Synthesis and styrene copolymerization of dimethyl, dimethoxy, and halogen ring-substituted isopropyl cyanophenylacrylates

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Abstract

Novel trisubstituted ethylenes, dimethyl, dimethoxy, and halogen ring-substituted isopropyl cyanophenylacrylates, RPhCH=C(CN)$CO_2CH(CH_3)_2$ (where R is 2,3-dimethyl, 2,4-dimethyl, 2,5-dimethyl, 2,6-dimethyl, 3,4-dimethyl, 3,5-dimethyl, 2,3-dimethoxy, 2,4-dimethoxy, 2,5-dimethoxy, 2-Br, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 2-F, 3-F, 4-F) were prepared and copolymerized with styrene. The monomers were synthesized by the piperidine catalyzed Knoevenagel condensation of ring-substituted benzaldehydes and isopropyl cyanoacetate and characterized by CHN elemental analysis, IR, ^{1}H- and ^{13}C-NMR. All the ethylenes were copolymerized with styrene in solution with radical initiation (ABCN) at 70°C. The composition of the copolymers was calculated from nitrogen analysis, and the structures were analyzed by IR, ^{1}H and ^{13}C-NMR, GPC, DSC, and TGA. Decomposition of

the copolymers in nitrogen occurred in two steps, first in the 219-500°C range with residue (0.9-5.6 % wt), which then decomposed in the 500-800ºC range.

1. Introduction

Cyanophenylacrylates continue to attract attention as components and products of organic synthesis. Thus, methoxy ring-substituted methyl cyanophenylacrylates, MCPA was used in synthesis of pyridotriazines and triazolopyridines [1]. There are a number of applications of ethyl cyanophenylacrylates (ECPA), which include studies of catalysis [2] and as potential antimicrobial and antioxidant agents [3]. 2,4-Dimethoxyphenyl ECPA was used in design, synthesis and study of anticancer activity of novel benzothiazole analogues [4], in synthesis of thiazacridine derivatives as anticancer agents against breast and hematopoietic neoplastic cells [5] and in DABCO-catalyzed Knoevenagel condensation, using hydroxy ionic liquid as a promoter [6]. This ECPA was involved in catalysis study of N,N'-dialkylimidazolium dimethyl phosphates [7], in synthesis and study of antimicrobial activity of some cyanoacrylates [8], as well as in synthesis of antiproliferative active 2-aminobenzimidazole derivatives [9]. 2-Bromo ring-substituted ECPA is reported in heterocyclic synthesis of novel antimicrobial agents [10], norepinephrine transporter imaging agents [11], as well as, in synthesis and anti-inflammatory activity of N and S-alkylated arylidene-thioxo-imidazolidinones [12]. 2-Bromo and 4-bromo isopropyl cyanophenylacrylate (ICPA) was used in organocatalyzed enantioselective synthesis [13, 14], as well, in cyclodimerization of 1,1-dicyanoalkenes and arylidenecyanoacetates [15]. 3-Bromo ICPA is reported in reductive dimerization

cyclization of arylmethylenecyanoacetates [16]. 2-Chloro ECPA was involved in application of prolinamide functionalized polyacrylonitrile fiber in catalysis [17] and in synthesis and studies of antifungal activities of novel polyheterocyclic spirooxindole derivatives [18]. 3-Chloro ECPA was reported in catalysis study [19] and DBU-promoted cascade annulation of nitroarylcyclopropane-1,1-dicarbonitriles and 3-aryl-2-cyanoacrylates [20]. 4-Chloro ICPA was prepared via cyanuric chloride-mediated reactions involving condensation/cyano hydration/esterification [21]. It was also involved in cyclodimerization of arylidenecyanoacetate promoted by samarium diiodide [22]. 4-Fluoro ICPA was reported in catalysis studies compartmentalization of incompatible polymers within metal-organic frameworks [23]. We have reported synthesis and styrene copolymerization of a number of dimethyl and dimethoxy ring-substituted esters of cyanophenylacrylates (CPA): methyl CPA [24, 25], ethyl CPA [26, 27], propyl CPA [28], and butyl CPA [29], as well as mono halogen phenyl-substituted CPA: methyl CPA [30], ethyl CPA [31], propyl CPA [32], butyl CPA [33], and isobutyl [34].

