Synthesis and styrene copolymerization of novel phenoxy ring-substituted isopropyl phenylcyanoacrylates

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Abstract

Phenoxy ring-substituted isopropyl phenylcyanoacrylates, RPhCH=C(CN)CO_2CH(CH_3)$_2$, where R is 2-(3-methoxyphenoxy), 2-(4-methoxyphenoxy), 3-(4-methoxyphenoxy), 3-(4-methylphenoxy), 4-(4-bromophenoxy), 4-(4-fluorophenoxy), 2-(4-chlorophenoxy), 3-(4-chlorophenoxy), 4-(3-chlorophenoxy), 4-(4-chlorophenoxy), 3-(3,4-dichlorophenoxy), 3-(3,5-dichlorophenoxy), 4-(2,4-dichlorophenoxy) were prepared and copolymerized with styrene. The acrylates were synthesized by the piperidine catalyzed Knoevenagel condensation of phenoxy ring-substituted benzaldehydes and isopropyl 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 at 70°C. The compositions of the copolymers were calculated from nitrogen analysis and the structures were analyzed by IR, ^{1}H and ^{13}C-NMR. Decomposition of the copolymers in nitrogen occurred in two steps, first in the 129-500ºC range with residue (2-10% wt.), which then decomposed in the 500-800ºC range.

1. Introduction

Ring–functionalized phenylcyanoacrylates continue to attract attention as intermediates and compounds with interesting properties. There are application reports exemplifying phenoxy ring substituted phenylcyanoacrylates, PCA [1-5]. Thus, 3-phenoxy phenyl-substituted PCA was used in microwave-assisted Knoevenagel condensation over triazine-based microporous network [1] as well as in condensation with imidazolium chloride immobilized SBA-15 [2]. This PCA was used also in N,N'-Dioxide-Lanthanum(III)-catalyzed asymmetric cyclopropanation of 2-cyano-3-arylacrylates with 2-bromomalonates [3], in synthesis of substitiuted tetrazoles [4], and in

synthesis of electrophilic TSEs using lipase as a biocatalyst [5]. 4-Phenoxy PCA was used in studies on quinolin-2(1H)-one derivatives [6], whereas 3-fluorophenoxy ring-substituted PCA was employed in synergistic reduction/cyclization of 2-aroylcyclopropane-1-carboxylates [7]. 2,6-Dimethoxy ring-substituted PCA was used in preparation of 2-cyanopropanoic acid, amide and ester derivatives as estrogen receptor selective NF-κB inhibitors for the treatment of sepsis [8] as well as in preparation of 2-cyanopropanoic acid amide and ester derivatives as estrogen receptor binding agents for use as antiinflammatory and immunomodulatory agents [9]. Chlorophenoxy ring-substituted PCAs were reported in a number of applications [10-20]. Thus, 3-chlorophenoxy ring-substituted PCAwas used in preparation of cinnamic acid hydroxyamides as histone deacetylase 8 inhibitors [10]. 4-Chlorophenoxy PCA was involved in preparation of substituted 2-(1,1-dioxoperhydro-1,4-thiazepin-7-yl)acetamides for treating inflammatory respiratory diseases [11] and preparation of substituted tetrazoles as multipurpose screening compounds [12]. Similar ring-substituted derivative was involved in Knoevenagel condensation catalyzed by triazine network [13] as well as by imidazolium chloride [14]. This derivative was also applied in asymmetric cyclopropanation of propenoates with 2-bromomalonates [15] and in synthesis of trisubstituted propenoates using lipase [16]. 4-Phenoxy phenyl-substituted cyanoacrylates were reported in studies on quinoline derivatives [17]. In relation to chloro-functionalized polymers of interest are reactions of poly(chlorostyrene) used as adsorbent with bifunctional ligand [18], application of N,N,N-tris(triethoxysilylpropyl) melamine in paper culture heritage conservation [19], as well as grafting of poly(p-chlorostyrene) from the surface of ramie fiber via RAFT polymerization [20]. We have reported synthesis and styrene copolymerization of various phenoxy ring-substituted methyl [21], ethyl [22], iso-propyl [23, 24], butyl [25], iso-butyl [26], methoxyethyl [27], octyl [28] phenylcyanoacrylates.

