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Synthesis and Styrene Copolymerization of Novel Oxy Ring-Disubstituted Isopropyl Phenylcyanoacrylates

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Abstract

Novel trisubstituted ethylenes, oxy ring-disubstituted isopropyl 3-(R-phenyl)-2-cyanoacrylates, $RPhCH=C(CN)CO_2CH(CH_3)_2$ (where R is 2,6-dimethoxy, 3,4-dimethoxy, 3,5-dimethoxy, 4-methoxy-2-methyl, 4-methoxy-3-methyl, 3-ethoxy-4-methoxy, 4-ethoxy-3-methoxy) were prepared and copolymerized with styrene. The monomers were synthesized by the piperidine catalyzed Knoevenagel condensation of ring-disubstituted benzaldehydes and isopropyl cyanoacetate and characterized by CHN elemental analysis, IR, ^1H- 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, ^1H and ^{13}C-NMR, GPC, DSC, and TGA.

Keywords: Trisubstituted ethylenes; Radical copolymerization; Styrene copolymers

Introduction

Ring–functionalized trisubstituted ethylenes (TSE), esters of 3-phenylcyanoacrylic acid, R1PhCH=C (CN) CO2R2 continue to attract attention as compounds with interesting properties and as comonomers for modification of commercial polymers. Thus, methoxy ring-substituted methyl ester of 2-cyano-3-phenyl-2-propenoate, MCPP was used in synthesis of pyridotriazines and triazolopyridines [1]. Dimethylamino ring-substituted MCPP was examined among other cyanovinylheteroaromatics in relation to organic nonlinear optics [2]. There are a number of applications of ethyl 2-cyano-3-phenyl-2-propenoate, ECPP and its ring-substituted derivatives which include studies of catalysis [3] and potential antimicrobial and antioxidant agents [4]. 2,4-Dimethoxyphenyl ECPP was used in design, synthesis and study of anticancer activity of novel benzothiazole analogues [5], in synthesis of thiazacridine derivatives as anticancer agents against breast and hematopoietic neoplastic cells [6] and in DABCO-catalyzed Knoevenagel condensation using hydroxy ionic liquid as a promoter [7]. This ECPP was involved in catalysis study of N,N'-dialkylimidazolium dimethyl phosphates [8], in synthesis and study of antimicrobial activity of some cyanoacrylates [9], as well as in synthesis of antiproliferative active 2-aminobenzimidazole derivatives [10]. 3, 4-Diethoxyphenyl ethyl cyanoacrylate was used in synthesis of 3-hydroxypyridines [11]. We have reported synthesis and styrene copolymerization of a number of dimethyl and dimethoxy ring-substituted esters of cyanophenylacrylates (CPA): methyl ester of CPA [12,13], ethyl CPA [14,15], propyl CPA [16], and butyl CPA [17]. In continuation of our exploration of novel isopropyl CPA compounds [18-20] with the objective to synthesize novel structures with a various functional groups and explore the feasibility of their copolymerization with styrene we have prepared some oxy ring-disubstituted isopropyl 3-(R-phenyl)cyanoacrylates (IPCA), $RPhCH=C(CN)CO_2CH(CH_3)_2$, where R is 2,6-dimethoxy, 3,4-dimethoxy, 3,5-dimethoxy, 4-methoxy-2-methyl, 4-methoxy-3-methyl, 3-ethoxy-4-methoxy, 4-ethoxy-3-methoxy. To the best of our knowledge, there have been no reports on either synthesis of these isopropyl 3-phenylcyanoacrylates, nor their copolymerization with styrene.

Experimental and Materials

2,6-Dimethoxy, 3,4-dimethoxy, 3,5-dimethoxy, 4-methoxy-2-methyl, 4-methoxy-3-methyl, 3-ethoxy-4-methoxy, 4-ethoxy-3-methoxybenzaldehydes, isopropyl cyanoacetate, piperidine, styrene, 1,1'-azobiscyclohexanecarbonitrile, (ABCN), and toluene supplied from Sigma-Aldrich Co., were used as received.

