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Synthesis and styrene copolymerization of halogen ring-substituted isopropyl cyanophenyl propanoates

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Abstract
Halogen ring-substituted isopropyl 2-cyano-3-phenyl-2-propenoates, RPhCH=C(CN)$CO_2CH(CH_3)_2$ (where R is 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 compounds were synthesized by the piperidine catalyzed Knoevenagel condensation of ring-substituted benzaldehydes and isopropyl cyanoacetate. All the propenoates were copolymerized with styrene in solution with radical initiation (ABCN) at 70°C. The monomers and copolymers were characterized by elemental analysis, FTIR, ^{1}H and ^{13}C-NMR. Thermal properties of the copolymers were estimated by DSC and TGA analyses.

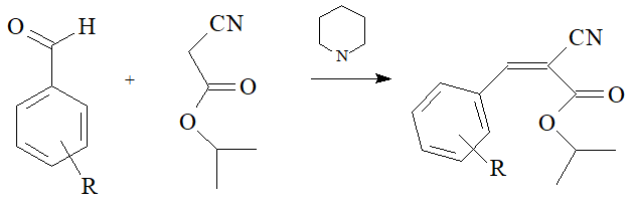
Keywords: knoevenagel condensation, trisubstituted ethylenes, radical copolymerization, styrene copolymers

1. Introduction
Halogen ring–functionalized trisubstituted ethylenes (TSE), esters of 2-cyano-3-phenyl-2-propenoic acid, R^1PhCH=C(CN)CO_2R^2 find a variety of applications in organic and polymer synthesis. Thus, 2-Br ring-substituted ethyl cyanophenyl propanoate (ECPP) was utilized in synthesis of novel antimicrobial agents [1] and transporter imaging agents [2], whereas 2-Cl ECPP was involved in catalysis [3], as well as in synthesis and antifungal activities of polyheterocyclic spirooxindole [4]. 3-Cl ECPP was used in synthesis of multifunctional polymer containing Ni-Pd nanoparticles [5] and highly functionalized cyclopentadiene [6], while 4-Cl ECPP was applied to metal-free synthesis of cyano acrylates [7]. Both 4-Cl and 4-F ECPP were used in synthesis of organocatalyzed enantioselective synthesis of 2-amino-4H-chromene derivatives [8]. We have reported earlier synthesis and styrene copolymerization of various halogen ring-substituted esters of cyanophenyl propanoates (CPP): methyl CPP [9, 10], ethyl CPP [11], propyl CPP [12], and butyl CPP [13].
With the objective to design novel compounds, that could serve as a spring board for further development of novel materials with new properties and applications, and in continuation of exploration of isopropyl CPP compounds [14-17], we have prepared halogen ring-substituted isopropyl 2-cyano-3-phenyl-2-propenoates,
RPhCH=C(CN)$CO_2CH(CH_3)_2$, where R is 2-Br, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 2-F, 3-F, 4-F, and explore the feasibility of their copolymerization with styrene. To the best of our knowledge, except for syntheses of 2-Br, 3-Br, 4-Br [8], 4-Cl [7], and 4-F [18], there have been no reports on either synthesis of these isopropyl 2-cyano-3-phenyl-2-propenoates, nor their copolymerization with styrene.

2 Experimental
2.1 Materials
2-Br (98%), 3-Br (97%), 4-Br (99%), 2-Cl (99%), 3-Cl (97%), 4-Cl (97%), 2-F (97%), 3-F (97%), 4-F (98%) -substituted benzaldehydes, isopropyl cyanoacetate (98%), piperidine (99.5%), styrene (99%), 1,1'-azobiscyclohexanecarbonitrile, (ABCN) (98%), and toluene (99.8%) supplied from Sigma-Aldrich Co., were used as received.