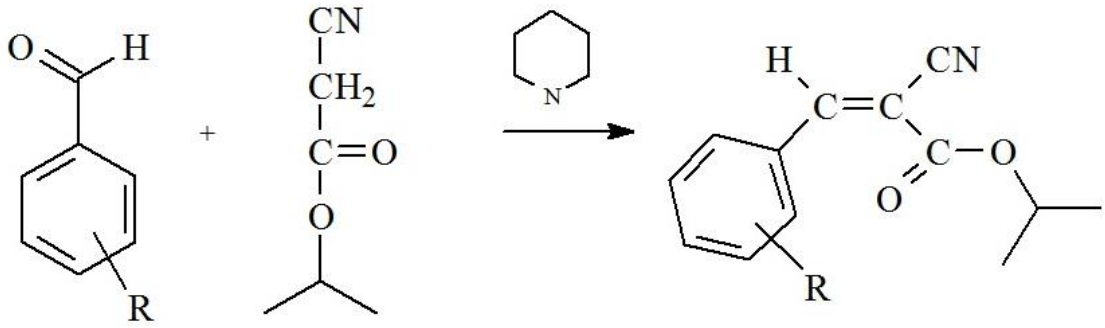
We have prepared phenoxy ring-substituted isopropyl phenylcyanoacrylates, IPCA, $RPhCH=C(CN)CO_2CH(CH_3)_2$, where R is 2-(3-methoxyphenoxy), 2-(4-methoxyphenoxy), 3-(4-methoxyphenoxy), 3-(4-methylphenoxy), 4-(4-bromophenoxy), 4-(4-fluorophenoxy), 2-(4-chlorophenoxy), 3-(4-chlorophenoxy), 4-(3-chlorophenoxy), 4-(4-chlorophenoxy), 3-(3,4-dichlorophenoxy), 3-(3,5-dichlorophenoxy), 4-(2,4-dichlorophenoxy) and copolymerized with styrene. To the best of our knowledge there have been no reports on either synthesis of these compounds, nor their copolymerization with styrene [29].

2. Experimental

2-(3-Methoxyphenoxy), 2-(4-methoxyphenoxy), 3-(4-methoxyphenoxy), 3-(4-methylphenoxy), 4-(4-bromophenoxy), 4-(4-fluorophenoxy), 2-(4-chlorophenoxy), 3-(4-chlorophenoxy), 4-(3-chlorophenoxy), 4-(4-chlorophenoxy), 3-(3,4-dichlorophenoxy), 3-(3,5-dichlorophenoxy), 4-(2,4-dichlorophenoxy)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 [30].

3. Synthesis of Monomers

All IPCA compounds were synthesized by Knoevenagel condensation [31] of appropriate benzaldehydes with isopropyl cyanoacetate, catalyzed by base, piperidine (Scheme 1).
The preparation procedure was essentially the same for all the monomers [30].



Scheme 1. Synthesis of isopropyl phenylcyanoacrylates, RPhCH = $C(CN)CO_2CH(CH_3)_2$ where R is 2-(3-methoxyphenoxy), 2-(4-methoxyphenoxy), 3-(4-methoxyphenoxy), 3-(4-methylphenoxy), 4-(4-bromophenoxy), 4-(4-fluorophenoxy), 2-(4-chlorophenoxy), 3-(4-chlorophenoxy), 4-(3-chlorophenoxy), 4-(4-chlorophenoxy), 3-(3,4-dichlorophenoxy), 3-(3,5-dichlorophenoxy), 4-(2,4-dichlorophenoxy).