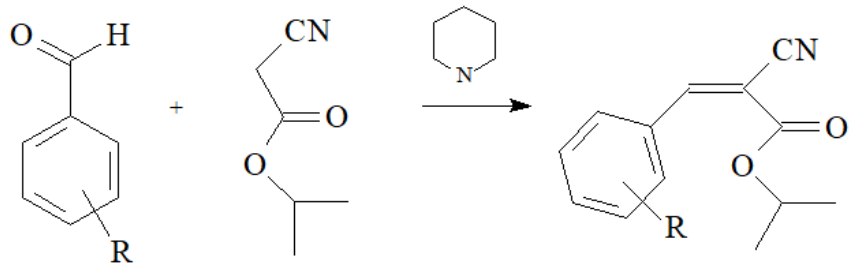
In continuation of our efforts in synthesis and copolymerization of ICPA compounds we have prepared dimethyl and dimethoxy ring-disubstituted and halogen ring monosubstituted ICPA compounds, $RPhCH=C(CN)CO_2CH(CH_3)_2$, where R is 2,3-dimethyl, 2,5-dimethyl, 2,6-dimethyl, 3,4-dimethyl, 2,3-dimethoxy, 2,4-dimethoxy, 2,5-dimethoxy, 2,6-dimethoxy 3,4-dimethoxy, 3,5-dimethoxy, 2-Br, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 2-F, 3-F, 4-F. To the best of our knowledge, except for syntheses of 2-Br, 4-Br, 4-Cl, and 4-F (13, 19, 20, 23) there have been no reports on either synthesis of these isopropyl cyanophenylacrylates, nor their copolymerization with styrene.

2. Experimental

2,3-Dimethyl, 2,5-dimethyl, 2,6-dimethyl, 3,4-dimethyl, 2,3-dimethoxy, 2,4-dimethoxy, 2,5-dimethoxy, 2,6-dimethoxy 3,4-dimethoxy, 3,5-dimethoxy, 2-Br, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 2-F, 3-F, 4-F-benzaldehydes, isopropyl cyanoacetate, piperidine, styrene, 1,1'-azobiscyclohexanecarbonitrile, (ABCN), and toluene supplied from Sigma-Aldrich Co., were used as received. Instrumentation is described in the first paper of this isopropyl esters' series [35].

Synthesis of isopropyl cyanophenylacrylates

The ICPA compounds were synthesized by Knoevenagel condensation [36] of a ring-substituted benzaldehyde with isopropyl cyanoacetate, catalyzed by base, piperidine (Scheme 1).



Scheme 1: Synthesis of isopropyl 2-cyano-3-phenyl-2-propenoates, where R is 2,3-dimethyl, 2,4-dimethyl, 2,5-dimethyl, 2,6-dimethyl, 3,4-dimethyl, 3,5-dimethyl, 2,3-dimethoxy, 2,4-dimethoxy 2,5-dimethoxy, 2-Br, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 2-F, 3-F, 4-F.

The preparation procedure was essentially the same for all the monomers. In a typical synthesis, equimolar amounts of isopropyl cyanoacetate and an appropriate ring-substituted 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 [35]. No stereochemical analysis of the novel ring-substituted ICPA was performed since no stereoisomers (*E* or/and *Z*) of known configuration were available.

3.1. Isopropyl cyano(2,3-dimethylphenyl)acrylate

Yield 92%; mp 114°C, ^{1}H-NMR δ 8.3 (s, 1H, CH=), 7.8, 7.2, 7.0 (m, 3H, Ph), 5.1 (m, 1H, OCH), 2.3 (d, 6H, CH_3) 1.3 (d, 6H, $CH(CH_3)_2$); ^{13}C-NMR δ 166 (C=O), 152 (HC=), 133, 131, 130, 126, 125 (Ph), 116 (CN), 104 (C=), 68 (OCH), 22 ($CH(CH_3)_2$), 20, 16 (CH_3); FTIR (cm^{-1}): 3028-2837 (m, C-H), 2226 (m, CN), 1728 (s, C=O), 1596 (C=C), 1246 (s, C-O-C), 968, 842 (s, C-H out of plane). Anal. Calcd. for $C_{15}H_{17}NO_2$: C, 74.05; H, 7.04; N, 5.76; Found: C, 72.32; H, 6.96; N, 5.91.