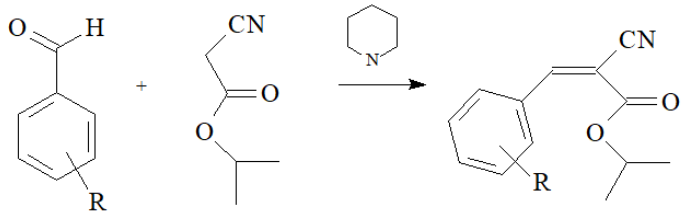
Instrumentation

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).

Results and Discussion

Synthesis of Monomers

The oxy ring-disubstituted isopropyl 3-phenylcyanoacrylates (IPCA) were synthesized by Knoevenagel condensation [21] of a ring-disubstituted benzaldehyde with isopropyl cyanoacetate, catalyzed by base, piperidine (Scheme 1).



Scheme 1: Synthesis of isopropyl 3-phenylcyanoacrylates, where R is 2, 6-dimethoxy, 3, 4-dimethoxy, 3,5-dimethoxy, 4-methoxy-2-methyl, 4-methoxy-3-methyl, 3-ethoxy-4-methoxy, 4-ethoxy-3-methoxy. 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.

Isopropyl 3-(2,6-dimethoxyphenyl)cyanoacrylate

Yield 82%; mp 118°C, ^{1}H-NMR δ 8.4 (s, 1H, CH=), 7.5-6.5 (m, 3H, Ph), 5.2 (m, 1H, OCH), 3.9 (d, 6H, CH_3O), 1.2 (d, 6H, $CH(CH_3)_2$); ^{13}C-NMR δ 159 (C=O), 148 (HC=), 133, 126, 121 (Ph), 116 (CN), 103 (C=), 71 (OCH), 70 (OCH_3), 22 ($CH(CH_3)_2$); FTIR (cm^{-1}): 3120-2790 (m, C-H), 2250 (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, 6.35; N, 4.99.

Isopropyl 3-(3,4-dimethoxyphenyl)cyanoacrylate

Yield 89%; mp 109°C, ^{1}H-NMR δ 8.1 (s, 1H, CH=), 7.8-6.8 (m, 3H, Ph), 5.2 (m, 1H, OCH), 3.9 (d, 6H, CH_3O), 1.4 (d, 6H, $CH(CH_3)_2$); ^{13}C-NMR δ 166 (C=O), 155 (HC=), 152, 149, 127, 98 (Ph), 116 (CN), 111 (C=), 71 (OCH), 56 (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, 63.46; H, 5.98; N, 4.85.

Isopropyl 3-(3,5-dimethoxyphenyl)cyanoacrylate

Yield 87%; mp 98°C, ^{1}H-NMR δ 8.1 (s, 1H, CH=), 7.3-6.5 (m, 3H, Ph), 5.2 (m, 1H, OCH), 3.8 (d, 6H, CH_3O), 1.4 (d, 6H, $CH(CH_3)_2$); ^{13}C-NMR δ 161 (C=O), 155 (HC=), 133, 108, 106 (Ph), 116 (CN), 104 (C=), 77 (OCH), 56, 55 (OCH_3), 22 ($CH(CH_3)_2$); FTIR (cm^{-1}): 3095-2807 (m, C-H), 2223 (m, CN), 1732 (s, C=O), 1609 (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, 62.68; H, 6.24; N, 5.20.

Isopropyl 3-(4-methoxy-2-methylphenyl)cyanoacrylate

Yield 92%; mp 123°C, ^{1}H-NMR δ 8.5 (s, 1H, CH=), 7.5 - 6.6 (m, 3H, Ph), 5.3 (m, 1H, OCH), 3.8 (s, 3H, OCH_3), 2.3 (s, 3H, CH_3), 1.3 (d, 6H, $CH(CH_3)_2$); ^{13}C-NMR δ 163 (C=O), 152 (HC=), 143, 131, 123, 112 (Ph), 116 (CN), 101 (C=), 71 (OCH), 55 (OCH_3), 22 ($CH(CH_3)_2$), 20 (CH_3); FTIR (cm^{-1}): 3052-2847 (m, C-H), 2218 (m, CN), 1717 (s, C=O), 1558 (C=C), 1279 (s, C-O-CH_3), 935, 844 (s, C-H out of plane). Anal. Calcd. for $C_{15}H_{17}NO_3$: C, 69.48; H, 6.61; N, 5.40; Found: C, 68.05; H, 6.61; N, 5.27.

