosphines via Pd-catalyzed alkoxycarbonylation of alkynes [10]; in synthesis of novel 1-phenyl-benzopyrrolizidin-3-one derivatives and evaluation of their cytoneuroprotective effects against NMDA-induced injury in PC12 cells [11]; in convenient synthetic route towards 2-(hetero)aryl-substituted thieno[3,2-b]indoles using Fischer indolization [12]; in photodriven transfer hydrogenation of olefins [13]; in synthesis and studies of anticonvulsant activity of 7-phenyl-6,7-dihydro-[1,2,4]triazolo[1,5-a]pyrimidin-5(4H)-ones and their derivatives [14]; in synthesis of amino-piperidine derivatives as C3aR ligands [15]; in synthesis and studies

of antitumor activities of piperidone farnesyltransferase inhibitors [16], and studies of oxidative rearrangements with thallium(III) nitrate (TTN) in trimethyl orthoformate [17]. We have prepared octyl ring-substituted cyanoacrylates, $RPhCH=C(CN)CO_2CH_2(CH_2)_6CH_3$, 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, 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].

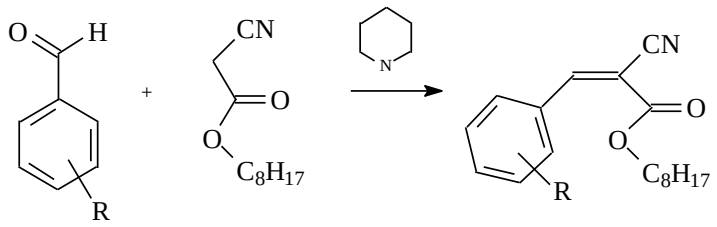
2. Experimental

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 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 is 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 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.

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 2-fluoro-3-methoxyphenylcyanoacrylate***

Yield 76%; mp 45.1°C; ^{1}H NMR δ 8.6 (s, 1H, CH=), 8.0-7.1 (m, 3H, Ph), 4.3 (t, 2H, CO_2CH_2), 3.9 (s, 3H, $PhOCH_3$), 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 162 (C=O), 154 (HC=), 151, 149, 148, 125, 121, 113 (Ph), 116 (CN), 105 (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 ($\underline{C}H_2CH_3$), 14 ($CH_3$); IR (cm^{-1}): 2929 (m, C-H), 2227 (m, CN), 1734 (s, C=O), 1615 (s, C=C), 1249 (s, C-O-CH_3), 752 (s, C-H out of plane). Anal. Calcd. for $C_{19}H_{24}FNO_3$: C, 68.45; H, 7.26; N, 4.20; Found: C, 67.08; H, 7.38; N, 4.62.

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

Yield 85%; mp 54.5°C; ^{1}H NMR δ 8.5 (s, 1H, CH=), 6.9-6.6 (m, 3H, Ph), 4.3 (t, 2H, CO_2CH_2), 3.9 (s, 3H, $PhOCH_3$), 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=), 147, 131, 112, 111 (Ph), 116, (CN), 102 (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 ($\underline{C}H_2CH_3$), 14 ($CH_3$); IR (cm^{-1}): 2937 (m, C-H), 2217 (m, CN), 1726 (s, C=O), 1607 (C=C), 1269 (s, C-O-CH_3), 821 (s, C-H out of plane). Anal. Calcd. for $C_{19}H_{24}FNO_3$: C, 68.45; H, 7.26; N, 4.20; Found: C, 67.14; H, 7.15; N, 4.34.

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

Yield 92%; ^{1}H NMR δ 8.5 (s, 1H, CH=), 8.0-7.0 (m, 3H, Ph), 4.3 (t, 2H, CO_2CH_2), 3.0 (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, $O(CH_2)_5(C\underline{H}_2)_2$), 0.9 (t, 3H, CH_3); ^{13}C NMR δ163 (C=O), 158 (HC=), 153, 147-112 (Ph), 117 (CN), 105 (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 ($\underline{C}H_2CH_3$), 13 ($CH_3$); IR ($cm^{-1}$): 2934 (m, C-H), 2225 (m, CN), 1731 (s, C=O), 1609 (C=C), 1272 (s, C-O-CH_3), 724 (s, C-H out of plane). Anal. Calcd. for $C_{19}H_{24}FNO_3$: C, 68.45; H, 7.26; N, 4.20; Found: C, 67.65; H, 7.12; N, 4.35.