3.2. Isoropyl cyano(2,4-dimethylphenyl)acrylate

Yield 84%; mp 55°C, ^{1}H-NMR δ 8.4 (s, 1H, CH=), 7.5, 7.0, 6.9 (t, 3H, Ph), 5.1 (m, 1H, OCH), 2.3 (d, 6H, CH_3) 1.3 (d, 6H, $CH(CH_3)_2$); ^{13}C-NMR δ 166 (C=O), 152 (HC=), 131, 130, 127, 126, 125 (Ph), 116 (CN), 104 (C=), 68 (OCH), 22 ($CH(CH_3)_2$), 21, 22 (CH_3); FTIR (cm^{-1}): 3122-2802 (m, C-H), 2224 (m, CN), 1724 (s, C=O), 1592 (C=C),

1273, 1268 (s, C-O-C), 923, 839 (s, C-H out of plane). Anal. Calcd. for $C_{15}H_{17}NO_2$: C, 74.05; H, 7.04; N, 5.76; Found: C, 73.76; H, 6.96; N, 5.91.

3.3. Isopropyl cyano(2,5-dimethylphenyl)acrylate

Yield 87%; mp 33°C, ^{1}H-NMR δ8.5 (s, 1H, CH=), 7.5 - 7.0 (m, 3H, Ph), 5.3 (m, 1H, OCH), 2.3 (d, 6H, CH_3) 1.3 (d, 6H, $CH(CH_3)_2$); ^{13}C-NMR δ 166 (C=O), 152 (HC=), 136, 133, 131, 130 (Ph), 116 (CN), 104 (C=), 68 (OCH), 22 ($CH(CH_3)_2$), 21, 20 (CH_3); FTIR (cm^{-1}): 3052-2847 (m, C-H), 2224 (m, CN), 1724 (s, C=O), 1558 (C=C), 1279 (s, C-O-CH_3), 935, 844 (s, C-H out of plane). Anal. Calcd. for $C_{15}H_{17}NO_2$: C, 74.05; H, 7.04; N, 5.76; Found: C, 72.30; H, 7.02; N, 5.69.

3.4. Isopropyl cyano(2,6-dimethylphenyl)acrylate

Yield 91%; mp 46°C, ^{1}H-NMR δ8.5 (s, 1H, CH=), 7.5 - 7.0 (m, 3H, Ph), 5.3 (m, 1H, OCH), 2.3 (d, 6H, CH_3) 1.3 (d, 6H, $CH(CH_3)_2$); ^{13}C-NMR δ 166 (C=O), 152 (HC=), 136, 133, 131, 130 (Ph), 116 (CN), 104 (C=), 68 (OCH), 22 ($CH(CH_3)_2$), 21, 20 (CH_3); FTIR (cm^{-1}): 3052-2847 (m, C-H), 2224 (m, CN), 1724 (s, C=O), 1558 (C=C), 1279 (s, C-O-CH_3), 935, 844 (s, C-H out of plane). Anal. Calcd. for $C_{15}H_{17}NO_2$: C, 74.05; H, 7.04; N, 5.76; Found: C, 71.39; H, 6.92; N, 5.66.