2.2 Instrumentation
Infrared spectra of the TSE monomers and polymers (NaCl plates) were determined with an ABB FTLA 2000 FT-IR spectrometer. The melting points of the monomers, the glass transition temperatures (T_g), of the copolymers were measured with TA (Thermal Analysis, Inc.) Model Q10 differential scanning calorimeter (DSC). The thermal scans were performed in a 25 to 200ºC range at heating rate of 10ºC/min. T_g was taken as a midpoint of a straight line between the inflection of the peak's onset and endpoint. The thermal stability of the copolymers was measured by thermogravimetric analyzer (TGA) TA Model Q50 from ambient temperature to 800ºC at 20ºC/min. The molecular weights of the polymers was determined relative to polystyrene standards in THF solutions with sample concentrations 0.8% (w/v) by gel permeation chromatography (GPC) using a Alltech 426 HPLC pump at an elution rate of 1.0 mL/min; Phenogel 5µ Linear column at 25ºC and Viscotek 302 detector. ^{1}H- and ^{13}C-NMR spectra were obtained on 10-25% (w/v) monomer or polymer solutions in $CDCl_3$ at ambient temperature using Bruker Avance 300 MHz spectrometer. Elemental analyses were performed by Midwest Microlab, LLC (IN).

3. Results and Discussion
3.1 Synthesis of Monomers
The halogen ring-substituted isopropyl 2-cyano-3-phenyl-2-propenoates (ICPP) were synthesized by Knoevenagel condensation [19] of a ring-substituted benzaldehyde with isopropyl cyanoacetate, catalyzed by base, piperidine.



Scheme 1: Synthesis of isopropyl 2-cyano-3-phenyl-2-propenoates, where R is 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. The syntheses of 2-Br, 3-Br, 4-Br [8], 4-Cl [7], and 4-F [18] ring-substituted ICPP were reported earlier.

3.1.1 Isopropyl 2-cyano-3-(2-bromophenyl)-2-propenoate
Yield 91%; mp 55.8°C, ^{1}H-NMR δ 8.7 (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.

3.1.2 Isopropyl 2-cyano-3-(3-bromophenyl)-2-propenoate
Yield 68%; mp 85.3°C, ^{1}H-NMR δ 8.2 (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.

3.1.3 Isopropyl 2-cyano-3-(4-bromophenyl)-2-propenoate
Yield 88%; mp 108.8°C, ^{1}H-NMR δ 8.3 (s, 1H, CH=), 8.0-6.2 (m, 4H, Ph), 5.3 (m, 1H, CH), 1.5 (d, 6H, CH_3); ^{13}C-NMR δ 165 (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.

3.1.4 Isopropyl 2-cyano-3-(2-chlorophenyl)-2-propenoate
Yield 78%; ^{1}H-NMR δ 8.7 (s, 1H, CH=), 8.3-7.3 (m, 4H, Ph), 5.3 (m, 1H, CH), 1.2 (d, 6H, CH_3); ^{13}C-NMR δ 164 (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.

3.1.5 Isopropyl 2-cyano-3-(3-chlorophenyl)-2-propenoate
Yield 84%; mp 159C°; ^{1}H-NMR δ 8.2 (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.

3.1.6 Isopropyl 2-cyano-3-(4-chlorophenyl)-2-propenoate
Yield 75%; mp 113.7C°; ^{1}H-NMR δ 8.2 (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.

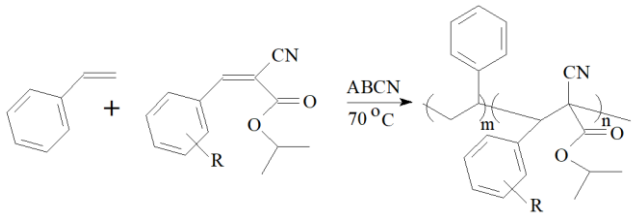
3.1.7 Isopropyl 2-cyano-3-(2-fluorophenyl)-2-propenoate
Yield 97%; mp 59.5°C; ^{1}H-NMR δ 8.5 (s, 1H, CH=), 8.4-7.0 (m, 4H, Ph), 5.3 (m, 1H, CH), 1.3 (d, 6H, CH_3); ^{13}C-NMR δ 164 (C=O), 142, 131, 130, 125, 119 (Ph), 116 (CN), 104 (C=), 68 (CH), 22 (CH_3); FTIR (cm^{-1}): 3096-2834 (m, C-H), 2222 (m, 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.