Isopropyl 3-(4-methoxy-3-methylphenyl)cyanoacrylate

Yield 81%; 123°C, ^{1}H-NMR δ 8.1 (s, 1H, CH=), 7.5 - 6.6 (m, 3H, Ph), 5.3 (m, 1H, OCH), 3.9 (s, 3H, OCH_3), 2.2 (s, 3H, CH_3), 1.4 (d, 6H, $CH(CH_3)_2$); ^{13}C-NMR δ 161 (C=O), 154 (HC=), 132, 131, 110 (Ph), 116 (CN), 99 (C=), 70 (OCH), 56 (OCH_3), 21 ($CH(CH_3)_2$), 16 (CH_3); FTIR (cm^{-1}): 3061-2832 (m, C-H), 2220 (m, CN), 1705 (s, C=O), 1562 (C=C), 1283 (s, C-O-CH_3), 927, 833 (s, C-H out of plane). Anal. Calcd. for $C_{15}H_{17}NO_3$: C, 69.48; H, 6.61; N, 5.40; Found: C, 69.64; H, 6.81; N, 5.52.

Isopropyl 3-(3-ethoxy-4-methoxyphenyl)cyanoacrylate

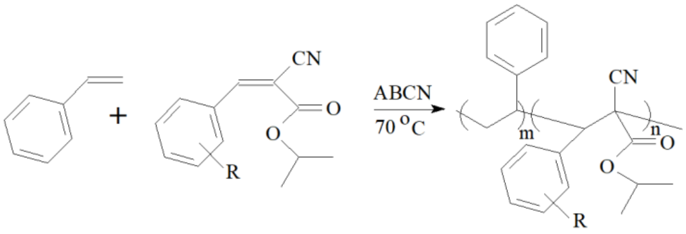
Yield 79%; mp 59°C, ^{1}H-NMR δ 8.2 (s, 1H, CH=), 7.4-6.6 (m, 3H, Ph), 5.1 (m, 1H, OCH), 4.2 (q, 2H, OCH_2), 3.8 (d, 3H, CH_3O), 1.3 (t, 3H, CH_3), 1.2 (d, 6H, $CH(CH_3)_2$); ^{13}C-NMR δ 163 (C=O), 153 (HC=), 153, 149, 126, 113, 111 (Ph), 116 (CN), 100 (C=), 68 (OCH), 64 (OCH_2), 56 (OCH_3), 22 ($CH(CH_3)_2$, 15 (CH_3); FTIR (cm^{-1}): 3021-2867 (m, C-H), 2228 (m, CN), 1712 (s, C=O), 1619 (C=C), 1254 (s, C-O-CH_3), 827 (s, C-H out of plane). Anal. Calcd. for $C_{16}H_{19}NO_4$: C, 66.42; H, 6.62; N, 4.84; Found: C, 65.78; H, 6.38; N, 4.29.

Isopropyl 3-(4-ethoxy-3-methoxyphenyl)cyanoacrylate

Yield 94%; mp 33°C, ^{1}H-NMR δ 8.2 (s, 1H, CH=), 7.6-6.3 (m, 3H, Ph), 5.2 (m, 1H, OCH), 4.1 (q, 2H, OCH_2), 3.7 (d, 3H, CH_3O), 1.3 (t, 3H, CH_3), 1.2 (d, 6H, $CH(CH_3)_2$); ^{13}C-NMR δ 164 (C=O), 151 (HC=), 153, 148, 125, 112, 111 (Ph), 116 (CN), 104 (C=), 69 (OCH), 65 (OCH_2), 55 (OCH_3), 21 ($CH(CH_3)_2$, 16 (CH_3); FTIR (cm^{-1}): 3067-2821 (m, C-H), 2232 (m, CN), 1730 (s, C=O), 1614 (C=C), 1243 (s, C-O-CH_3), 821 (s, C-H out of plane). Anal. Calcd. for $C_{16}H_{19}NO_4$: C, 66.42; H, 6.62; N, 4.84; Found: C, 65.66; H, 6.58; N, 4.86.