3.5. Isopropyl cyano(3,4-dimethylphenyl)acrylate

Yield 79%; mp 83°C, ^{1}H-NMR δ8.6 (s, 1H, CH=), 8.2 - 7.0 (m, 3H, Ph), 5.3 (m, 1H, OCH), 2.3 (d, 6H, CH_3) 1.3 (d, 6H, $CH(CH_3)_2$); ^{13}C-NMR δ 166 (C=O), 154 (HC=), 137, 136, 131, 130, 125 (Ph), 116 (CN), 104 (C=), 68 (OCH), 22 ($CH(CH_3)_2$), 19 (CH_3); FTIR (cm^{-1}): 3164-2850 (m, C-H), 2222 (m, CN), 1722 (s, C=O), 1602 (C=C), 1245 (s,

C-O-CH_3), 849 (s, C-H out of plane). Anal. Calcd. for $C_{15}H_{17}NO_2$: C, 74.05; H, 7.04; N, 5.76; Found: C, 72.83; H, 7.14; N, 5.69.

3.6. Isopropyl cyano(3,5-dimethylphenyl)acrylate

Yield 82%; mp 72°C, ^{1}H-NMR δ8.2 (s, 1H, CH=), 7.3 - 7.0 (m, 3H, Ph), 5.3 (m, 1H, OCH), 2.4 (d, 6H, CH_3) 1.3 (d, 6H, $CH(CH_3)_2$); ^{13}C-NMR δ 166 (C=O), 154 (HC=), 137, 136, 131, 130, 125 (Ph), 116 (CN), 104 (C=), 68 (OCH), 22 ($CH(CH_3)_2$), 19 (CH_3); FTIR (cm^{-1}): 3164-2850 (m, C-H), 2224 (m, CN), 1720 (s, C=O), 1610 (C=C), 1249 (s, C-O-CH_3), 835 (s, C-H out of plane). Anal. Calcd. for $C_{15}H_{17}NO_2$: C, 74.05; H, 7.04; N, 5.76; Found: C, 72.66; H, 6.95; N, 5.67.

3.7. Isopropyl cyano(2,3-dimethoxyphenyl)acrylate

Yield 96%; mp 66°C, ^{1}H-NMR δ8.6 (s, 1H, CH=), 7.9-6.9 (m, 3H, Ph), 5.1 (m, 1H, OCH), 3.8 (d, 6H, CH_3O), 1.3 (d, 6H, $CH(CH_3)_2$); ^{13}C-NMR δ 166 (C=O), 152 (HC=), 152, 127, 126, 121 (Ph), 116 (CN), 111 (C=), 68 (OCH), 60, 56 (OCH_3), 22 ($CH(CH_3)_2$); FTIR (cm^{-1}): 3120-2790 (m, C-H), 2224 (m, CN), 1724 (s, C=O), 1615 (C=C), 1250 (s, C-O-CH_3), 810, 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, 63.89; H, 6.19; N, 4.95.

3.8. Isopropyl cyano(2,4-dimethoxyphenyl)acrylate

Yield 87%; mp 62°C, ^{1}H-NMR δ8.6 (s, 1H, CH=), 7.6-6.9 (m, 3H, Ph), 5.1 (m, 1H, OCH), 3.8 (d, 6H, CH_3O), 1.3 (d, 6H, $CH(CH_3)_2$); ^{13}C-NMR δ 166 (C=O), 152 (HC=), 152, 131, 106, 98 (Ph), 116 (CN), 96 (C=), 68 (OCH), 56, 55 (OCH_3), 22 ($CH(CH_3)_2$); FTIR (cm^{-1}): 3982-2867 (m, C-H), 2224 (m, CN), 1723 (s, C=O), 1607 (C=C), 1286 (s,

C-O-CH_3), 842 (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, 67.37; H, 6.64; N, 5.65.

3.9. Isopropyl cyano(2,5-dimethoxyphenyl)acrylate

Yield 77%; mp 87°C, ^{1}H-NMR δ8.7 (s, 1H, CH=), 7.9-6.6 (m, 3H, Ph), 5.2 (m, 1H, OCH), 3.9 (d, 6H, CH_3O), 1.3 (d, 6H, $CH(CH_3)_2$); ^{13}C-NMR δ 166 (C=O), 152 (HC=), 152, 131, 106, 98 (Ph), 116 (CN), 96 (C=), 68 (OCH), 56, 55 (OCH_3), 22 ($CH(CH_3)_2$); FTIR (cm^{-1}): 3095-2807 (m, C-H), 2222 (m, CN), 1718 (s, C=O), 1611 (C=C), 1264 (s, C-O-CH_3), 854 (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, 65.51; H, 6.31; N, 5.06.