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

Yield 78%; ^1H NMR δ8.3 (s, 1H, CH=), 7.5-6.6 (m, 3H, Ph), 4.3 (t, 2H, CO_2CH_2), 3.9 (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, $O(CH_2)_5(C\underline{H}_2)_2$), 0.9 (t, 3H, CH_3); ^{13}C NMR δ163 (C=O), 159 (HC=), 147, 134-118 (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 ($\underline{C}H_2CH_3$), 13 ($CH_3$); IR ($cm^{-1}$): 2930 (m, C-H), 2230 (m, CN), 1729 (s, C=O), 1616 (C=C), 1272 (s, C-O-CH_3), 751 (s, C-H out of plane). Anal. Calcd. for $C_{19}H_{24}FNO_3$: C, 68.45; H, 7.26; N, 4.20; Found: C, 69.26; H, 7.62; N, 4.39.

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

Yield 93%; mp 65.7°C; ^1H NMR δ8.1 (s, 1H, CH=), 7.9-7.0 (m, 3H, Ph), 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 δ163 (C=O), 153 (HC=), 152, 130-113 (Ph), 117 (CN), 101 (C=), 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}): 2914 (m, C-H), 2220 (m, CN), 1715 (s, C=O), 1601 (s, C=C), 1273 (s, C-O-CH_3), 862 (s, C-H out of plane). Anal. Calcd. for $C_{19}H_{24}NO_3$: C, 68.45; H, 7.26; N, 4.20; Found: C, 67.64; H, 7.29; N, 4.31.

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

Yield 79%; mp 53.9°C; ^{1}H NMR δ8.3 (s, 1H, CH=), 7.9-7.1 (m, 3H, Ph), 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 δ163 (C=O), 154 (HC=), 149-113 (Ph), 117 (CN), 103 (C=), 68 (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 ($cm^{-1}$): 2928 (m, C-H), 2223 (m, CN), 1733 (s, C=O), 1612 (s, C=C), 1259 (s, C-O-CH_3), 843 (s, C-H out of plane). Anal. Calcd. for $C_{19}H_{24}FNO_3$: C, 68.45; H, 7.26; N, 4.20; Found: C, 67.97; H, 7.38; N, 4.27.

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

Yield 87%; ^{1}H NMR δ8.5 (s, 1H, CH=), 8.2-7.0 (m, 3H, Ph), 4.3 (t, 2H, CO_2CH_2), 2.3 (s, 3H, $PhCH_3$), 1.8-1.7 (q, 2H, $OCH_2C\underline{H}_2$), 1.5-1.4 (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 δ163 (C=O), 153 (HC=), 162, 158, 147-112 (Ph), 116 (CN), 103 (C=), 68 (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 ($\underline{C}H_2CH_3$), 14 ($PhCH_3$), 13 ($CH_3$); IR ($cm^{-1}$): 2928 (m, C-H), 2226 (m, CN), 1733 (s, C=O), 1609 (s, C=C), 1267 (s, C-O-CH_3), 820 (s, C-H out of plane). Anal. Calcd. for $C_{19}H_{24}FNO_2$: C, 71.90; H, 7.62; N, 4.41; Found: C, 71.75; H, 7.68; N, 4.51.

3.1.8. ***Octyl 2-fluoro-6-methylphenylcyanoacrylate.***

Yield 91%; ^{1}H NMR δ8.3 (s, 1H, CH=), 7.5-7.0 (m, 3H, Ph), 4.3 (t, 2H, CO_2CH_2), 2.3 (s, 3H, $PhCH_3$), 1.8-1.7 (q, 2H, $OCH_2C\underline{H}_2$), 1.5-1.4 (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 δ162 (C=O), 150 (HC=), 162, 140-115 (Ph), 116 (CN), 103 (C=), 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 ($\underline{C}H_2CH_3$), 14 ($PhCH_3$), 13 ($CH_3$); IR ($cm^{-1}$): 2933 (m, C-H), 2232 (m, CN), 1739 (s, C=O), 1616 (s, C=C), 1256 (s, C-O-CH_3), 767 (s, C-H out of plane). Anal. Calcd. for $C_{19}H_{24}FNO_2$: C, 71.90; H, 7.62; N, 4.41; Found: C, 70.87; H, 7.71; N, 4.60.

3.1.9. ***Octyl 3-fluoro-4-methylphenylcyanoacrylate.***

Yield 87%; mp 83.6°C; ^{1}H NMR δ8.2 (s, 1H, CH=), 7.8-7.2 (m, 3H, Ph), 4.3 (t, 2H, CO_2CH_2), 2.4 (s, 3H, $PhCH_3$), 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 δ163 (C=O), 153 (HC=), 160, 133-118 (Ph), 116 (CN), 103 (C=), 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 ($\underline{C}H_2CH_3$), 14 ($PhCH_3$), 13 ($CH_3$); IR ($cm^{-1}$): 2928 (m, C-H), 2220 (m, CN), 1720 (s, C=O), 1606 (s, C=C), 1278 (s, C-O-CH_3), 766 (s, C-H out of plane). Anal. Calcd. for $C_{19}H_{24}FNO_2$: C, 71.90; H, 7.62; N, 4.41; Found: C, 70.91; H, 7.64; N, 4.44.

