Synthesis and styrene copolymerization of novel methyl and oxy ring-disubstituted tert-butyl phenylcyanoacrylates

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Abstract

Novel ring-disubstituted tert-butyl phenylcyanoacrylates, RPhCH=C(CN)$CO_2C(CH_3)_3$, where R is 2,5-dimethyl, 3,4-dimethyl, 2,3-dimethoxy, 2,5-dimethoxy, 3,5-dimethoxy, 4-methoxy-2-methyl, 4-methoxy-3-methyl, 3-ethoxy-4-methoxy, 3-ethoxy-4-hydroxy, 3-ethoxy-2-hydroxy, 3-benzyloxy-4-methoxy, 4-benzyloxy-3-methoxy, 2,3-(methylenedioxy) were prepared and copolymerized with styrene. The acrylates were synthesized by the piperidine catalyzed Knoevenagel condensation of ring-substituted benzaldehydes and tret-butyl cyanoacetate, and characterized by CHN analysis, IR, ^1H and ^{13}C NMR. All the

acrylates were copolymerized with styrene in solution with radical initiation at 70°C. The compositions of the copolymers were calculated from nitrogen analysis.

Introduction

3,4-Dimethyl ring-substituted ethyl phenylcyanoacrylate (PCA) is reported in catalyst-free [3+3] annulation/oxidation of cyclic amidines with activated olefins [1], and in N'N-dioxide-Lanthanum(III)-catalyzed asymmetric cyclopropanation of 2-cyano-3-arylacrylates with 2-bromomalonates. [2]. 3,4-Dimethyl ring-substituted *t*-butyl PCA is mentioned in development of the first two-pore domain potassium channel twik-related k+ channel 1-selective agonist possessing in vivo antinociceptive activity [3]. 3-Methoxyphenyl 1-methylethyl ester (*2E*) PCA is reported in organocatalyzed enantioselective synthesis of 2-amino-4h-chromene derivatives, and in organocatalyzed enantioselective synthesis of 2-amino-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carboxylates [4]. 4-Methoxy-3-methylphenyl ethyl PCA is mentioned in organocatalyzed enantioselective synthesis of 2-amino-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carboxylates [5]; in synthesis of potent, orally bioavailable pyrimidine-5-carbonitrile-6-alkyl CXCR2 receptor antagonists [6], and in synthesis of methoxytolylsuccinic acids [7]. 4-Methoxy-3-(1-methylethoxy)phenyl PCA is used in synthesis of 4-benzyl-2-imidazolidinones from N-[(1-cyano-2-phenyl)ethyl] carbamates [8]. 2-Hydroxy-3-methoxyphenyl methyl PCA is reported in synthesis and study of x-ray crystal structure of (*E*)-alkyl 2-cyano-3-(2-hydroxyphenyl)propenoates [9], and in synthesis of 4H-chromenes [10]. 3-Methoxy-4-(phenylmethoxy)phenyl ethyl is

mentioned in Knoevenagel condensation reaction under microwave irradiation in presence of antimony trichloride [11], and in solvent-free microwave enhanced condensation of ethyl cyanoacetate with aldehydes [12]. 4-Methoxy-3-(phenylmethoxy) phenyl ethyl PCA is reported in synthesis and copolymerization of ring-substituted ethyl 2-cyano-3-phenyl-2-propenoates [13]. 3-(1,3-Benzodioxol-5-yl) 2-ethylhexyl PCA I used in sensitive color photothermographic compositions containing ultraviolet absorber [14], and in silver halide photographic material and image formation system [15]. 1,3-Benzodioxol-5-yl methyl PCA is reported in pentanidium-catalyzed direct assembly of vicinal all-carbon quaternary stereocenters through C(sp3)-C(sp3) bond formation [16]; in oxidative cleavage reactions of vicinal diols by silica gel and paraperiodic acid [17], and in synthesis of pyrido[2,1-c][1,2,4]triazine, 1,2,4-triazolo[4,3-a]pyridine and 2-(pyrazolyl)nicotinonitrile and study of their effect on Biomphalaria alexandrina snail enzymes [18]. In this work we have prepared *tert*-butyl ring-disubstituted phenylcyanoacrylates (TBCA), $RPhCH{=}C(CN)CO_2C(CH_3)_3$, where R is 2,5-dimethyl, 3,4-dimethyl, 2,3-dimethoxy, 2,4-dimethoxy, 2,5-dimethoxy, 3,4-dimethoxy, 3,5-dimethoxy, 4-methoxy-2-methyl, 4-methoxy-3-methyl, 3-ethoxy-4-methoxy, 4-ethoxy-3-methoxy, 3-ethoxy-4-hydroxy, 3-ethoxy-2-hydroxy, 3-benzyloxy-4-methoxy, 4-benzyloxy-3-methoxy, 2,3-(methylenedioxy), and explored the feasibility of their copolymerization with styrene. To the best of our knowledge except 3,4-dimethyl [3], there have been no reports on either synthesis of these compounds, nor their copolymerization with styrene [19].