3.10. Isopropyl cyano(2-bromophenyl)acrylate

Yield 91%; mp 55.8°C, ^{1}H NMR δ8.7 (s, 1H, CH=), 8.3-7.2 (m, 4H, Ph), 5.2 (m, 1H, CH), 1.4 (d, 6H, CH_3); ^{13}C NMR δ 166 (C=O), 152 (HC=), 137, 133, 131, 130, 128 (Ph), 116 (CN), 106 (C=), 68 (CH), 22 (CH_3); FTIR (cm^{-1}): 3015-2836 (m, C-H), 2226 (m, CN), 1726 (s, C=O), 1594 (C=C), 1253 (s, C-O-CH_3), 766-741 (s, C-H out of plane). Anal. Calcd. for $C_{13}H_{12}BrNO_2$: C, 53.08; H, 4.11; N, 4.76; Found: C, 52.79; H, 4.42; N, 5.03.

3.11. Isopropyl cyano(3-bromophenyl)acrylate

Yield 68%; mp 85.3°C, ^{1}H NMR δ8.2 (s, 1H, CH=), 8.1-7.3 (m, 4H, Ph), 5.2 (m, 1H, CH), 1.8 (d, 6H, CH_3); ^{13}C NMR δ 162 (C=O), 153 (HC=), 137, 134, 131, 123 (Ph), 115 (CN), 104 (C=), 68 (CH), 22 (CH_3); FTIR (cm^{-1}): 3038-2869 (m, C-H), 2223 (m, CN),

1724 (s, C=O), 1607 (C=C), 1248 (s, C-O-CH_3), 788, 750 (s, C-H out of plane). Anal. Calcd. for $C_{13}H_{12}BrNO_2$: C, 53.08; H, 4.11; N, 4.76; Found: C, 51.37; H, 4.21; N, 4.81.

3.12. Isopropyl cyano(4-bromophenyl)acrylate

Yield 88%; mp 108.8°C, ^{1}H NMR δ8.3 (s, 1H, CH=), 8.0-6.2 (m, 4H, Ph), 5.3 (m, 1H, CH), 1.5 (d, 6H, CH_3); ^{13}C NMR δ165 (C=O), 154 (HC=), 133, 132, 131, 128 (Ph), 116 (CN), 114 (C=), 68 (CH), 22 (CH_3); FTIR (cm^{-1}): 3016-2807 (m, C-H), 2226 (m, CN), 1717 (s, C=O), 1241 (s, C-O-C), 818 (s, C-H out of plane). Anal. Calcd. for $C_{13}H_{12}BrNO_2$: C, 53.08; H, 4.11; N, 4.76; Found: C, 52.39; H, 4.34; N, 4.82.

3.13. Isopropyl cyano(2-chlorophenyl)acrylate

Yield 78%; ^{1}H NMR δ8.7 (s, 1H, CH=), 8.3-7.3 (m, 4H, Ph), 5.3 (m, 1H, CH), 1.2 (d, 6H, CH_3); ^{13}C NMR δ164 (C=O), 152 (HC=), 137, 132, 131, 130, 127 (Ph), 116 (CN), 116 (C=), 68 (CH), 22 (CH_3); FTIR (cm^{-1}): 3072-2815 (m, C-H), 2226 (m, CN), 1730 (s, C=O), 1609 (C=C), 1248 (s, C-O-C), 760 (s, C-H out of plane). Anal. Calcd. for $C_{13}H_{12}ClNO_2$: C, 62.53; H, 4.84; N, 5.61; Found: C, 62.49; H, 4.93; N, 5.81.

