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Synthesis and styrene copolymerization of novel trisubstituted ethylenes: Chlorophenoxy ring-substituted isopropyl 2-cyano-3-phenyl-2-propenoates

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Abstract

Novel trisubstituted ethylenes, chlorophenoxy ring-substituted isopropyl 2-cyano-3-phenyl-2-propenoates, $RPhCH{=}C(CN)CO_2CH(CH_3)_2$ (where R is 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 ethylenes were synthesized by the piperidine catalyzed Knoevenagel condensation of ring-substituted benzaldehydes and isopropyl cyanoacetate, and characterized by CHN analysis, FTIR, ^1H 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 FTIR, ^1H and ^{13}C NMR. Decomposition of the copolymers in nitrogen occurred in two steps, first in the 250-500ºC range with residue (4.9-9.8% wt), which then decomposed in the 500-800ºC range.

Keywords: trisubstituted ethylene monomers, styrene copolymers, 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 substitiuted tetrazoles [4], and in synthesis of electrophilic TSEs using lipase as a biocatalyst [5]. 4-Phenoxy ECPP was used in studies on quinolin-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 electrophylic 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], propyl [15], and butyl 2-cyano-3-phenyl-2-propenoates [16].

Our purposes in exploration of novel isopropyl chlorophenoxy-ring substituted 2-cyano-3-phenyl-2-propenoates were twofold: (1) to utilize aldol condensation for synthesis of alkenes with a variety of potentially reactive functional groups; (2) to employ conventional radical copolymerization of novel functional comonomers with a commercial monomer styrene. Thus, in continuation of our investigation of novel functional compounds we have prepared chlorophenoxy ring-substituted isopropyl 2-cyano-3-phenyl-2-propenoates, ICPP, $RPhCH{=}C(CN)CO_2CH(CH_3)_2$, where R is 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 explored 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-(4-Chlorophenoxy) 97%, 3-(4-chlorophenoxy) 97%, 4-(3-chlorophenoxy) 97%, 4-(4-chlorophenoxy) 97%, 3-(3,4-dichlorophenoxy) 94%, 3-(3,5-dichlorophenoxy) 95%, 4-(2,4-dichlorophenoxy) (97%) –benzaldehydes, isopropyl cyanoacetate (98.0%), piperidine (99.5%), styrene (99%), 1,1'-azobiscyclohexanecarbonitrile, (ABCN) (98%), and toluene (99.8%) supplied from Sigma-Aldrich Co., were used as received.

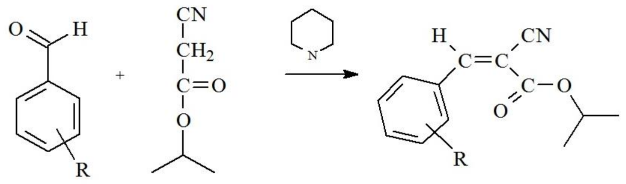
2.2 General Procedures

Infrared spectra of the ICPP compounds and polymers (KBr plates) were determined with an ABB FTLA 2000 FTIR spectrometer. The melting points of the ICPP compounds and 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 150ºC range on second heat 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 in the flow of nitrogen (20 mL/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 RI detector. ^{1}H and ^{13}C-NMR spectra were obtained on 10-25% (w/v) ICPP or polymer solutions in $CDCl_3$ at ambient temperature using Avance 300 MHz spectrometer. Elemental analyses of ICPP compounds and the copolymers were performed by Midwest Microlab, LLC (IN).

3. Results and Discussion

3.1 Synthesis of ICPP compounds

All ICPP compounds were synthesized by Knoevenagel condensation [17] 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-(4-chlorophenoxy), 3-(4-chlorophenoxy), 4-(3-chlorophenoxy), 4-(4-chlorophenoxy), 3-(3,4-dichlorophenoxy), 3-(3,5-dichlorophenoxy), 4-(2,4-dichlorophenoxy).

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. Melting points of the compounds in crystalline state were measured by DSC. The compounds were characterized by FTIR, ^{1}H and ^{13}C NMR spectroscopies. No stereochemical analysis of the novel chlorophenoxy ring-substituted ICPP was performed since no stereoisomers (*E* or/and *Z*) of known configuration were available.

3.1.1 Isopropyl 2-cyano-3-[2-(4-chlorophenoxy)phenyl]-2-propenoate

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.

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

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.

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

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.

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

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.

3.1.5 Isopropyl 2-cyano-3-[3-(3,4-chlorophenoxy) phenyl]-2-propenoate

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.

3.1.6 Isopropyl 2-cyano-3-[3-(3,5-dichlorophenoxy) phenyl]-2-propenoate

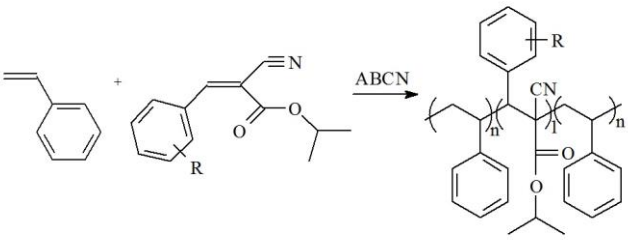
ield 76%; mp 89°C; ^{1}H-NMR δ 8.2 (s, 1H, CH=), 8.0-6.7 (m, 7H, Ph), 5.2 (m, 1H, OCH), 1.4 (d, 6H, (CH_3); ^{13}C-NMR δ 165 (C=O), 154 (HC=), 159, 153, 131, 124, 119, 115 (Ph), 116 (CN), 104 (C=), 68 (OCH), 22 (CH_3); IR (cm^{-1}): 3012-2778 (m, C-H), 2225 (m, CN), 1724 (s, C=O), 1558 (C=C), 1279 (s, 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.