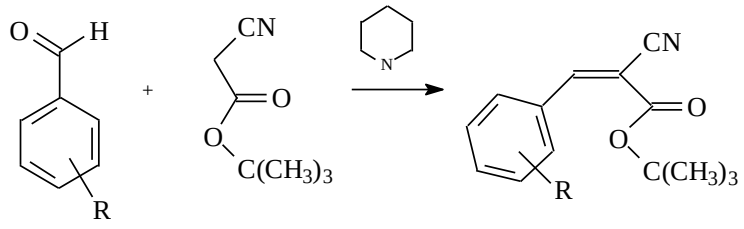
2. Experimental

2,5-Dimethyl, 3,4-dimethyl, 2,3-dimethoxy, 2,4-dimethoxy, 2,5-dimethoxy, 3,4-dimethoxy, 3,5-dimethoxy, 4-methoxy-2-methyl, 4-methoxy-3-methyl, 3-ethoxy-4-methoxy, 4-ethoxy-3-methoxy, 3-ethoxy-4-hydroxy, 3-ethoxy-2-hydroxy, 3-benzyloxy-4-methoxy, 4-benzyloxy-3-methoxy, 2,3-(methylenedioxy) benzaldehydes, tert-butyl 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 was reported in [20].

3. Results and discussion

3.1. Synthesis and characterization of tert-butyl phenylcyanoacrylates

All tert-butyl phenylcyanoacrylates (TBCA) compounds were synthesized by Knoevenagel condensation [21] of appropriate benzaldehydes with tert-butyl cyanoacetate, catalyzed piperidine (Scheme 1).



Scheme 1. Synthesis of tert-butyl phenylcyanoacrylates where R is 2,5-dimethyl, 3,4-dimethyl, 2,3-dimethoxy, 2,4-dimethoxy, 2,5-dimethoxy, 3,4-dimethoxy, 3,5-dimethoxy, 4-methoxy-2-methyl, 4-methoxy-3-methyl, 3-ethoxy-4-methoxy, 4-ethoxy-3-methoxy, 3-

ethoxy-4-hydroxy, 3-ethoxy-2-hydroxy, 3-benzyloxy-4-methoxy, 4-benzyloxy-3-methoxy, 2,3-(methylenedioxy).

The preparation procedure was essentially the same for all the monomers. In a typical synthesis, equimolar amounts of tert-butyl 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 compounds were characterized by IR, ^{1}H and ^{13}C NMR, and elemental analysis. No stereochemical analysis of the novel compounds was performed since no stereoisomers (*E* or/and *Z*) of known configuration were available.

