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Synthesis and styrene copolymerization of novel phenoxy ring-substituted isopropyl 2-cyano-3-phenyl-2-propenoates

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Abstract
Trisubstituted ethylenes, phenoxy ring-substituted isopropyl 2-cyano-3-phenyl-2-propenoates, $RPhCH=C(CN)CO_2CH(CH_3)_2$ where R is 2-(3-methoxyphenoxy), 2-(4-methoxyphenoxy), 3-(4-methoxyphenoxy), 3-(4-methylphenoxy), 4-(4-bromophenoxy), 4-(4-fluorophenoxy) were prepared and copolymerized with styrene. The monomers 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 ethylenes were copolymerized with styrene in solution with radical initiation (ABCN) 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 270-500ºC range with residue (2-7% wt.), which then decomposed in the 500-800ºC range.

Keywords: knoevenagel condensation, trisubstituted ethylenes, styrene radical copolymerization

1. Introduction
Ring–functionalized trisubstituted ethylenes (TSE), esters of 2-cyano-3-R^1-phenyl-2-propenoic acid, $R^1PhCH=C(CN)CO_2R^2$ continue to attract attention as compounds with interesting properties and as comonomers for modification of commercial polymers. There are application reports exemplifying phenoxy ring substituted ethyl 2-cyano-3-phenyl-2-propenoates, ECPP [1-5]. Thus, 3-phenoxy phenyl-substituted ECPP 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 ECPP was used also in N,N'-Dioxide-Lanthanum(III)-catalyzed asymmetric cyclopropanation of 2-cyano-3-arylacrylates with 2-bromomalonates [3], in synthesis of substituted tetrazoles [4], and in synthesis of electrophilic TSEs using lipase as a biocatalyst [5]. 4-Phenoxy ECPP was used in studies on quinoline-2(1H)-one derivatives [6], whereas 3-fluorophenoxy ring-substituted ECPP was employed in synergistic reduction/cyclization of 2-aroylcyclopropane-1-carboxylates [7].

It was shown that electrophilic TSEs are particularly useful in delineating the transition from radical chemistry to ionic chemistry [8]. Previous studies showed that TSE containing substituents larger than fluorine have very low reactivity in radical homopolymerization due to polar and steric reasons. Although steric difficulties preclude homopolymerization of most TSE monomers, their copolymerization with a monosubstituted alkene makes it possible to overcome these steric problems [9]. Copolymerization of electrophilic TSE having double bonds substituted with halo, cyano, and carbonyl groups and electron-rich monosubstituted ethylenes such as styrene, *N*-vinylcarbazole, and vinyl acetate [10-12] show a tendency toward the formation of alternating copolymers. We have reported synthesis and styrene copolymerization of various phenoxy ring-substituted methyl [13], ethyl [14], and butyl 2-cyano-3-phenyl-2-propenoates [15].

With the objective to design novel structures, that could serve as a spring board for further development of novel materials with new properties and applications, and in continuation of our studies of the monomer structure-reactivity correlation in the radical copolymerization of TSE monomers we have prepared some phenoxy ring-substituted isopropyl 2-cyano-3-phenyl-2-propenoates, ICPP, $RPhCH=C(CN)CO_2CH(CH_3)_2$, where R is 2-(3-methoxyphenoxy), 2-(4-methoxyphenoxy), 3-(4-methoxyphenoxy), 3-(4-methylphenoxy), 4-(4-bromophenoxy), 4-(4-fluorophenoxy), and explore 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.

2 Experimental
2.1 Materials
2-(3-Methoxyphenoxy), 2-(4-methoxyphenoxy), 3-(4-methoxyphenoxy), 3-(4-methylphenoxy), 4-(4-bromophenoxy), 4-(4-fluorophenoxy) benzaldehydes, isopropyl cyanoacetate, piperidine, styrene, 1,1'-azobiscyclohexanecarbonitrile, (ABCN), and toluene supplied from Sigma-Aldrich Co., were used as received.