3.1. Isopropyl 2-(3-methoxyphenoxy)phenylcyanoacrylate

Yield 79%; mp 100°C; ^{1}H-NMR δ8.8 (s, 1H, CH=), 8.4-6.5 (m, 8H, Ph), 5.2 (m, 1H, OCH), 3.8 (s, 3H, OCH_3), 1.4 (d, 6H, $(CH_3)_2$); ^{13}C-NMR δ166 (C=O), 152 (HC=), 161, 131, 130, 122, 115, 114, 105, 109 (Ph), 116 (CN), 111 (C=), 68 (OCH), 55 (OCH_3) 22 ($(CH_3)_2$); IR (cm^{-1}): 3067-2829 (m, C-H), 2227 (m, CN), 1748 (s, C=O), 1269 (s, C-O-CH_3), 867, 789 (s, C-H out of

plane). Anal. Calcd. for $C_{20}H_{19}NO_4$: C, 71.20; H, 5.68; N, 4.15; Found: C, 70.66; H, 5.90; N, 4.21.

3.2. Isopropyl 2-(4-methoxyphenoxy)phenylcyanoacrylate

Yield 89%; mp 77°C; ^{1}H-NMR δ 8.8 (s, 1H, CH=), 8.4-6.6 (m, 8H, Ph), 5.2 (m, 1H, OCH), 3.8 (s, 3H, OCH_3), 1.4 (d, 6H, $(CH_3)_2$); ^{13}C-NMR δ 166 (C=O), 152 (HC=), 155, 148, 131, 130, 122, 120, 115 (Ph), 116 (CN), 111 (C=), 68 (OCH), 55 (OCH_3) 22 ($(CH_3)_2$); IR (cm^{-1}): 3032-2843 (m, C-H), 2224 (m, CN), 1724 (s, C=O), 1228 (s, C-O-CH_3), 876, 756 (s, C-H out of plane). Anal. Calcd. for $C_{20}H_{19}NO_4$: C, 71.20; H, 5.68; N, 4.15; Found: C, 71.08; H, 5.78; N, 4.19.

3.3. Isopropyl 3-(4-methoxyphenoxy)phenylcyanoacrylate

Yield 72%; ^{1}H-NMR δ 8.1 (s, 1H, CH=), 7.8-6.7 (m, 8H, Ph), 5.2 (m, 1H, OCH), 3.8 (s, 3H, OCH_3), 1.4 (d, 6H, $(CH_3)_2$); ^{13}C-NMR δ 166 (C=O), 154 (HC=), 156, 152, 133, 127, 122, 115 (Ph), 116 (CN), 104 (C=), 68 (OCH), 55 (OCH_3) 22 ($(CH_3)_2$); IR (cm^{-1}): 3094-2856 (m, C-H), 2226 (m, CN), 1727 (s, C=O), 1243 (s, C-O-CH_3), 865, 767 (s, C-H out of plane). Anal. Calcd. for $C_{20}H_{19}NO_4$: C, 71.20; H, 5.68; N, 4.15; Found: C, 68.92; H, 5.58; N, 4.08.

3.4. Isopropyl 3-(4-methylphenoxy)phenylcyanoacrylate

Yield 73%; ^{1}H-NMR δ 8.1 (s, 1H, CH=), 7.8-6.5 (m, 8H, Ph), 5.2 (m, 1H, OCH), 2.3 (s, 3H, CH_3), 1.4 (d, 6H, $(CH_3)_2$); ^{13}C-NMR δ 166 (C=O), 154 (HC=), 158, 155, 133, 130, 119, 114 (Ph), 116 (CN), 104 (C=), 68 (OCH), 22 ($(CH_3)_2$), 21 (CH_3); IR (cm^{-1}): 3087-2838 (m, C-H), 2225 (m, CN), 1744 (s, C=O), 1229 (s, C-O-CH_3), 879, 762 (s, C-H out of plane). Anal. Calcd. for $C_{20}H_{19}NO_3$: C, 74.75; H, 5.96; N, 4.36; Found: C, 73.82; H, 6.23; N, 4.57.