3.1.1. ***Tert-butyl 2,5-dimethylphenylcyanoacrylate***

Yield 96%; mp 94.1°C; ^{1}H NMR δ 8.5 (s, 1H, CH=), 8.0-7.1 (m, 3H, Ph), 2.4 (s, 6H, $Ph(CH_3)_2$), 1.6 (s, 9H, CH_3); ^{13}C NMR δ 162 (C=O), 154 (HC=), 143, 138, 132, 131, 129 (Ph), 116 (CN), 103 (C=), 84 (OC), 28 (CH_3), 20 ($PhCH_3$); IR (cm^{-1}): 2982 (m, C-H), 2225 (m, CN), 1708 (s, C=O), 1591 (s, C=C), 1259 (s, C-O-CH_3), 788 (s, C-H out of plane). Anal. Calcd. for $C_{16}H_{19}NO_2$: C, 74.68; H, 7.44; N, 5.44; Found: C, 72.23; H, 7.12; N, 5.39.

3.1.2. ***Tert-butyl 3,4-dimethylphenylcyanoacrylate***.

Yield 96.6%; mp 42.8°C; ^{1}H NMR δ 8.1 (s, 1H, CH=), 7.7-7.0 (m, 3H, Ph), 1.6 (s, 9H, CH_3); ^{13}C NMR δ 162 (C=O), 154 (HC=), 143, 138, 132, 131, 129 (Ph), 116 (CN), 103

(C=), 84 (OC), 29 (CH_3), 20 ($PhCH_3$); IR (cm^{-1}): 2982 (m, C-H), 2225 (m, CN), 1709 (s, C=O), 1561 (C=C), 1199 (s, C-O-CH_3), 874 (s, C-H out of plane). Anal. Calcd. for $C_{16}H_{19}ClNO_2$: C, 74.68; H, 7.44; N, 5.44; Found: C, 72.64; H, 6.60; N, .17.

3.1.3. ***Tret-butyl 2,3-dimethoxyphenoxy)phenylcyanoacrylate***.

Yield 53%; mp 53.0°C; ^{1}H NMR δ8.6 (s, 1H, CH=), 7.9-7.0 (m, 3H, Ph), 3.9 (s, 3H, $PhOCH_3$), 1.6 (s, 9H, CH_3); ^{13}C NMR δ161 (C=O), 156 (HC=), 151, 150, 127, 124, 121 (Ph), 117 (CN), 103 (C=), 62, 56 ($PhOCH_3$), 28 (CH_3); IR (cm^{-1}): 2922 (m, C-H), 2225 (m, CN), 1724 (s, C=O), 1502 (C=C), 1269 (s, C-O-CH_3), 872 (s, C-H out of plane). Anal. Calcd. for $C_{16}H_{19}NO_4$: C, 66.42; H, 6.62; N, 4.84; Found: C, 65.12; H, 7.00; N, 4.91.

3.1.4. ***Tret-butyl 2,5-dimethoxyphenylcyanoacrylate***.

Yield 92%; mp 74.8°C; ^{1}H NMR δ8.6 (s, 1H, CH=), 7.8-6.9 (m, 3H, Ph), 3.8 (s, 6H, $PhOCH_3$), 1.6 (s, 9H, CH_3); ^{13}C NMR δ163 (C=O), 154 (HC=), 153, 148, 122, 121, 113, 112 (Ph), 116 (CN), 104 (C=), 84 (OCO<u>C</u>), 56 ($PhOCH_3$), 28 $(CH_3)_3$; IR (cm^{-1}): 2930 (m, C-H), 2221 (m, CN), 1720 (s, C=O), 1595 (s, C=C), 1230 (s, C-O-CH_3), 841 (s, C-H out of plane). Anal. Calcd. for $C_{16}H_{19}NO_4$: C, 66.42; H, 6.62; N, 4.84; Found: C, 65.79; H, 6.54; N, 4.91.

