Synthesis and styrene copolymerization of novel alkoxy ring-substituted isobutyl phenylcyanoacrylates

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Abstract

Novel alkoxy ring-substituted isobutyl phenylcyanoacrylates, RPhCH=C(CN)$CO_2CH_2CH(CH_3)_2$ (where R is 2-methoxy, 3-methoxy, 4-methoxy, 2-ethoxy, 3-ethoxy, 4-ethoxy, 4-propoxy, 4-butoxy, 4-hexyloxy) were prepared and copolymerized with styrene. The acrylates were synthesized by the piperidine catalyzed Knoevenagel condensation of ring-substituted benzaldehydes and isobutyl cyanoacetate and characterized by CHN elemental analysis, IR, ^{1}H- and ^{13}C-NMR. All the acrylates 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, ^{1}H and ^{13}C-NMR. Thermal properties of the copolymers are characterized by DSC and TGA. Decomposition of the copolymers in nitrogen occurred in two steps, first in the 200-500ºC range with residue (1.8-3.3% wt.), which then decomposed in the 500-800ºC range.

1. Introduction

Alkoxy ring–functionalized phenylcyanoacrylates (PCA) are reported in a variety of applications [4-11]. Thus, 2-methoxy ring-substituted methyl PCA was used in pyrrolizinone synthesis [1], as well as in molecular design for linear and nonlinear optical response [2, 3]. 3-Methoxy ring-substituted methyl PCA was employed in diastereoselective syntheses of polysubstituted cyclohexanes and cyclopentenes [4] and in enhancement of the hyperpolarizability of styrene [5]. Propyl PCA with 4-methoxy ring-substitution was used in synthesis of cyanoacrylates [6] and in technology related to antenna dyes [7]. 4-Propoxy ring-substituted propyl PCA was synthesized in MgO-based catalyzed Knoevenagel reaction [8]. 4-Butoxy phenyl-substituted ethyl PCA was an intermediate in synthesis of 6-amino-4-(4-butoxyphenyl)-3,5-dicyanopyridine-2(1H)-thione [9], as well as in synthesis of (arylmethylene)cyanothioacetamides [10]. 4-Hexyloxy ring-substituted ethyl PCA was mentioned in preparation of prostaglandin E synthase inhibitors [11].

Earlier we have reported synthesis and styrene copolymerization a number of alkoxy ring-substituted PCAs, such esters as methyl [12], ethyl [13], propyl [14], isopropyl [15], butyl [16], and tert-butyl [17].

In continuation of our investigation of novel PCA compounds we have prepared isobutyl phenylcyanoacrylates, $RPhCH=C(CN)CO_2CH_2CH(CH_3)_2$, where R is 2-methoxy, 3-methoxy, 4-methoxy, 2-ethoxy, 3-ethoxy, 4-ethoxy, 4-propoxy, 4-butoxy, 4-hexyloxy, 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 phenylcyanoacrylates, nor their copolymerization with styrene [18].

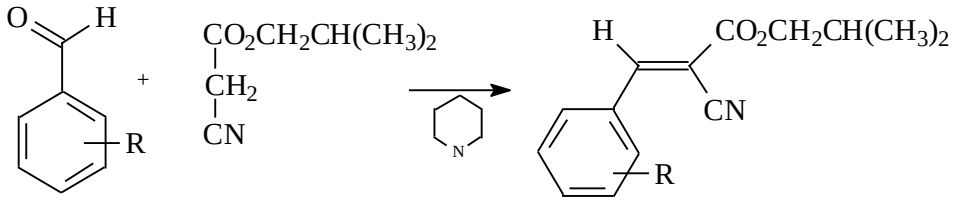
2. Experimental

2-Methoxy, 3-methoxy, 4-methoxy, 2-ethoxy, 3-ethoxy, 4-ethoxy, 4-propoxy, 4-butoxy, 4-hexyloxybenzaldehydes, isobutyl cyanoacetate, styrene, 1,1'-azobiscyclohexanecarbonitrile, (ABCN), and toluene supplied from Sigma-Aldrich Co., were used as received. Instrumentation is described in [19].

3. Synthesis and characterization of isobutyl phenylcyanoacrylates

The alkoxy ring-substituted isobutyl phenylcyanoacrylates (IPCA) were synthesized by Knoevenagel condensation [20] of a ring-substituted benzaldehyde with isobutyl cyanoacetate, catalyzed by base, piperidine (Scheme 1). Equimolar amounts of the benzaldehyde and isobutyl cyanoacetate were mixed in a 20 mL vial. Piperidine (0.1 mL)

was added with stirring. The IPCA was isolated by filtration and purified by crystallization from 2-propanol.