3.14. Isopropyl cyano(3-chlorophenyl)acrylate

Yield 84%; mp 159C°; ^{1}H NMR δ8.2 (s, 1H, CH=), 8.0-7.2 (m, 4H, Ph), 5.1 (m, 1H, CH), 1.3 (d, 6H, CH_3); ^{13}C NMR δ 162 (C=O), 154 (HC=), 135, 133, 128 (Ph), 116 (CN), 104 (C=), 68 (CH), 22 (CH_3); FTIR (cm^{-1}): 3026-2817 (m, C-H), 2223 (m, CN), 1699 (s, C=O), 1597 (C=C), 1268 (s, C-O-C), 748 (s, C-H out of plane). Anal. Calcd. for $C_{13}H_{12}ClNO_2$: C, 62.53; H, 4.84; N, 5.61; Found: C, 62.69; H, 4.96; N, 5.68.

3.15. Isopropyl cyano(4-chlorophenyl)acrylate

Yield 75%; mp 113.7C°; ^{1}H NMR δ8.2 (s, 1H, CH=), 8.0-7.2 (m, 4H, Ph), 5.3 (m, 1H, CH), 1.2 (d, 6H, CH_3); ^{13}C NMR δ 166 (C=O), 154 (HC=), 138, 132, 129 (Ph), 116 (CN), 114 (C=), 68 (CH), 22 (CH_3); FTIR (cm^{-1}): 3016-2891 (m, C-H), 2225 (m, CN), 1731 (s, C=O), 1585 (C=C), 1222 (s, C-O-C), 815, 766 (s, C-H out of plane). Anal. Calcd. for $C_{13}H_{12}ClNO_2$: C, 62.53; H, 4.84; N, 5.61; Found: C, 61.47; H, 4.97; N, 5.49.

3.16 Isopropyl cyano(2-fluorophenyl)acrylate

Yield 97%; mp 59.5°C; ^{1}H NMR δ8.5 (s, 1H, CH=), 8.4-7.0 (m, 4H, Ph), 5.3 (m, 1H, CH), 1.3 (d, 6H, CH_3); ^{13}C NMR δ164 (C=O), 142, 131, 130, 125, 119 (Ph), 116 (CN), 104 (C=), 68 (CH), 22 (CH_3); FTIR (cm^{-1}): 3096-2834 (m, C-H), 2222 (m, CN), 1720 (s, C=O), 1578 (C=C), 1228 (s, C-O-C), 820 (s, C-H out of plane). Anal. Calcd. for $C_{13}H_{12}FNO_2$: C, 66.94; H, 5.19; N, 6.01; Found: C, 65.80; H, 5.36; N, 6.47.

3.17 Isopropyl cyano(3-fluorophenyl)acrylate

Yield 82%; mp 87.7°C; ^{1}H NMR δ8.3 (s, 1H, CH=), 7.9-7.2 (m, 4H, Ph), 5.3 (m, 1H, CH), 1.3 (d, 6H, CH_3); ^{13}C NMR δ 166 (C=O), 154 (HC=), 162, 135, 131 (Ph), 116 (CN), 104 (C=), 68 (CH), 22 (CH_3); FTIR (cm^{-1}): 3174-2754 (m, C-H), 2222 (m, CN), 1717 (s, C=O), 1612 (C=C), 1268 (s, C-O-C), 835, 763 (s, C-H out of plane). Anal. Calcd. for $C_{13}H_{12}FNO_2$: C, 66.94; H, 5.19; N, 6.01; Found: C, 64.64; H, 5.20; N, 6.03.

3.18. Isopropyl cyano(4-fluorophenyl)acrylate

Yield 92%; mp 91.2°C; ^{1}H NMR δ8.2 (s, 1H, CH=), 8.1-7.1 (m, 4H, Ph), 5.3 (m, 1H, CH), 1.3 (2, 6H, CH_3); ^{13}C NMR δ166 (C=O), 154 (HC=), 134, 131, 129, 117 (Ph), 116