3.1.5. ***Tret-butyl 3,4-dimethoxyphenylcyanoacrylate***

Yield 89.8 %; mp 100.5°C; ^{1}H NMR δ8.0 (s, 1H, CH=), 7.7-6.8 (m, 3H, Ph), 4.2, 3.9. (s, 6H, $PhO(CH_3)_2$) , 1.5 (s, 9H, $(CH_3)_3$); ^{13}C NMR δ162 (C=O), 154 (HC=), 153, 149, 127, 125, 112 (Ph), 116 (CN), 101 (C=), 83 (OCO<u>C</u>), 56 ($PhOCH_3$), 28 $(CH_3)_3$; IR (cm^{-1}):

2937 (m, C-H), 2218 (m, CN), 1717 (s, C=O), 1591 (s, C=C), 1242 (s, C-O-CH_3), 751 (s, C-H out of plane). Anal. Calcd. for $C_{16}H_{19}NO_4$: C, 66.42; H, 6.62; N, 4.84; Found: C, 64.66; H, 6.49; N, 4.84.

3.1.6. ***Tert-butyl 3,5-dimetoxyphenylcyanoacrylate***

Yield 92%; mp 86.8°C; ^{1}H NMR δ 8.1 (s, 1H, CH=), 7.3-6.3 (m, 3H, Ph), 3.8 (s, 6H, $PhOCH_3$), 1.5 (s, 9H, $(CH_3)_3$); ^{13}C NMR δ 161 (C=O), 154 (HC=), 160, 133, 108, 105 (Ph), 116 (CN), 104 (C=), 84 (OC), 56 ($PhOCH_3$), 28 (CH_3); IR (cm^{-1}): 2941 (m, C-H), 2224 (m, CN), 1718 (s, C=O), 1583 (s, C=C), 1279 (s, C-O-CH_3), 853 (s, C-H out of plane). Anal. Calcd. for $C_{16}H_{19}NO_4$: C, 66.42; H, 6.62; N, 4.84; Found: C, 65.54; H, 6.59; N, 3.95.

3.1.7. ***Tret-butyl 4-methoxy-2-methylphenylcyanoacrylate***

Yield 76 %; mp 58°C; ^{1}H NMR δ 8.4 (s, 1H, CH=), 8.3-6.7 (m, 3H, Ph), 3.8. (s, 3H, $PhOCH_3$), 2.6 (s, 3H, CH_3), 1.5 (s, 9H, $(CH_3)_3$); ^{13}C NMR δ 163 (C=O), 152 (HC=), 151, 131, 123, 118, 112 (Ph), 116 (CN), 102 (C=), 83 (OCO<u>C</u>), 55 ($PhOCH_3$), 28 $(CH_3)_3$, 19 ($PhCH_3$); IR (cm^{-1}): 2974 (m, C-H), 2214 (m, CN), 1715 (s, C=O), 1599 (s, C=C), 1252 (s, C-O-CH_3), 772 (s, C-H out of plane). Anal. Calcd. for $C_{16}H_{19}NO_3$: C, 70.31; H, 7.01; N, 5.12; Found: C, 68.61; H, 6.85; N, 4.01.

3.1.8. ***Tret-butyl 4-methoxy-3-methylphenylcyanoacrylate***

Yield 96 %; mp 104°C; ^{1}H NMR δ 8.1 (s, 1H, CH=), 7.9-6.7 (m, 3H, Ph), 3.9. (s, 3H, $PhOCH_3$), 2.2 (s, 3H, CH_3), 1.5 (s, 9H, $(CH_3)_3$); ^{13}C NMR δ 162 (C=O), 154 (HC=), 134, 132, 128, 124, 114 (Ph), 116 (CN), 100 (C=), 83 (OCO<u>C</u>), 55 ($PhOCH_3$), 28 $(CH_3)_3$, 16

($PhCH_3$); IR (cm^{-1}): 2975 (m, C-H), 2221 (m, CN), 1717 (s, C=O), 1597 (s, C=C), 1257 (s, C-O-CH_3), 784 (s, C-H out of plane). Anal. Calcd. for $C_{16}H_{19}NO_3$: C, 70.31; H, 7.01; N, 5.12; Found: C, 67.02; H, 7.00; N, 4.93.