Scheme 1. Synthesis of isobutyl phenylcyanoacrylates, where R is 2-methoxy, 3-methoxy, 4-methoxy, 2-ethoxy, 3-ethoxy, 4-ethoxy, 4-propoxy, 4-butoxy, 4-hexyloxy.

3.1. ***Isobutyl 2-methoxyphenylcyanoacrylate***

Yield: 73.6%; mp 74.5°C; ^{1}H NMR: δ 8.8 (s, 1H, CH=), 8.3-6.9 (m, 4H, Ph), 4.2 (d, 2H, CH_2), 3.9 (s, 3H, CH_3O), 2.1 (m, 1H, CH), 1.0 (d, 6H, CH_3); ^{13}C NMR: δ 163 (C=O), 155 (HC=), 134, 131, 130, 122 (Ph), 115 (CN), 111 (C=), 73 (CH_2), 63 (OCH_3), 28 (CH), 20 (CH_3); FTIR: (cm^{-1}) 3004-2822 (m, C-H), 2218 (m, CN), 1724 (s, C=O), 1587 (s, C=C), 1288 (s, C-O-CH_3), 754, 752 (s, C-H out of plane). Anal. calcd. for $C_{15}H_{16}NO_3$: C, 69.75; H, 6.24; N, 5.42; Found: C, 68.76; H, 6.76; N, 5.63.

3.2. ***Isobutyl 3-methoxyphenylcyanoacrylate***

Yield 84%; ^{1}H NMR δ 8.2 (s, 1H, CH=), 7.6-7.0 (m, 4H, Ph), 4.1 (d, 2H, CH_2), 3.9 (s, 3H, CH_3O), 2.1 (m, 1H, CH), 1.0 (d, 6H, CH_3); ^{13}C NMR δ 163 (C=O), 155 (HC=), 150, 138, 133, 128, 124, 120, 119 (Ph), 115 (CN), 103 (C=), 72, 69 (CH_2), 56 (OCH_3), 31, 27 (CH), 19 (CH_3); IR (cm^{-1}): 2143 (m, CN), 1740 (s, C=O), 1670, 1474 (C=C), 1223 (s, C-

O-CH_3), 882, 788 (s, C-H out of plane). Anal. Calcd. for $C_{15}H_{16}NO_3$: C, 69.75; H, 6.24; N, 5.42; Found: C, 67.44; H, 6.27; N, 5.66.

3.3. ***Isobutyl 4-methoxyphenylcyanoacrylates***

Yield 83%; mp 79.4°C; ^{1}H NMR δ8.2 (s, 1H, CH=), 8.0-7.0 (m, 4H, Ph), 4.1 (d, 2H, CH_2), 3.9 (s, 3H, CH_3O), 2.1 (m, 1H, CH), 1.0 (d, 6H, CH_3); ^{13}C NMR δ 164 (C=O), 155 (HC=), 150, 138, 134, 124, 119 (Ph), 116, 115 (CN), 99 (C=), 73 (CH_2), 56 (OCH_3), 28 (CH), 19 (CH_3); IR (cm^{-1}): 2961, 2937 (m, C-H), 2221 (m, CN), 1713 (s, C=O), 1595 (C=C), 1229 (s, C-O-CH_3), 837 (s, C-H out of plane). Anal. Calcd. for $C_{15}H_{16}NO_3$: C, 69.75; H, 6.24; N, 5.42; Found: C, 69.11; H, 6.94; N, 5.50.

3.4. ***Isobutyl 2-ethoxyphenylcyanoacrylate***

Yield 81%; mp 78.3°C; ^{1}H NMR δ8.8 (s, 1H, CH=), 8.3-6.8 (m, 4H, Ph), 4.1 (m, 2H, $CH_3C\underline{H}_2O$ & 2H, OCH_2), 2.1 (m, 1H, CH), 1.5 (t, 3H, CH_3), 1.0 (d, 6H, $(CH_3)_2$); ^{13}C NMR δ 163 (C=O), 159 (HC=), 135, 129, 121, 112 (Ph), 116 (CN), 102 (C=), 73 (CH_2), 65 ($CH_3\underline{C}H_2O$), 28 (CH), 19 $(CH_3)_2$, 14 ($\underline{C}H_3CH_2O$); IR (cm^{-1}): 2918 (m, C-H), 2222 (m, CN), 1707 (s, C=O), 1593 (s, C=C), 1248 (s, C-O-CH_3), 764 (s, C-H out of plane). Anal. Calcd. for $C_{16}H_{19}NO_3$: C, 70.31; H, 7.01; N, 5.12; Found: C, 70.23; H, 7.10; N, 5.29.