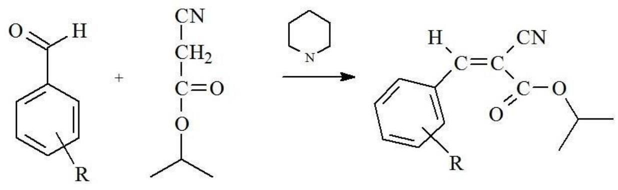
2.2 Instrumentation
Infrared spectra of the TSE monomers and polymers (NaCl plates) were determined with an ABB FTLA 2000 FT-IR spectrometer. The melting points of the monomers, the glass transition temperatures (T_g), of the copolymers were measured with TA (Thermal Analysis, Inc.) Model Q10 differential 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 Altech 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 Avance 300 MHz spectrometer. Elemental analyses were performed by Midwest Microlab, LLC (IN).

3. Results and Discussion

3.1 Synthesis of Monomers

All ICPP compounds were synthesized by Knoevenagel condensation [16] of appropriate benzaldehydes with isopropyl cyanoacetate, catalyzed by base, piperidine (Scheme 1).



Scheme 1: Synthesis of isopropyl 2-cyano-3-phenyl-2-propenoates $RPhCH = C(CN)CO_2CH(CH_3)_2$ where R is 2-(3-methoxyphenoxy), 2-(4-methoxyphenoxy), 3-(4-methoxyphenoxy), 3-(4-methylphenoxy), 4-(4-bromophenoxy), 4-(4-fluorophenoxy).

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.

3.1.1 Isopropyl 2-cyano-3-[2-(3-methoxyphenoxy) phenyl]-2-propenoate

Yield 79%; mp 100°C; ^{1}H-NMR δ 8.8 (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 δ 166 (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.

3.1.2 Isopropyl 2-cyano-3-[2-(4-methoxyphenoxy) phenyl]-2-propenoate

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.

3.1.3 Isopropyl 2-cyano-3-[3-(4-methoxyphenoxy) phenyl]-2-propenoate.

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.

3.1.4 Isopropyl 2-cyano-3-[3-(4-methylphenoxy) phenyl]-2-propenoate

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.

3.1.5 Isopropyl 2-cyano-3-[4-(4-bromophenoxy)phenyl)-2-propenoate

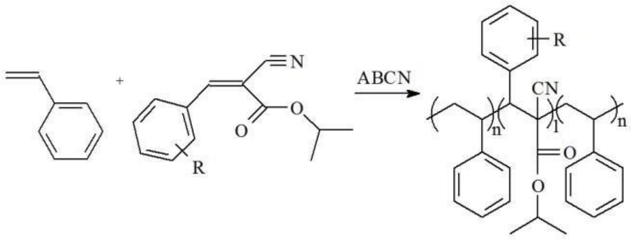
Yield 90%; mp 60°C; ^{1}H-NMR δ 8.2 (s, 1H, CH=), 8.1-6.8 (m, 8H, Ph), 5.2 (m, 1H, OCH), 1.4 (d, 6H, $(CH_3)_2$); ^{13}C-NMR δ 166 (C=O), 154 (HC=), 156, 132, 131, 120, 119 (Ph), 116 (CN), 100 (C=), 68 (OCH), 21 (CH_3); IR (cm^{-1}): 3089-2822 (m, C-H), 2222 (m, CN), 1722 (s, C=O), 1557 (C=C), 1269 (s, 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.

3.1.6 Isopropyl 2-cyano-3-[4-(4-fluorophenoxy)phenyl)-2-propenoate

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

3.2 Copolymerization

Copolymers of the ST and the ICPP monomers 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 (Table 1). The composition of the copolymers was determined based on the nitrogen content. Since ICPP monomers do not homopolymerize, the most likely structure of the copolymers would be isolated ICPP monomer units alternating with short ST sequences (Scheme 2).



Scheme 2: Copolymerization of styrene and the ring-substituted isopropyl 2-cyano-3-phenyl-2-propenoates, 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).