3.1.8 Isopropyl 2-cyano-3-(3-fluorophenyl)-2-propenoate
Yield 82%; mp 87.7°C; ^{1}H-NMR δ 8.3 (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.

3.1.9 Isopropyl 2-cyano-3-(4-fluorophenyl)-2-propenoate
Yield 92%; mp 91.2°C; ^{1}H-NMR δ 8.2 (s, 1H, CH=), 8.1-7.1 (m, 4H, Ph), 5.3 (m, 1H, CH), 1.3 (2, 6H, CH_3); ^{13}C-NMR δ 166 (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.

3.2 Copolymerization
None of the polymers of the ICPP monomers was reported before this study. Copolymers of styrene (ST) and the ICPP monomers, P(ST-*co*-ICPP) were prepared (Scheme 2) in 25-mL glass screw cap vials at ST/ICPP = 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 10 and 20% to minimize compositional drift. The composition of the

copolymers was determined based on the nitrogen content.



Scheme 2: Copolymerization of styrene and halogen ring-substituted ICPP monomers, where R is 2-Br, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 2-F, 3-F, 4-F

The compounds were characterized by nitrogen elemental analysis, FTIR, ^{1}H- and ^{13}C-NMR spectroscopies. Thermal behavior was studied by DSC and TGA.

3.2.1 Styrene - isopropyl 2-cyano-3-(2-bromophenyl)-2-propenoate copolymer
Yield 11%; ^{1}H-NMR δ 8.3-7.2 (Ph), 5.2 (CH), 1.4 (CH_3); ^{13}C NMR δ 166 (C=O), 137-128 (Ph), 116 (CN), 68 (CH), 22 (CH_3); FTIR (cm^{-1}): 3015-2836 (m, C-H), 2239 (m, CN), 1736 (s, C=O), 1253 (s, C-O-CH_3), 770 (s, C-H out of plane). Anal. Calcd. for N, 2.94.

3.2.2 Styrene - isopropyl 2-cyano-3-(3-bromophenyl)-2-propenoate copolymer
Yield 14%; ^{1}H-NMR δ 8.2-7.2 (Ph), 5.2 (CH), 1.8 (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}): 3045-2873 (m, C-H), 2243 (m, CN), 1734 (s, C=O), 1238 (s, C-O-CH_3), 785 (s, C-H out of plane). Anal. Calcd. for N, 2.58.

3.2.3 Styrene - isopropyl 2-cyano-3-(4-bromophenyl)-2-propenoate copolymer
Yield 18%; ^{1}H-NMR δ 8.0-6.0 (Ph), 5.3 (CH), 1.5 (CH_3); ^{13}C-NMR δ 165 (C=O), 133-128 (Ph), 116 (CN), 68 (CH), 22 (CH_3); FTIR (cm^{-1}): 3016-2807 (m, C-H), 2241 (m, CN), 1736 (s, C=O), 1247 (s, C-O-C), 828 (s, C-H out of plane). Anal. Calcd. For N, 2.59.

3.2.4 Styrene - isopropyl 2-cyano-3-(2-chlorophenyl)-2-propenoate copolymer
Yield 17%; ^{1}H-NMR δ 8.4-7.3 (Ph), 5.3 (CH), 1.2 (CH_3); ^{13}C-NMR δ 164 (C=O), 139-127 (Ph), 116 (CN), 68 (CH), 22 (CH_3); FTIR (cm^{-1}): 3012-2805 (m, C-H), 2241 (m, CN), 1738 (s, C=O), 1268 (s, C-O-C), 860 (s, C-H out of plane). Anal. Calcd. for N, 2.93.