3.5. Isopropyl 4-(4-bromophenoxy)phenylcyanoacrylate

Yield 90%; mp 60°C; ^{1}H-NMR δ 8.2 (s, 1H, CH=), 8.1-6.8 (m, 8H, Ph), 5.2 (m, 1H, OCH), 1.4 (d, 6H, $(CH_3)_2$); ^{13}C-NMR δ 166 (C=O), 154 (HC=), 156, 132, 131, 120, 119 (Ph), 116 (CN), 100 (C=), 68 (OCH), 21 (CH_3); IR (cm^{-1}): 3089-2822 (m, C-H), 2222 (m, CN), 1722 (s, C=O), 1557 (C=C), 1269 (s, C-O-CH_3), 834 (s, C-H out of plane). Anal. Calcd. for $C_{19}H_{16}BrNO_3$: C, 59.08; H, 4.18; N, 3.63; Found: C, 58.93; H, 4.94; N, 3.83.

3.6. Isopropyl 4-(4-fluorophenoxy)phenylcyanoacrylate

Yield 51%; mp 88°C; ^{1}H-NMR δ 8.2 (s, 1H, CH=), 8.0-7.2 (m, 8H, Ph), 5.2 (m, 1H, OCH), 1.4 (d, 6H, $(CH_3)_2$); ^{13}C-NMR δ 166 (C=O), 154 (HC=), 159, 154, 131, 125, 119, 115 (Ph), 116 (CN), 100 (C=), 68 (OCH), 22 (CH_3); IR (cm^{-1}): 3023-2878 (m, C-H), 2224 (m, CN), 1745 (s,

C=O), 1558 (C=C), 1267 (s, C-O-CH_3), 872 (s, C-H out of plane). Anal. Calcd. for $C_{19}H_{16}FNO_3$: C, 70.14; H, 4.96; N, 4.31; Found: C, 69.81; H, 5.2

3.7. Isopropyl 2-(4-chlorophenoxy)phenylcyanoacrylate

Yield 76%; mp 102°C; ^{1}H-NMR δ 8.4 (s, 1H, CH=), 7.5-6.8 (m, 8H, Ph), 5.2 (m, 1H, OCH), 1.4 (d, 6H, CH_3); ^{13}C-NMR δ 165 (C=O), 151 (HC=), 160, 131, 130, 122, 121, 115, 114, 105, 109 (Ph), 116 (CN), 108 (C=), 67 (OCH), 22 (CH_3); IR (cm^{-1}): 3107-2852 (m, C-H), 2224 (m, CN), 1724 (s, C=O), 1267 (s, C-O-CH_3), 862, 779 (s, C-H out of plane). Anal. Calcd. for $C_{19}H_{16}ClNO_3$: C, 66.77; H, 4.72; N, 4.10; Found: C, 66.60; H, 4.70; N, 4.05.

3.8. Isopropyl 3-(4-chlorophenoxy)phenylcyanoacrylate

Yield 88%; mp 84°C; ^{1}H-NMR δ 8.2 (s, 1H, CH=), 7.8-6.8 (m, 8H, Ph), 5.2 (m, 1H, OCH), 1.4 (d, 6H, (CH_3); ^{13}C-NMR δ 164 (C=O), 152 (HC=), 155, 148, 142, 131, 129, 122, 120, 116 (Ph), 116 (CN), 108 (C=), 68 (OCH), 22 (CH_3); IR (cm^{-1}): 3062-2849 (m, C-H), 2226 (m, CN), 1726 (s, C=O), 1232 (s, C-O-CH_3), 896, 756 (s, C-H out of plane). Anal. Calcd. for $C_{19}H_{16}ClNO_3$: C, 66.77; H, 4.72; N, 4.10; Found: C, 65.73; H, 5.01; N, 4.05.