Copolymerization

To the best of our knowledge, there have been no reports on copolymerization of the oxy-ring-substituted IPCA compounds. Copolymers of the ST and the IPCA monomers were prepared 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. The composition of the copolymers was determined based on the nitrogen content.



Scheme 2: ST-IPCA copolymer synthesis, R = 2,6-dimethoxy, 3,4-dimethoxy, 3,5-dimethoxy, 4-methoxy-2-methyl, 4-methoxy-3-methyl, 3-ethoxy-4-methoxy, 4-ethoxy-3-methoxy. The ST-IPCA copolymers were characterized by nitrogen elemental analysis, FTIR, ^{1}H- and ^{13}C-NMR spectroscopies. Thermal behavior was studied by DSC and TGA.

Styrene - isopropyl 3-(2, 6-dimethoxyphenyl) cyanoacrylate copolymer

Yield 13%; ^{1}H-NMR δ 7.7 – 6.4 (8H, Ph), 5.4 - 5.1 (1H, OCH), 4.1 – 3.6 (1H, CHPh –ST), 3.8-3.6 (6H, CH_3O), 1.5 - 1.2 (2H, CH_2), 2.6 - 2.3 (1H, CH-ICPP), 1.4 - 1.1 (6H, $CH(CH_3)_2$); ^{13}C-NMR δ 173-167 (C=O), 152 - 101 (Ph), 117 - 114 (CN), 68 - 56 (OCH), 60 - 56 (OCH_3), 52 - 42 (CH, CH_2), 25 - 22 ($CH(CH_3)_2$); FTIR (cm^{-1}): 3062-2856 (m, C-H), 2242 (m, CN), 1738 (s, C=O), 1237 (s, C-O-C), 982 (s, C-H out of plane). Nitrogen content 2.71%.

Styrene - isopropyl 3-(3, 4-dimethoxyphenyl)cyanoacrylate copolymer

Yield 15%; ^{1}H-NMR δ 7.8 – 6.5 (8H, Ph), 5.5 - 5.1 (1H, OCH), 4.2 – 3.6 (1H, CHPh –ST), 3.8-3.4 (6H, CH_3O), 1.3 - 1.2 (2H, CH_2), 2.6 - 2.4 (1H, CH-ICPP), 1.4 - 1.2 (6H, $CH(CH_3)_2$); ^{13}C-NMR δ 172-167 (C=O), 152 - 103 (Ph), 116 - 114 (CN), 68 - 58 (OCH), 63 - 56 (OCH_3), 52 - 43 (CH, CH_2), 26 - 22 ($CH(CH_3)_2$); FTIR (cm^{-1}): 3029-2855 (m, C-H), 2243 (m, CN), 1743 (s, C=O), 1247 (s, C-O-C), 987 (s, C-H out of plane). Nitrogen content 2.36%.

Styrene - isopropyl 3-(3, 5-dimethoxyphenyl) cyanoacrylate copolymer

Yield 11%; ^{1}H-NMR δ 7.6 – 6.3 (8H, Ph), 5.4 - 5.2 (1H, OCH), 4.2 – 3.5 (1H, CHPh –ST), 3.9-3.5 (6H, CH_3O), 1.6 - 1.3 (2H, CH_2), 2.7 - 2.4 (1H, CH-ICPP), 1.5 - 1.2 (6H, $CH(CH_3)_2$); ^{13}C-NMR δ 174-166 (C=O), 152 - 100 (Ph), 117 - 115 (CN), 68 - 58 (OCH), 60 - 54 (OCH_3), 54 - 41 (CH, CH_2), 25 - 23 ($CH(CH_3)_2$); FTIR (cm^{-1}): 3077-2869 (m, C-H), 2243 (m, CN), 1740 (s, C=O), 1238 (s, C-O-C), 978 (s, C-H out of plane). Nitrogen content 2.2%.