3.1.9. ***Tret-butyl 3-ethoxy-4-methoxyphenylcyanoacrylate***

Yield 87 %; mp 77.3°C; ^{1}H NMR δ 8.1 (s, 1H, CH=), 7.7-6.9 (m, 3H, Ph), 4.2 (s, 2H, $PhOCH_2$), 3.9 (s, 3H, $PhOCH_3$), 1.6 (s, 9H, $(CH_3)_3$); ^{13}C NMR δ 162 (C=O), 154 (HC=), 149, 148, 130, 127, 126, 125, 113, 111 (Ph), 116 (CN), 101 (C=), 83 (OCO<u>C</u>), 64 ($PhOCH_2$), 56 ($PhOCH_3$), 28 $(CH_3)_3$, 14 ($PhCH_2\underline{C}H_3$); IR (cm^{-1}): 2980 (m, C-H), 2215 (m, CN), 1718 (s, C=O), 1589 (s, C=C), 1267 (s, C-O-CH_3), 824 (s, C-H out of plane). Anal. Calcd. for $C_{17}H_{21}NO_4$: C, 67.31; H, 6.98; N, 4.62; Found: C, 66.06; H, 7.13; N, 4.87.

3.1.10. ***Tret-butyl 4-ethoxy-3-methoxyphenylcyanoacrylate***

Yield 93 %; mp 100.4°C; ^{1}H NMR δ 8.0 (s, 1H, CH=), 7.8-6.8 (m, 3H, Ph), 4.2 (s, 2H, $PhOCH_2$), 3.9 (s, 3H, $PhOCH_3$), 1.5 (s, 9H, $(CH_3)_3$); ^{13}C NMR δ 162 (C=O), 154 (HC=), 153, 149, 127, 125, 112 (Ph), 116 (CN), 101 (C=), 83 (OCO<u>C</u>), 65 ($PhOCH_2$), 56, 53 ($PhOCH_3$), 28 $(CH_3)_3$, 15 ($PhCH_2\underline{C}H_3$); IR (cm^{-1}): 2982 (m, C-H), 2216 (m, CN), 1717 (s, C=O), 1589 (s, C=C), 1298 (s, C-O-CH_3), 858 (s, C-H out of plane). Anal. Calcd. for $C_{17}H_{21}NO_4$: C, 67.31; H, 6.98; N, 4.62; Found: C, 66.13; H, 7.22; N, 4.72.

3.1.11. ***Tret-butyl 3-ethoxy-4-hydroxyphenylcyanoacrylate***

Yield 57 %; ^{1}H NMR δ 8.0 (s, 1H, CH=), 7.9 (s, 1H, OH), 7.5-6.7 (m, 3H, Ph), 4.2 (s, 2H, $PhOCH_2$), 1.6 (s, 9H, $(CH_3)_3$), 1.5 (CH_3); ^{13}C NMR δ 162 (C=O), 154 (HC=), 151,

146, 128, 124, 115, 111 (Ph), 116 (CN), 100 (C=), 83 (OCOC), 65 ($PhOCH_2$), 28 $(CH_3)_3$, 15 ($PhCH_2CH_3$); IR (cm^{-1}): 2987 (m, C-H), 2218 (m, CN), 1717 (s, C=O), 1582 (s, C=C), 1277 (s, C-O-CH_3), 873 (s, C-H out of plane). Anal. Calcd. for $C_{16}H_{19}NO_4$: C, 66.42; H, 6.62; N, 4.84; Found: C, 62.51; H, 6.45; N, 4.81.

3.1.12. ***Tret-butyl 3-ethoxy-2-hydroxyphenylcyanoacrylate***

Yield 96 %; ^{1}H NMR δ 8.3 (s, 1H, CH=), 7.9 (s, 1H, OH), 7.5-6.7 (m, 3H, Ph), 4.2 (s, 2H, $PhOCH_2$), 1.6 (s, 9H, $(CH_3)_3$), 1.4 (CH_3); ^{13}C NMR δ 161 (C=O), 153 (HC=), 150, 148, 128, 124, 115, 112 (Ph), 116 (CN), 100 (C=), 84 (OCOC), 64 ($PhOCH_2$), 28 $(CH_3)_3$, 15 ($PhCH_2CH_3$); IR (cm^{-1}): 2980 (m, C-H), 2219 (m, CN), 1736 (s, C=O), 1680 (s, C=C), 1277 (s, C-O-CH_3), 884 (s, C-H out of plane). Anal. Calcd. for $C_{16}H_{19}NO_4$: C, 66.42; H, 6.62; N, 4.84; Found: C, 63.92; H, 6.60; N, 4.39.