3.9. Isopropyl 4-(3-chlorophenoxy)phenylcyanoacrylate

Yield 92%; mp 108°C; ^{1}H-NMR δ 8.2 (s, 1H, CH=), 7.4-6.8 (m, 8H, Ph), 5.2 (m, 1H, OCH), 1.4 (d, 6H, (CH_3); ^{13}C-NMR δ 166 (C=O), 154 (HC=), 156, 151, 133, 132, 127, 122, 115 (Ph), 116 (CN), 103 (C=), 68 (OCH), 22 (CH_3); IR (cm^{-1}): 3092-2859 (m, C-H), 2264 (m, CN), 1745 (s, C=O), 1248 (s, C-O-CH_3), 895, 763 (s, C-H out of plane). Anal. Calcd. for $C_{19}H_{16}ClNO_3$: C, 66.77; H, 4.72; N, 4.10; Found: C, 67.62; H, 4.58; N, 4.28.

3.10. Isopropyl 4-(4-chlorophenoxy)phenylcyanoacrylate

Yield 86%; mp 82°C; ^{1}H-NMR δ 8.2 (s, 1H, CH=), 8.1-7.0 (m, 8H, Ph), 5.2 (m, 1H, OCH), 1.4 (d, 6H, (CH_3); ^{13}C-NMR δ 165 (C=O), 153 (HC=), 158, 156, 134, 131, 118, 114 (Ph), 116 (CN), 103 (C=), 68 (OCH), 21 (CH_3); IR (cm^{-1}): 3098-2848 (m, C-H), 2222 (m, CN), 1720 (s, C=O), 1231 (s, C-O-CH_3), 876, 768 (s, C-H out of plane). Anal. Calcd. for $C_{19}H_{16}ClNO_3$: C, 66.77; H, 4.72; N, 4.10; Found: C, 66.91; H, 4.79; N, 4.11.

3.11. Isopropyl 3-(3,4-chlorophenoxy)phenylcyanoacrylate

Yield 92%; mp 58°C; ^{1}H-NMR δ 8.2 (s, 1H, CH=), 8.1-6.8 (m, 7H, Ph), 5.2 (m, 1H, OCH), 1.4 (d, 6H, CH_3); ^{13}C-NMR δ 162 (C=O), 152 (HC=), 156, 134, 132, 131, 120, 119 (Ph), 116 (CN), 100 (C=), 68 (OCH), 21 (CH_3); IR (cm^{-1}): 3089-2822 (m, C-H), 2225 (m, CN), 1726 (s, C=O),

1553 (C=C), 1261 (s, C-O-CH_3), 832 (s, C-H out of plane). Anal. Calcd. for $C_{19}H_{15}Cl_2NO_3$: C, 60.66; H, 4.02; N, 3.72; Found: C, 59.96; H, 4.38; N, 4.39.

3.12. Isopropyl 3-(3,5-dichlorophenoxy)phenylcyanoacrylate

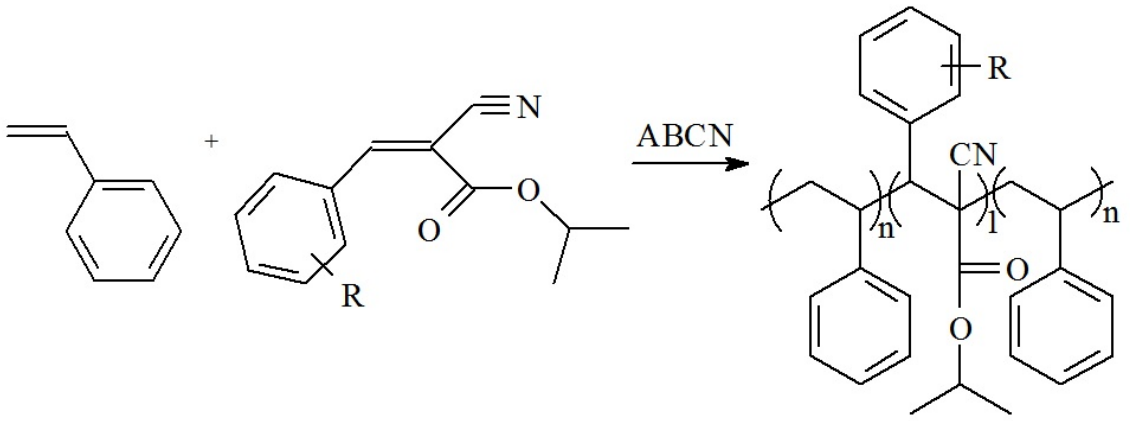
Yield 76%; mp 89°C; ^{1}H-NMR δ 8.2 (s, 1H, CH=), 8.0-6.7 (m, 7H, Ph), 5.2 (m, 1H, OCH), 1.4 (d, 6H, (CH_3); ^{13}C-NMR δ 165 (C=O), 154 (HC=), 159, 153, 131, 124, 119, 115 (Ph), 116 (CN), 104 (C=), 68 (OCH), 22 (CH_3); IR (cm^{-1}): 3012-2778 (m, C-H), 2225 (m, CN), 1724 (s, C=O), 1558 (C=C), 1279 (s, C-O-CH_3), 862 (s, C-H out of plane). Anal. Calcd. for $C_{19}H_{15}Cl_2NO_3$: C, 60.66; H, 4.02; N, 3.72; Found: C, 60.38; H, 4.07; N, 3.78.