Styrene - isopropyl 3-(4-methoxy-2-methylphenyl)cyanoacrylate copolymer

Yield 12%; ^{1}H-NMR δ 7.5 - 6.6 (Ph), 5.3-5.2 (OCH), 3.8-3.7 (OCH_3), 2.3-2.2 (CH_3), 1.3-1.1 ($CH(CH_3)_2$); ^{13}C-NMR δ 163-161 (C=O), 153-112 (Ph), 116-114 (CN), 71-69 (OCH), 55-52 (OCH_3), 22-20 ($CH(CH_3)_2$), 20-16 (CH_3); FTIR (cm^{-1}): 3045-2823 (m, C-H), 2243 (m, CN), 1727 (s, C=O), 1279 (s, C-O-CH_3), 932-842 (s, C-H out of plane). Nitrogen content 2.17%.

Styrene - isopropyl 3-(4-methoxy-3-methylphenyl)cyanoacrylate copolymer

Yield 11%; ^{1}H-NMR δ 7.7-6.3 (Ph), 5.3-5.1 (OCH), 3.9-3.7 (OCH_3), 2.4-2.1 (CH_3), 1.4-1.2 ($CH(CH_3)_2$); ^{13}C-NMR δ 163-160 (C=O), 136-110 (Ph), 116-112 (CN), 70-68 (OCH), 57-53 (OCH_3), 21-19 ($CH(CH_3)_2$), 16-13 (CH_3); FTIR (cm^{-1}): 3087-2821 (m, C-H), 2232 (m, CN), 1720 (s, C=O), 1283-1010 (s, C-O-CH_3), 930-823 (s, C-H out of plane). Nitrogen content 2.45%.

Styrene isopropyl 3-(3-ethoxy-4-methoxyphenyl)cyanoacrylate copolymer

Yield 14%; ^{1}H-NMR δ 7.8-6.3 (Ph), 5.2-4.9 (OCH), 4.2-3.0 (OCH_2), 3.8-3.6 (CH_3O), 1.3-1.0 (CH_3), 1.2-0.9 ($CH(CH_3)_2$); ^{13}C-NMR δ 165-159 (C=O), 155-109 (Ph), 116-114 (CN), 68-65 (OCH), 64-62 (OCH_2), 56-53 (OCH_3), 22-20 ($CH(CH_3)_2$, 15-11 (CH_3); FTIR (cm^{-1}): 3042-2878 (m, C-H), 2237 (m, CN), 1742-1732 (s, C=O), 1254-1107 (s, C-O-CH_3), 827-734 (s, C-H out of plane). Nitrogen content 0.68%.

Styrene isopropyl 3-(4-ethoxy-3-methoxyphenyl)cyanoacrylate copolymer

Yield 11%; ^{1}H-NMR δ 7.8-6.2 (Ph), 5.2-4.9 (OCH), 4.1-3.9 (OCH_2), 3.7-3.5 (CH_3O), 1.3-1.1 (CH_3), 1.2-0.9 ($CH(CH_3)_2$); ^{13}C-NMR δ 167-163 (C=O), 154-110 (Ph), 116-112 (CN), 69-67 (OCH), 65-63 (OCH_2), 55-50 (OCH_3), 21-18 ($CH(CH_3)_2$, 16-12 (CH_3); FTIR (cm^{-1}): 3071-2832 (m, C-H), 2238 (m, CN), 1732-1712 (s, C=O), 1249-1119 (s, C-O-CH_3), 834-785 (s, C-H out of plane). Nitrogen content 0.79%. Copolymerization (Scheme 1) of ST and the oxy ring-substituted IPCA resulted in formation of copolymers (Table 1) with weight-average molecular masses 56 to 65 kD. Since IPCA monomers do not homopolymerize, the most likely structure of the copolymers would be isolated IPCA 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 5.6 and 30.1 mol% of IPCA monomer is present in the copolymers prepared at ST/IPCA = 3 (mol). 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 [22]:

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

Table 1: *Molecular characteristics of P (ST-co-IPCA) copolymers.*

R	Nitrogen wt%	% mole ST	% mole IPCA	$1/r_1$	M_W kD
2,6-$(OCH_3)_2$	2.7	70	30	2.27	63.2
3,4-$(OCH_3)_2$	2.4	75	25	1.46	56.3
3,5-$(OCH_3)_2$	2.2	78	22	1.21	52.5
4-OCH_3-2-CH_3	2.2	79	21	1.11	62.8
4-OCH_3-3-CH_3	2.5	75	25	1.50	59.8
3-OC_2H_5-4-OCH_3	0.7	94	6	0.19	62.2
4-OC_2H_5-3-OCH_3	0.8	93	7	0.23	57.5