3.1.7 Isopropyl 2-cyano-3-[4-(2,4-chlorophenoxy)phenyl] -2-propenoate

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.

3.2 Synthesis of styrene – ICPP copolymers

Copolymers of styrene (ST) and the ICPP compounds, 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 (Table 1). The composition of the copolymers was determined based on the nitrogen content. The compounds were characterized by nitrogen elemental analysis, IR, ^{1}H- and ^{13}C-NMR spectroscopies. Thermal behavior was studied by DSC and TGA. 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). 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 25.9 and 29.5 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.



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-(4-chlorophenoxy), 3-(4-chlorophenoxy), 4-(3-chlorophenoxy), 4-(4-chlorophenoxy), 3-(3,4-dichlorophenoxy), 3-(3,5-dichlorophenoxy), 4-(2,4-dichlorophenoxy).

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-(4-ClOPhO)	12.1	2.24	26.8	18.9	118	124	301	364	4.9
3-(4-ClOPhO)	13.2	2.28	27.6	19.4	125	136	292	390	9.5
4-(3-ClOPhO)	10.6	2.30	28.0	24.3	127	176	291	323	5.1
4-(4-CH_3PhO)	10.7	2.34	28.8	22.2	122	129	278	345	5.2
3-(3,4-ClPhO)	11.6	2.22	29.0	21.1	137	156	287	362	9.8
3-(3,5-ClPhO)	12.2	2.24	29.5	19.2	136	154	276	369	5.3
4-(2,4-ClPhO)	12.8	2.08	25.9	25.4	142	125	288	366	7.1

^{a}Polymerization time was 5 h

Relative reactivities of ST and the ICPP monomers in the copolymerization can be estimated by application of the copolymerization equation for the terminal copolymerization model [9]

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

where m_1 and m_2 are mole fractions of ST and ICPP monomer units in the copolymer, $[M_1]$ and $[M_2]$ are concentrations of ST and an ICPP in the monomer feed, and r_1 and r_2 are monomer reactivity ratios, $r_1 = k_{ST\text{-}ST}/k_{ST\text{-}ICPP}$ and $r_2 = k_{ICPP\text{-}ICPP}/k_{ICPP\text{-}ST}$. In the absence of self-propagation of ICPP monomers ($k_{ICPP\text{-}ICPP} = 0$, $r_2 = 0$), the Eq. 1 yields

$$m_1/m_2 = r_1\,([M_1]/[M_2]) + 1 \qquad (2)$$

Equation 2 assumes a minimal copolymer compositional drift during a copolymerization reaction, i.e., a low conversion. The fact that ICPP monomers do not self-propagate allows the use of Eq. 2 for a single-point estimation of the relative reactivity of ICPP monomers with respect to ST; it is represented by the $1/r_1 = k_{ST\text{-}ICPP}/k_{ST\text{-}ST}$ ratio (the rate constant ratio of attaching an ICPP molecule vs. a ST molecule to a ST-ending growing polymer chain). Thus relative reactivities ($1/r_1$) for the ICPP monomers increase in the following row R = 4-(2,4-dichlorophenoxy) (1.62) > 2-(4-chlorophenoxy) (1.73) > 3-(4-chlorophenoxy) (1.85) > 4-(3-chlorophenoxy) (1.91) > 4-(4-chlorophenoxy) (2.04) > 3-(3,4-dichlorophenoxy) (2.07) > 3-(3,5-dichlorophenoxy) (2.15). These ratios indicate that all chlorophenoxy ring-substituted ICPP monomers are more reactive than styrene in the addition to a ST-ended polymer radical.

3.4 Copolymer structure

The structure of ST-ICPP copolymers was characterized by FTIR and NMR spectroscopy. A comparison of the spectra of the monomers, copolymers and polystyrene shows, that the reaction between the ICPP monomers and ST is a copolymerization. FTIR spectra of the copolymers show overlapping bands in 3350-2680 cm^{-1} region corresponding to C-H stretch vibrations. The bands for the ICPP monomer unit are 2240-2228 (w, CN), 1756-1710 (s, C=O), and 1280-1210 cm^{-1} (m, C-O). Phenyl rings of both monomers show ring stretching bands at 1516-1320 cm^{-1} as well as a doublet 778-610 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 groups.

Our earlier microstructure analysis of ST copolymers with

2-phenyl-1,1-dicyanoethene [18], as deduced from high resolution ^{1}H and ^{13}C-NMR spectroscopy (DEPT, HETCOR, NOESY and JMODXH), demonstrated the formation of both head-to-tail and head-to-head alternating monomer structures, as well as short ST sequences. 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 [18]. 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 [18]. 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 (4.9-9.8% 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, chlorophenoxy 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, ^{1}H and ^{13}C-NMR. The thermal gravimetric analysis indicated that the copolymers decompose in two steps, first in the 270-500ºC range with residue (2-7%wt), which then decomposed in the 500-800ºC range.

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