3.13. Isopropyl 4-(2,4-chlorophenoxy)phenylcyanoacrylate

Yield 79%; mp 90°C; ^{1}H-NMR δ 8.2 (s, 1H, CH=), 8.0-6.8 (m, 7H, Ph), 5.2 (m, 1H, OCH), 1.4 (d, 6H, CH_3); ^{13}C-NMR δ 163 (C=O), 151 (HC=), 157, 133, 132, 131, 125, 120, 119 (Ph), 116 (CN), 98 (C=), 68 (OCH), 21 (CH_3); IR (cm^{-1}): 3123-2787 (m, C-H), 2223 (m, CN), 1729 (s, C=O), 1559 (C=C), 1243 (s, C-O-CH_3), 812, 765 (s, C-H out of plane). Anal. Calcd. for $C_{19}H_{15}Cl_2NO_3$: C, 60.66; H, 4.02; N, 3.72; Found: C, 60.96; H, 3.98; N, 3.32.

4. Copolymerization

Copolymers of the ST and the IPCA monomers were prepared (Scheme 2) in 25-mL glass screw cap vials at ST/IPCA = 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 (Table 1). The composition of the copolymers was determined based on the nitrogen content. Since IPCA monomers do not homopolymerize, the most likely structure of the copolymers would be isolated IPCA monomer units alternating with short ST sequences (Scheme 2).



Scheme 2. Copolymerization of styrene and the ring-substituted phenylcyanoacrylates, RPhCH = $C(CN)CO_2CH(CH_3)_2$. R is 2-(3-methoxyphenoxy), 2-(4-methoxyphenoxy), 3-(4-methoxyphenoxy), 3-(4-methylphenoxy), 4-(4-bromophenoxy), 4-(4-fluorophenoxy), 2-(4-chlorophenoxy), 3-(4-chlorophenoxy), 4-(3-chlorophenoxy), 4-(4-chlorophenoxy), 3-(3,4-dichlorophenoxy), 3-(3,5-dichlorophenoxy), 4-(2,4-dichlorophenoxy).

Copolymerization of ST and the phenoxy ring-substituted IPCA resulted in formation of copolymers (Table 1) with weight-average molecular masses 17 to 35 kD. According to the nitrogen elemental analysis, between 25.9 and 33.4 mol% of TSE monomer is present in the copolymers prepared at ST/IPCA = 3 (mol), which is indicative of relatively high reactivity of the monomers towards ST.