3.1.13. ***Tret-butyl 3-benzyloxy-4-methoxyphenylcyanoacrylate***

Yield 85 %; mp 123.4°C; ^{1}H NMR δ 8.0 (s, 1H, CH=), 7.8-6.7 (m, 8H, Ph), 5.2 (s, 2H, $PhOCH_2$), 3.9 (s, 3H, $PhOCH_3$), 1.6 (s, 9H, $(CH_3)_3$); ^{13}C NMR δ 162 (C=O), 154 (HC=), 153, 148, 136, 128, 126, 125, 114, 111 (Ph), 116 (CN), 101 (C=), 83 (OCOC), 71 ($PhOCH_2$), 56 ($PhOCH_3$), 28 $(CH_3)_3$; IR (cm^{-1}): 2980 (m, C-H), 2222 (m, CN), 1717 (s, C=O), 1588 (s, C=C), 1269 (s, C-O-CH_3), 864 (s, C-H out of plane). Anal. Calcd. for $C_{22}H_{23}NO_4$: C, 72.31; H, 6.34; N, 3.83; Found: C, 71.62; H, 6.50; N, 3.89.

3.1.14. ***Tret-butyl 4-benzyloxy-3-methoxyphenylcyanoacrylate***

Yield 88 %; mp 113.2°C; ^{1}H NMR δ 8.0 (s, 1H, CH=), 7.8-6.8 (m, 8H, Ph), 5.2 (s, 2H, $PhOCH_2$), 4.0 (s, 3H, $PhOCH_3$), 1.6 (s, 9H, $(CH_3)_3$); ^{13}C NMR δ 162 (C=O), 154 (HC=),

153, 150, 136, 129, 127, 125, 113, 112 (Ph), 116 (CN), 101 (C=), 83 (OCOC), 71 ($PhOCH_2$), 56 ($PhOCH_3$), 28 $(CH_3)_3$; IR (cm^{-1}): 2983 (m, C-H), 2224 (m, CN), 1717 (s, C=O), 1573 (s, C=C), 1272 (s, C-O-CH_3), 821 (s, C-H out of plane). Anal. Calcd. for $C_{22}H_{23}NO_4$: C, 72.31; H, 6.34; N, 3.83; Found: C, 71.18; H, 6.71; N, 3.97.

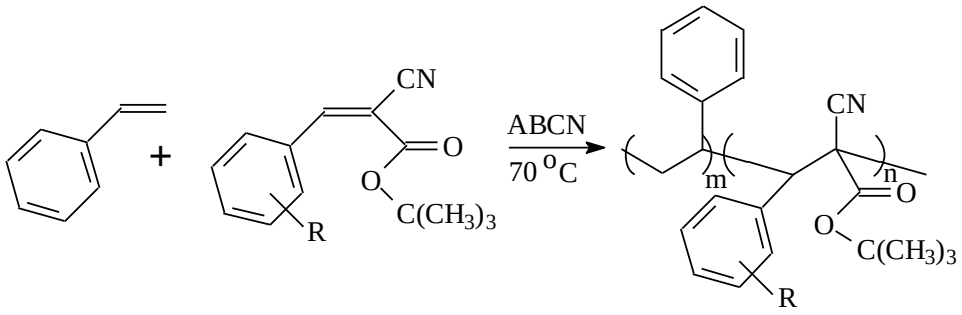
3.1.15. ***Tret-butyl 2,3-(methylenedioxy)phenylcyanoacrylate***