3.2.5 Styrene - isopropyl 2-cyano-3-(3-chlorophenyl)-2-propenoate copolymer
Yield 18%; ^{1}H-NMR δ 8.2-7.2 (Ph), 5.2 (CH), 1.3 (CH_3); ^{13}C-NMR δ 162 (C=O), 135-128 (Ph), 116 (CN), 68 (CH), 22 (CH_3); FTIR (cm^{-1}): 3023-2841 (m, C-H), 2243 (m, CN), 1730 (s, C=O), 1248 (s, C-O-C), 832, 748 (s, C-H out of plane). Anal. Calcd. for N, 2.86.

3.2.6 Styrene - isopropyl 2-cyano-3-(4-chlorophenyl)-2-propenoate copolymer
Yield 19%; ^{1}H-NMR δ 8.0-7.2 (Ph), 5.3 (CH), 1.2 (CH_3); ^{13}C-NMR δ 166 (C=O), 138-129 (Ph), 116 (CN), 68 (CH), 22 (CH_3); FTIR (cm^{-1}): 3156-2750 (m, C-H), 2241 (m, CN), 1736 (s, C=O), 1232 (s, C-O-C), 926 (s, C-H out of plane). Anal. Calcd. for N, 2.73.

3.2.7 Styrene- isopropyl 2-cyano-3-(2-fluorophenyl)-2-propenoate
Yield 10%; ^{1}H-NMR δ 8.4-7.0 (Ph), 5.3 (CH), 1.3 (CH_3); ^{13}C-NMR δ 164 (C=O), 144-119 (Ph), 116 (CN), 68 (CH), 22 (CH_3); FTIR (cm^{-1}): 3096-2834 (m, C-H), 2242 (m, CN), 1736 (s, C=O), 1256 (s, C-O-C), 920 (s, C-H out of plane). Anal. Calcd. for N, 3.03.

3.2.8 Styrene - isopropyl 2-cyano-3-(3-fluorophenyl)-2-propenoate copolymer
Yield 11.8%; ^{1}H-NMR δ 7.9-7.2 (Ph), 5.3 (CH), 1.3 (CH_3); ^{13}C-NMR δ 166 (C=O), 165-131 (Ph), 116 (CN), 68 (CH), 22 (CH_3); FTIR (cm^{-1}): 3174-2754 (m, C-H), 2241 (m, CN), 1734 (s, C=O), 1278 (s, C-O-C), 746, 698 (s, C-H out of plane). Anal. Calcd. for N, 2.88.

3.2.9 Styrene - isopropyl 2-cyano-3-(4-fluorophenyl)-2-propenoate copolymer
Yield 12%; ^{1}H-NMR δ 8.1-7.1 (Ph), 5.3 (CH), 1.3 (CH_3); ^{13}C-NMR δ 166 (C=O), 134-117 (Ph), 116 (CN), 68 (CH), 22 (CH_3); FTIR (cm^{-1}): 3140-2782 (m, C-H), 2242 (m, CN), 1740 (s, C=O), 1224 (s, C-O-C), 760, 698 (m, C-H out of plane). Anal. Calcd. for N, 2.65.
Copolymerization (Scheme 2) of ST and the halogen ring-substituted ICPP resulted in formation of copolymers (Table 1) with weight-average molecular masses 51.1 to 66.9 kD. Since ICPP monomers do not homopolymerize, the most likely structure of the copolymers would be isolated ICPP 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 26.0 and 36.3 mol% of TSE monomer is present in the copolymers prepared at ST/ICPP = 3 (mol), which is indicative of relatively high reactivity of the monomers towards ST.

Table 1: Molecular characteristics of P(ST-co-ICPP) copolymers[a].