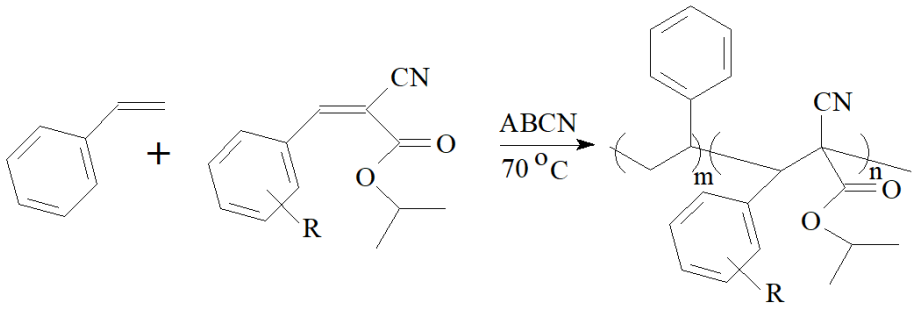
(CN), 108 (C=), 68 (CH), 22 (CH_3); FTIR (cm^{-1}): 3142-2782 (m, C-H), 2242 (m, CN), 1728 (s, C=O), 1608 (C=C), 1214 (s, C-O-C), 810 (m, C-H out of plane). Anal. Calcd. for $C_{13}H_{12}FNO_2$: C, 66.94; H, 5.19; N, 6.01; Found: C, 65.78; H, 5.09; N, 5.87.

4. Copolymerization

Copolymers of the ST and the ICPA monomers were prepared in 25-mL glass screw cap vials at ST/ICPA = 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 conversion of the copolymers was kept between below 20% to minimize compositional drift. The composition of the copolymers was determined based on the nitrogen content. The ST-ICPA copolymers were characterized by nitrogen elemental analysis, FTIR, ^{1}H- and ^{13}C-NMR spectroscopies. Thermal behavior was studied by DSC and TGA.

Copolymerization (Scheme 1) of ST and the ring-substituted ICPA resulted in formation of copolymers (Table 1) with weight-average molecular masses 13.5 - 69.5kD. Since ICPA monomers do not homopolymerize, the most likely structure of the copolymers would be isolated ICPA monomer units (n = 1) alternating with short ST (m = 1 - 4) 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. According to the nitrogen elemental analysis, between 13.5 and 31.2

mol% of ICPA monomer is present in the copolymers, which is indicative of relatively high reactivity of the monomers towards ST.



Scheme 2. ST-ICPA copolymer synthesis, R = 2,3-dimethyl, 2,4-dimethyl, 2,5-dimethyl, 2,6-dimethyl, 3,4-dimethyl, 3,5-dimethyl, 2,3-dimethoxy, 2,4-dimethoxy 2,5-dimethoxy, 2-Br, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 2-F, 3-F, 4-F.

						TGA			
R	Yield[a] wt%	N wt%	ICPA in pol., mol %	M_W kD	T_g ºC	Onset of dec., ºC	10% wt loss, ºC	50% wt loss, ºC	Residue at 500ºC, wt%
2,3-$(CH_3)_2$	12.1	2.44	23.9	63.2	127	279	306	338	4.9
2,4-$(CH_3)_2$	13.3	1.97	18.2	56.3	128	287	318	343	3.8
2,5-$(CH_3)_2$	11.4	2.96	31.1	52.5	131	286	312	346	3.9
2,6-$(CH_3)_2$	13.3	1.54	13.5	62.8	136	291	321	369	4.6

3,4-$(CH_3)_2$	17.2	2.73	27.8	59.8	129	295	299	374	5.1
3,5-$(CH_3)_2$	11.7	2.54	25.2	62.2	133	282	331	359	4.4
2,3-$(CH_3O)_2$	13.7	2.53	27.2	57.5	131	297	308	352	4.5
2,4-$(CH_3O)_2$	12.4	2.26	23.2	62.3	125	297	309	353	5.6
2,5-$(CH_3O)_2$	16.4	2.27	23.3	61.4	132	290	309	357	3.9
2-Br	12.3	2.94	29.5	46.2	162	257	312	341	2.9
3-Br	16.9	2.58	27.4	68.9	166	269	320	348	4.7
4-Br	18.2	2.59	28.1	65.5	161	271	312	340	2.9
2-Cl	17.2	2.93	31.2	42.5	161	267	314	342	3.2
3-Cl	18.3	2.86	30.6	20.0	111	230	206	369	0.9
4-Cl	19.2	2.73	30.1	50.4	127	219	308	351	3.5
2-F	10.3	3.03	30.0	62.2	158	258	313	337	1.1
3-F	11.8	2.88	28.6	69.5	155	260	306	333	1.4
4-F	12.4	2.65	27.0	46.3	156	244	304	335	1.5

[a]Conditions: ST/ICAA: 3 (mol) / Toluene / 70ºC / 5 hrs.