Table 1. Copolymerization of styrene and ring-substituted isopropyl phenylcyanoacrylate

						TGA			
R	Yield[a] wt%	N wt %	IPCA mol%	M_W kD	T_g °C	Onset of decomp., °C	10% wt loss, °C	50% wt loss, °C	Residue at 500 °C, wt%
2-(3-CH_3OPhO)	13.3	2.3	28.1	25	108	189	298	362	3
2-(4-CH_3OPhO)	15.6	2.2	26.2	16	95	195	271	377	2
3-(4-CH_3OPhO)	10.7	2.3	27.7	35	77	178	273	381	7
3-(4-CH_3PhO)	11.8	2.3	27.1	17	72	198	298	389	7
3-(4-BrPhO)	12.5	2.4	33.4	24	73	197	296	384	7
3-(4-FPhO)	17.2	2.5	30.7	23	97	199	305	386	4
2-(4-ClOPhO)	12.1	2.2	26.8	19	118	124	301	364	5
3-(4-ClOPhO)	13.2	2.3	27.6	19	125	136	292	390	10
4-(3-ClOPhO)	10.6	2.3	28.0	24	127	176	291	323	5
4-(4-ClPhO)	10.7	2.3	28.8	22	122	129	278	345	5
3-(3,4-ClPhO)	11.6	2.2	29.0	21	137	156	287	362	10
3-(3,5-ClPhO)	12.2	2.2	29.5	19	136	154	276	369	5
4-(2,4-ClPhO)	12.8	2.1	25.9	25	142	125	288	366	7

[a]Polymerization time was 5 h

5. Structure and Thermal Properties

The structure of ST-IPCA 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 propenoates and ST is a copolymerization. IR spectra of the copolymers show overlapping bands in 3332-2687 cm^{-1} region corresponding to C-H stretch vibrations. The bands for the IPCA monomer unit are 2247-2230 (w, CN), 1768-1731 (s, C=O), and 1241-1231 cm^{-1} (m, C-

O). Phenyl rings of both monomers show ring stretching bands at 1508-1472 and 1508-1489 cm^{-1} as well as a doublet 787-752 cm^{-1}, associated with C-H out-of-plane deformations. These bands can be readily identified in styrene copolymers with the propenoates containing cyano and carbonyl electron withdrawing groups. The ^{1}H-NMR spectra of the ST-IPCA copolymers show a broad double peak in a 6.2-8.2 ppm region corresponding to phenyl ring protons. A resonance at 5.1-4.4 ppm is assigned to the methineoxy proton of isopropyl ester. Broad overlapping resonances at 3.3-2.1 ppm are assigned to the methine proton and CH_2Ph of IPCA, and methine and methylene protons of ST monomer unit close to the acrylate unit, which are more subjected to deshielding than the ones in polystyrene. The low and high field components of the signal are associated with IPCA monomer unit in head-to-tail and head-to-head structures [32]. A broad resonance peak in 0.7-2.8 ppm range is attributed to the methine and methylene protons of styrene monomer sequences, as well as to isopropyl ester and alkyl-Ph protons of IPCA. The ^{13}C-NMR spectra also support the suggested skeletal structure of the copolymers. Thus, the assignment of the peaks is as follows: 168-160 ppm (C=O), 155-134 ppm (quaternary carbons of both phenyls), 141-122 ppm (phenyl carbons), 121-111 ppm (CN), 64-51 ppm (methine, quaternary carbons and IPCA carbons), 49-42 ppm (ST methine), and 44-40 ppm (ST methylene), 36-21 ppm alkyl carbons of IPCA. Broadening of the NMR signals in the spectra of the copolymers is apparently associated with head-to-tail and head-to-head structures, which formed though the attack of a styrene-ended radical on both sides of the propenoates [32]. The IR and NMR data showed that these are true copolymers, composed of both the acrylates and ST monomer units.

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. They are amorphous and show no crystalline DSC endotherm. Results of thermal analysis of ST-IPCA copolymers are presented in Table 1. Information on the degradation of the copolymers was obtained from thermogravimetric analysis. Decomposition of the copolymers in nitrogen occurred in two steps, first in the 129-500ºC range with residue (2-10% 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.

6. Conclusions

Novel trisubstituted ethylenes, phenoxy ring-substituted isopropyl phenylcyanoacrylates 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 two steps, first in the 129-500°C range with residue (2-10%wt), which then decomposed in the 500-800ºC range.

Acknowledgments

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