R	Nitrogen wt%	% mole ST	% mole ICPP	$1/r_1$	M_w[b] kD
2-Bromo	2.94	63.7	36.3	3.99	66.9
3-Bromo	2.58	70.5	29.5	2.16	51.1
4-Bromo	2.59	70.3	29.7	2.19	58.9
2-Chloro	2.93	68.7	31.3	2.52	65.5
3-Chloro	2.86	69.7	30.3	2.30	56.8
4-Chloro	2.73	71.6	28.4	1.96	53.1
2-Fluoro	3.03	68.8	31.2	2.50	61.4
3-Fluoro	2.88	70.9	29.1	2.09	60.1
4-Fluoro	2.65	74.0	26.0	1.63	52.4

[av]Conditions: ST/ICPP: 3 (mol) / Toluene / 70ºC / 5 hrs. [b]by GPC in THF

In an attempt to qualitatively correlate the observed monomer reactivities, we considered copolymer composition data. The relative reactivity of ST in copolymerization with ICPP monomers can be estimated by assuming applicability of the copolymerization equation (Eq. 1) of the terminal copolymerization model [20]:

$$m_1/m_2 = [M_1](r_1[M_1] + [M_2])/[M_2]([M_1] + r_2[M_2]) \quad (1)$$

m_1 and m_2 are the mole fractions of ST and ICPP monomer units in the copolymer, respectively, $[M_1]$ and $[M_2]$ are the

concentrations of ST and a ICPP in the monomer feed, respectively. The monomer reactivity ratios, r_1 and r_2 are k_{11}/k_{12} and k_{22}/k_{21}, respectively. In the absence of the self-propagation of ICPP monomers (k_{22}= 0, r_2 = 0), and at the monomer feed ([M_1]/[M_2] = 3), the above equation yields:

$$r_1 = (m_1/m_2 - 1)/3 \quad (2)$$

or the equation for the relative reactivity of styrene radical k_{12}/k_{11} with ICPP monomers

$$1/r_1 = 3/(m_1/m_2) - 1 \quad (3)$$

Consideration of monomer reactivities according to Equation 3 also involves the assumption of minimal copolymer compositional drift at given conversion. This non-rigorous kinetic treatment [20] allows estimation of the reactivity of a ST-ended polymer radical in reaction with ICPP monomer. The order of relative reactivity ($1/r_1$) for the PCPP monomers is 2-Br (3.99) > 2-Cl (2.52) > 2-F (2.50) > 3-Cl (2.30) > 4-Br (2.19) > 3-Br (2.16) > 3-F (2.09) > 4-Cl (1.96) > 4-F (1.63). More detailed information on the copolymer composition at different monomer feed ratios would be necessary for the application of copolymerization models that would allow prediction of copolymer composition.

3.3 Thermal behavior

Thermal transitions of the ST-ICPP copolymers were analyzed by differential scanning calorimetry. All the copolymers were amorphous and show no crystalline DSC endotherm on repeated heating and cooling cycles. The glass transition temperatures T_g of the copolymers were measured by DSC. The second heating results were obtained in all cases so that the samples become more dry without "thermal memory". Table 2 shows glass transition values for the ST-ICPP copolymers prepared in this work with no correlation to the size and position of the ICPP ring substitution apparently due to non-uniform composition, monomer unit distribution, and/or molecular weight and MWD.

Table 2: Thermal behavior of P(ST-co-ICPP) copolymers

R	T_g ºC	Onset of decomp., ºC	10% wt loss, ºC	50% wt loss, ºC	Residue at 500 ºC, wt%
2-Bromo	116	281	302	348	5.5
3-Bromo	154	274	309	325	3.6
4-Bromo	137	282	316	336	4.6
2-Chloro	123	290	302	335	4.5
3-Chloro	134	294	282	355	4.1
4-Chloro	136	289	307	322	5.4
2-Fluoro	136	290	311	354	4.6
3-Fluoro	129	285	323	339	4.2
4-Fluoro	130	280	317	321	4.8

A single T_g value was observed for all the copolymers with values higher than polystyrene (104ºC). Information on thermal stability of the copolymers was obtained from thermogravimetric analysis (Table 1). Decomposition of the copolymers in nitrogen occurred in two steps, first in the 250-500ºC range with residue (3.6-5.5% 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.

4. Conclusions

Novel trisubstituted ethylenes, halogen ring-substituted isopropyl 2-cyano-3-phenyl-2-propenoates 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 200-500°C range with residue (3.6-5.5 wt%), which then decomposed in the 500-800ºC range.

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