Yield 99 %; mp 161.2°C; ^{1}H NMR δ8.3 (s, 1H, CH=), 7.9-6.8 (m, 3H, Ph), 6.0 (s, 2H, OCH_2O), 1.6 (s, 9H, $(CH_3)_3$); ^{13}C NMR δ161 (C=O), 152 (HC=), 149, 146, 122, 120, 114, 112 (Ph), 116 (CN), 111 (C=), 104 (CH_2), 84 (OCOC), 28 (CH_3); IR (cm^{-1}): 2975 (m, C-H), 2225 (m, CN), 1705 (s, C=O), 1456 (s, C=C), 1250 (s, C-O-CH_3), 789 (s, C-H out of plane). Anal. Calcd. for $C_{15}H_{15}NO_4$: C, 65.92; H, 5.53; N, 5.13; Found: C, 65.38; H, 5.36; N, 5.13.

3.3. ***Synthesis and characterization of styrene – TBCA copolymers***

Copolymers of the ST and the TBCA compounds, P(ST-co-TBCA) were prepared in 25-mL glass screw cap vials at ST/TBCA = 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 TBCA). The novel synthesized TBCA 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 tert-butyl phenylcyanoacrylates, where R is 2,5-dimethyl, 3,4-dimethyl, 2,3-dimethoxy, 2,4-dimethoxy, 2,5-dimethoxy, 3,4-dimethoxy, 3,5-dimethoxy, 4-methoxy-2-methyl, 4-methoxy-3-methyl, 3-ethoxy-4-methoxy, 4-ethoxy-3-methoxy, 3-ethoxy-4-hydroxy, 3-ethoxy-2-hydroxy, 3-benzyloxy-4-methoxy, 4-benzyloxy-3-methoxy, 2,3-(methylenedioxy).

Table 1. Copolymerization of styrene and tert-butyl phenylcyanoacrylates.

R	Yield[a] (wt%)	N (wt%)	ST in copol. (mol%)	TBCA in copol. (mol%)
2,5-Dimethyl	12.5	2.07	78.8	21.2
3,4-Dimethyl	12.2	2.11	78.3	21.7
2,3-Dimethoxy	13.8	2.01	79.7	20.3
2,5-Dimethoxy	12.4	2.32	75.1	24.9
4-Methoxy-2-methyl	17.1	1.59	85.4	14.6
4-Methoxy-3-methyl	14.2	2.08	79.4	20.6
3-Ethoxy-4-methoxy	15.2	1.79	82.2	17.8
3-Ethoxy-4-hydroxy	11.5	1.86	81.7	18.3
3-Ethoxy-2-hydroxy	16.1	1.29	88.4	11.6
3-Benzyloxy-4-methoxy	12.4	1.97	76.9	23.1
4-Benzyloxy-3-methoxy	13.7	2.09	74.6	25.4
2,3-(Methylenedioxy)	15.3	2.18	78.0	22.0

Nitrogen elemental analysis showed that between 11.6 and 25.4 mol% of TBCA is present in the copolymers prepared at ST/TBCA = 3 (mol), which is indicative of relatively high reactivity of the TBCA monomers towards ST radical which is typical of alkoxy ring-substituted TBCA. Since TBCA monomers do not homopolymerize, the most likely structure of the copolymers would be isolated TBCA 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 tert-butyl phenylcyanoacrylates, $RPhCH=C(CN)CO_2C(CH_3)_3$ (where R is 2,5-dimethyl, 3,4-dimethyl, 2,3-dimethoxy, 2,4-dimethoxy, 2,5-dimethoxy, 3,4-dimethoxy, 3,5-dimethoxy, 4-methoxy-2-methyl, 4-methoxy-3-methyl, 3-ethoxy-4-methoxy, 4-ethoxy-3-methoxy, 3-ethoxy-4-hydroxy, 3-ethoxy-2-hydroxy, 3-benzyloxy-4-methoxy, 4-benzyloxy-3-methoxy, 2,3-(methylenedioxy)) were prepared and copolymerized with styrene.

Acknowledgments

The authors are grateful to acknowledge that the project was partly supported by Chicago Society of Coating Technology.

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