5. Structure and Thermal Properties

The structure of ST- ICPA copolymers was characterized by IR and NMR spectroscopy. A comparison of the spectra of the monomers, copolymers and polystyrene shows, that the reaction between the trisubstituted ethylenes and styrene is a copolymerization. IR spectra of the copolymers show overlapping bands in 3250-2700 cm^{-1} region

corresponding to C-H stretch vibrations. The bands for the ICPA monomer unit are 2231-2225 (w, CN), 1740-1722 (s, C=O), and 1252-1220 cm^{-1} (m, C-O). Benzene rings of both monomers show ring stretching bands at 1511-1462 and 1521-1462 cm^{-1} as well as a doublet 781-671 cm^{-1}, associated with C-H out of plane deformations. These bands can be readily identified in styrene copolymers with trisubstituted ethylene monomers containing cyano and carbonyl electron withdrawing groups.

The ^{1}H-NMR spectra of the ST- ICPA copolymers show a broad double peak in a 6.0-8.0 ppm region corresponding to phenyl ring protons. A resonance at 5.4-4.9 ppm is assigned to the methine protons of isopropyl group. A broad resonance at 4.2-3.8 ppm is methoxy protons, 3.8-2.0 ppm is assigned to the methine protons of ICPA, and methine and methylene protons of ST monomer unit close to the propenoate unit, which are more subjected to deshielding than the ones in polystyrene. The low and high field components of the signal are associated with ICPA monomer unit in head-to-tail and head-to-head structures. A broad resonance peak in 0.9-2.4 ppm range is attributed to the methine and methylene protons of styrene monomer sequences, as well as to methyl groups of isopropyl ester and alkyl-Ph protons of ICPA. The ^{13}C-NMR spectra also support the suggested skeletal structure of the copolymers. Thus, the assignment of the peaks is as follows: 167-160 ppm (C=O), 157-130 ppm (quaternary carbons of both phenyls), 118-112 ppm (CN), 60-50 ppm (methine, quaternary carbons and alkoxy ICPA carbons), 47-45 ppm (ST methine), and 44-40 ppm (ST methylene), 36-14 ppm alkyl carbons of ICPA. The copolymers prepared in the present work are all soluble in ethyl acetate, THF, DMF and CHCl3 and insoluble in methanol, ethyl ether, and petroleum ether.

All the copolymers were amorphous and show no crystalline DSC endotherm on repeated heating and cooling cycles. Table 2 shows glass transition values for the ST-ICPA copolymers prepared in this work with no correlation to the size and position of the ICPA ring substitution apparently due to non-uniform composition, monomer unit distribution, and/or molecular weight and MWD. A single Tg was observed for all the copolymers with values 111-166ºC. Information on thermal stability of the copolymers (Table 2) was obtained from thermogravimetric analysis (Table 2). Decomposition of the copolymers in nitrogen occurred in two steps, first in the 219-500ºC range with residue (0.9-5.6% wt), which then decomposed in the 500-800ºC range. The decomposition products were not analyzed in this study, and the mechanism has yet to be investigated.

Conclusion

Novel dimethyl, dimethoxy, and halogen ring-substituted isopropyl cyanophenylacrylates were prepared and copolymerized with styrene. The compositions of the copolymers were calculated from nitrogen analysis and the structures were analyzed by IR, H^1 and ^{13}C-NMR. The thermal gravimetric analysis indicated that the copolymers decompose in in two steps, first in the 219-500°C range with residue (0.9-5.6 % wt), which then decomposed in the 500-800ºC range.

Acknowledgments

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

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