Table 2*: Thermal behavior of P (ST-co-IPCA) copolymers.*

R	T_g (ºC)	Onset of decom. (ºC)	10 wt% loss (ºC)	50 wt% loss (ºC)	Residue Wt. %)
2,6-$(OCH_3)_2$	105	222	287	339	1
3,4-$(OCH_3)_2$	124	202	289	353	4
3,5-$(OCH_3)_2$	117	210	290	328	4
4-OCH_3-2-CH_3	99	240	296	339	3
4-OCH_3-3-CH_3	96	210	278	344	4
3-OC_2H_5-4-OCH_3	89	172	215	362	2
4-OC_2H_5-3-OCH_3	105	180	250	374	2

M1 and m_2 are the mole fractions of ST and IPCA monomer units in the copolymer, respectively, $[M_1]$ and $[M_2]$ are the concentrations of ST and an IPCA 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 IPCA 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 IPCA 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 [22] allows estimation of the reactivity of a ST-ended polymer radical in reaction with IPCA monomer. The order of relative reactivity ($1/r_1$) for the IPCA monomers is 2, 6-dimethoxy (2.27) > 4-methoxy-3-methyl (1.50) > 3, 4-dimethoxy (1.46) > 3, 5-dimethoxy (1.21) > 4-methoxy-2-methyl (1.11) > 4-ethoxy-3-methoxy (0.23) > 3-ethoxy-4-methoxy (0.19). 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.

Thermal behavior

Thermal transitions of the ST-IPCA copolymers were analyzed by differential scanning calorimetry (DSC). 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 drier without "thermal memory". Table 2 shows glass transition values for the ST-IPCA copolymers prepared in this work with no correlation to the size and position of the IPCA ring substitution apparently due to non-uniform composition, monomer unit distribution, and/or molecular weight and MWD. 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 (1-4% 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 trisubstituted ethylenes, oxy ring-disubstituted isopropyl 3-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 in two steps, first in the 200-500°C range with residue (1-4% wt), which then decomposed in the 500-800ºC range.