3.1.10. ***Octyl 4-fluoro-2-methylphenylcyanoacrylate***.

Yield 87%; mp 61.0°C; ^{1}H NMR δ8.5 (s, 1H, CH=), 8.3-6.9 (m, 3H, Ph), 4.3 (t, 2H, CO_2CH_2), 2.4 (s, 3H, $PhCH_3$), 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=), 160, 133-117 (Ph), 116 (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 ($\underline{C}H_2CH_3$), 14 ($PhCH_3$), 13 ($CH_3$); IR ($cm^{-1}$): 2927 (m, C-H), 2224 (m, CN), 1730 (s, C=O), 1621 (s, C=C), 1283 (s, C-O-CH_3), 821 (s, C-H out of plane). Anal. Calcd. for $C_{19}H_{24}FNO_2$: C, 71.90; H, 7.62; N, 4.41; Found: C, .71.83; H, 7.782; N, 4.53.

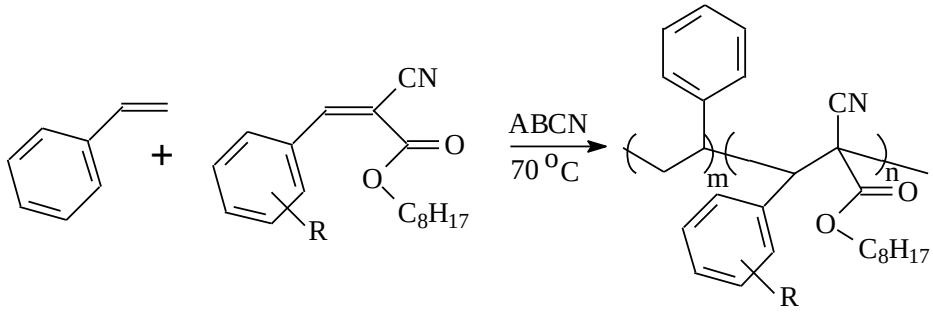
3.1.11. ***Octyl 4-fluoro-3-methylphenylcyanoacrylate***.

Yield 87%; mp 37.4°C; ^{1}H NMR δ8.2 (s, 1H, CH=), 8.0-7.0 (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 δ163 (C=O), 153 (HC=), 136-118 (Ph), 116 (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 ($\underline{C}H_2CH_3$), 22 ($PhCH_3$), 14 ($CH_3$); IR ($cm^{-1}$): 2927 (m, C-H), 2224 (m, CN), 1723 (s, C=O), 1657 (s, C=C), 1271 (s, C-O-CH_3), 828 (s, C-H out of plane). Anal. Calcd. for $C_{19}H_{24}FNO_2$: C, 71.90; H, 7.62; N, 4.41; Found: C, 72.37; H, 7.77; N, 4.60.

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 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.

Table 1. Copolymerization of styrene and octyl phenylcyanoacrylates.

R	Yield[a] (wt%)	N (wt%)	ST in copol. (mol%)	OPCA in copol. (mol%)
2-Fluoro-3-methoxy	12.3	2.86	60.1	39.9
2-Fluoro-4-methoxy	19.5	2.64	65.5	34.5
2-Fluoro-5-methoxy	11.2	3.06	54.5	45.5
2-Fluoro-6-methoxy	12.3	2.03	77.4	22.6
3-Fluoro-4-methoxy	14.5	2.41	70.4	29.6
4-Fluoro-3-methoxy	11.1	2.59	66.6	33.4
2-Fluoro-5-methyl	12.7	2.61	67.8	32.2
2-Fluoro-6-methyl	12.8	2.10	77.1	22.9
3-Fluoro-4-methyl	16.2	2.36	72.6	27.4
4-Fluoro-2-methyl	11.1	2.07	77.6	22.4
4-Fluoro-3-methyl	14.8	1.92	79.9	20.1

Nitrogen elemental analysis showed that between 20.1 and 45.5 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 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, fluoro, methyl and methoxy octyl phenylcyanoacrylates, $RPhCH=C(CN)CO_2CH_2(CH_2)_6CH_3$ (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) were prepared and copolymerized with styrene.

Acknowledgments

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