Copolymerization of ST and the phenoxy ring-substituted ICPP resulted in formation of copolymers (Table 1) with weight-average molecular masses 16.4 to 34.5 kD.

Table 1: Copolymerization of styrene (M_1) and ring-substituted isopropyl 2-cyano-3-phenyl-2-propenoates (M_2).

						TGA			
R	**Yield[a] wt%**	**N wt%**	**m_2 in pol., mol%**	**M_W kD**	**T_g ºC**	**Onset of decomp., ºC**	**10% wt loss, ºC**	**50% wt loss, ºC**	**Residue at 500 ºC, wt%**
2-(3-CH_3OPhO)	13.3	2.32	28.1	24.9	108	189	298	362	3
2-(4-CH_3OPhO)	15.6	2.22	26.2	16.4	95	195	271	377	2
3-(4-CH_3OPhO)	10.7	2.30	27.7	34.5	77	178	273	381	7
3-(4-CH_3PhO)	11.8	2.33	27.1	17.2	72	198	298	389	7
3-(4-BrPhO)	12.5	2.36	33.4	24.1	73	197	296	384	7
3-(4-FPhO)	17.2	2.50	30.7	23.1	97	199	305	386	4

[a] Polymerization time was 5 h

According to the nitrogen elemental analysis, between 26.2 and 33.4 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.

In an attempt to qualitatively correlate the observed monomer reactivities, we considered copolymer composition data. The relative reactivity of ST in copolymerization with these monomers can be estimated by assuming applicability of the copolymerization equation (Eq. 1) of the terminal copolymerization model [9]:

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

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:

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

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

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

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 [9] 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 ICPP monomers is 4-(4-bromophenoxy) (3.02) > 4-(4-fluorophenoxy) (2.38) > 2-(3-methoxyphenoxy) (1.92) > 3-(4-methoxyphenoxy) (1.86) > 3-(4-methylphenoxy) (1,77) > 2-(4-methoxyphenoxy) (1.65). 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 Structure and Thermal Properties

The structure of ST-ICPP 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 TSE monomers and ST is a copolymerization. IR spectra of the copolymers show overlapping bands in 3340-2690 cm^{-1} region corresponding to C-H stretch vibrations. The bands for the ICPP monomer unit are 2245-2232 (w, CN), 1762-1734 (s, C=O), and 1249-1233 cm^{-1} (m, C-O). Phenyl rings of both monomers show ring stretching bands at 1518-1483 and 1516-1481 cm^{-1} as well as a doublet 785-765 cm^{-1}, associated with C-H out-of-plane deformations. These bands can be readily identified in styrene copolymers with TSE monomers containing cyano and carbonyl electron withdrawing groups.

The ^{1}H-NMR spectra of the ST-ICPP copolymers show a broad double peak in a 6.6-8.1 ppm region corresponding to phenyl ring protons. A resonance at 5.2-4.8 ppm is assigned to the methineoxy proton of isopropyl ester. Broad overlapping resonances at 3.7-2.3 ppm are assigned to the methine proton and CH_2Ph of ICPP, 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 ICPP monomer unit in head-to-tail and head-to-head structures [17]. A broad resonance peak in 0.8-2.9 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 ICPP. The ^{13}C-NMR spectra also support the suggested skeletal structure of the copolymers. Thus, the assignment of the peaks is as follows: 167-162 ppm (C=O), 159-138 ppm (quaternary carbons of both phenyls), 140-120 ppm (phenyl carbons), 120-110 ppm (CN), 65-52 ppm (methine, quaternary carbons and ICPP carbons), 49-43 ppm (ST methine), and 43-41 ppm (ST methylene), 35-10 ppm alkyl carbons of ICPP. 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 TSE monomer [17]. The IR and NMR data showed that these are true copolymers, composed of both TSE 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-ICPP 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 270-500ºC range with residue (2-7% 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, phenoxy 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 two steps, first in the 270-500°C range with residue (2-7%wt), which then decomposed in the 500-800ºC range.

5. Acknowledgments

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