References

1. Zaki MEA, Fathalla OA, Swelam SA, Aly HF. Synthesis of pyrido[2,1-c][1,2,4]triazine, 1,2,4-triazolo[4,3-a]pyridine and 2-(pyrazolyl)nicotinonitrile and their effect on Biomphalaria alexandrina snail enzymes. Acta Poloniae Pharmaceutica. 2004; 61: 55-64.
2. Matsuoka M, Takao M, Kitao T, Fujiwara T, Nakatsu K. Molecular Crystals and Liquid Crystals. 1990; 182: 71.
3. Burate PA, Javle BR, Desale PH, Kinage AK. Amino acid amide based ionic liquid as an efficient organo-catalyst for solvent-free Knoevenagel condensation at room temperature. Catalysis Lett. 2019; 149: 2368-2375.
4. Medyouni R, Hamdi N, Ben Said R, Ayed AS, Zagrouba F. Clean Procedure and DFT tudy for the synthesis of 2-amino-3-ethoxycarbonyl-4-(aryl)-4H-pyrano-[3,2-c]-chromene-5-ones derivatives: A novel class of potential Antimicrobial and antioxidant agents. J Chem. 2013; 1-9.
5. Hassan AY, Sarg MT, Hussein EM. Design synthesis and anticancer activity of novel benzothiazole analogues. J Heter Chem. 2019; 56: 1437-1457.
6. Moacyr JB, Melo R, Wanessa LB, Sena D, Ricardo O, Moura D, et al. Synthesis and anticancer evaluation of thiazacridine derivatives reveals new selective Molecules to hematopoietic neoplastic cells. Combinatorial Chemistry & High Throughput Screening. 2017; 20: 713-718.
7. Meng D, Qiao Y, Wang X, Wen W, Zhao S. DABCO-catalyzed Knoevenagel condensation of aldehydes with ethyl cyanoacetate using hydroxy ionic liquid as a promoter. RSC Advances. 2018; 8: 30180-30185.
8. Brica S, Freimane L, Kulikovska L, Zicmanis A. N, N'-dialkylimidazolium dimethyl phosphates - promising media and catalysts at the same time for condensation reactions. Chem Scie Int J. 2017; 19: 1-9.
9. Bhuiyan M, Mosharef H, Rahman KM, Alam MA, Mahmud M. Microwave assisted Knoevenagel condensation: synthesis and antimicrobial activities of some α-cyanoacrylates. Pak J Scie Ind Res Seri A: Phy Sci. 2013; 56: 131-137.
10. Nowicka A, Liszkiewicz H, Nawrocka WP, Wietrzyk J, Kempinska K, Drys A. Synthesis and antiproliferative activity in vitro of new 2-aminobenzimidazole derivatives. Reaction of 2-arylideneaminobenzimidazole with selected nitriles containing active methylene group. Cen Eur J Chem. 2014; 12: 1047-1055.
11. Popp FD. Synthesis of 3-hydroxypyridines. I. Condensation of aromatic aldehydes with ethyl cyanoacetate. J Org Chem. 1960; 25: 646-647.
12. Kharas GB, Christensen JL, Cichanski DJ, Goldman KE, Gordon CL, Knowles LM, et al. Novel copolymers of styrene and dialkoxy ring-substituted Methyl 2-cyano-3-phenyl-2-propenoates. J Macromol Sci. 2005; 7: 989-994.
13. Kharas GB, Shahbein A, Fabbri J, Fanter CE, Garcia DR, Ibarra MG, et al. Novel copolymers of styrene. 14. Some ring-disubstituted methyl 2-cyano-3-phenyl-2-propenoates. J Macromol Sci. 2014; 51: 394-398.
14. Kharas GB, Molina ES, Pierce EE, Cocjin SAB, Cruz C, Fair KM, et al. Novel copolymers of styrene. 4. Alkyl ring-substituted ethyl 2-cyano-3-phenyl-2-propenoates. J Macromol Sci. 2013; 2: 144-148.
15. Kharas GB, Delgado AA, Anderson NE, Bajor A, Colbert AC, Coleman A, et al. Novel copolymers of styrene. 6. Alkoxy ring-substituted ethyl 2-cyano-3-phenyl-2-propenoates. J Macromol Sci. 2013; 50: 276-280.
16. Kharas GB, Barros WMB, Affaneh A, Alyahya LA, Ansari AS, Asztalos MJ, et al. Novel copolymers of styrene. 5. Alkyl and alkoxy ring-disubstituted propyl 2-cyano-3-phenyl-2-propenoates. J Macromol Sci. 2016; 53: 664-668.
17. Kharas GB, Feng H, Arendt LA, Belton SE, Edwards MQ, Franz EK, et al. Novel copolymers of styrene. 5. Methyl and methoxy ring-disubstituted butyl 2- cyano-3-phenyl-2-propenoates. J Macromol Sci. 2015; 52: 976-981.
18. Pride RL, Anderson CJ, Aelion MS, Barry OS, Berry M, Blankemeyer E, et al. Synthesis and styrene copolymerization of novel trisubstituted ethylenes: 1. Alkyl ring-Substituted isopropyl 2-cyano-3-phenyl-2-propenoates. J Macromol Sci Part A: Pure Appl Chem. 2018; 55: 355-361.
19. Shinde N, Jody JK, Mosher EK, Kaur N, Oriol AAR, Perez DM, et al. Synthesis and styrene copolymerization of novel trisubstituted ethylenes: 3. Alkoxy ring-substituted isopropyl 2-cyano-3-phenyl-2-propenoates. Designed Monomers and Polymers. 2018; 21: 163-171.
20. Zepeda JL, Coston RL, Flores MA, Graham A, Guzzo F, Manigault NS, et al. Synthesis and styrene copolymerization of novel trisubstituted ethylenes: Chlorophenoxy ring-substituted isopropyl 2-cyano-3-phenyl-2-propenoates. Int J Chem Stu. 2019; 3: 53-57.
21. Smith MB, March J. Addition to carbon-hetero multiple bonds, In March's Advanced Organic Chemistry J Wiley & Sons: New York. 2001; 16: 1225.
22. Odian G. Principles of Polymerization, 4th Ed., Wiley-Interscience: New York. 2004.