3.5. ***Isobutyl 3-ethoxyphenylcyanoacrylates***

Yield 94%; mp 67.7°C; ^{1}H NMR δ8.2 (s, 1H, CH=), 7.6-7.0 (m, 4H, Ph), 4.1 (m, 2H, $CH_3C\underline{H}_2O$ & 2H, OCH_2), 2.1 (m, 1H, CH), 1.4 (t, 3H, CH_3), 1.0 (d, 6H, $(CH_3)_2$); ^{13}C NMR δ163 (C=O), 160 (HC=), 155, 132, 130, 124, 120 (Ph), 115 (CN), 103 (C=), 73 (CH_2), 64 ($CH_3\underline{C}H_2O$), 28 (CH), 19 $(CH_3)_2$, 15 ($\underline{C}H_3CH_2O$); IR (cm^{-1}): 2928 (m, C-H),

2221 (m, CN), 1728 (s, C=O), 1609 (s, C=C), 1277 (s, C-O-CH_3), 768, 762 (s, C-H out of plane). Anal. Calcd. for $C_{16}H_{19}NO_3$: C, 70.31; H, 7.01; N, 5.12; Found: C, 68.96; H, 7.46; N, 5.35.

3.6. ***Isobutyl 4-ethoxyphenylcyanoacrylate***

Yield 76%; mp 79.3°C; ^{1}H NMR δ8.1 (s, 1H, CH=), 7.9-6.9 (m, 4H, Ph), 4.1 (m, 2H, $CH_3C\underline{H}_2O$ & 2H, OCH_2), 2.1 (m, 1H, CH), 1.4 (t, 3H, CH_3), 1.0 (d, 6H, $(CH_3)_2$); ^{13}C NMR δ163 (C=O), 155 (HC=), 133, 124 (Ph), 116 (CN), 99 (C=), 73 (CH_2), 64 ($CH_3\underline{C}H_2O$), 28 (CH), 19 $(CH_3)_2$, 15 ($\underline{C}H_3CH_2O$); IR (cm^{-1}): 2928-2878 (m, C-H), 2222 (m, CN), 1717 (s, C=O), 1560 (s, C=C), 1271 (s, C-O-CH_3), 841 (s, C-H out of plane). Anal. Calcd. for $C_{16}H_{19}NO_3$: C, 70.31; H, 7.01; N, 5.12; Found: C, 69.14; H, 7.11; N, 5.20.

3.7. ***Isobutyl 4-propoxyphenylcyanoacrylate***

Yield 79%; mp 75.9°C; ^{1}H NMR δ8.2 (s, 1H, CH=), 8.1-6.9 (m, 4H, Ph), 4.1 (t, 2H, $CH_3CH_2C\underline{H}_2O$), 3.9 (d, 2H, CH_2O), 2.1 (m, 1H, CH), 1.8 (m, 2H, $CH_3C\underline{H}_2CH_2O$), 1.0 (m, 6H, $CH(C\underline{H}_3)_2$ & 3H, $C\underline{H}_3CH_2CH_2$); ^{13}C NMR δ 163 (C=O), 155 (HC=), 134, 124 (Ph), 115 (CN), 99 (C=), 73 ($CH_3CH_2\underline{C}H_2O$), 70 ($OCH_2$), 28 (CH) 23 ($CH_3\underline{C}H_2CH_2O$), 19 $(CH_3)_2$, 10 (CH_3); IR (cm^{-1}): 3035-2805 (m, C-H), 2217 (m, CN), 1717 (s, C=O), 1507 (C=C), 1271 (s, C-O-CH_3), 841 (s, C-H out of plane). Anal. Calcd. for $C_{17}H_{21}NO_3$: C, 71.06; H, 7.37; N, 4.87; Found: C, 71.08; H, 7.45; N, 4.99.

3.8. ***Isobutyl 4-butoxyphenylcyanoacrylates***

Yield 73; mp 56.9°C; ^{1}H NMR δ8.2 (s, 1H, CH=), 7.3, 7.0 (m, 4H, Ph), 4.1 (m, 2H, OCH_2 & 2H, $C_3H_7C\underline{H}_2O$), 2.2 (d, 1H, CH), 1.8 (m, 2H, $C_2H_5C\underline{H}_2CH_2O$), 1.5 (m, 2H, $CH_3C\underline{H}_2CH_2CH_2O$), 1.0 (d, 6H, $(CH_3)_2$ & (t, 3H, $C\underline{H}_3CH_2CH_2CH_2O$); ^{13}C NMR δ 164 (C=O), 155 (HC=), 134, 124 (Ph), 116 (CN), 99 (C=), 73 (CH), 68 ($C_3H_7\underline{C}H_2O$), 31 ($C_2H_5\underline{C}H_2CH_2O$), 19 $(CH_3)_2$, 19 ($CH_3\underline{C}H_2CH_2CH_2O$), 14 ($C\underline{H}_3CH_2CH_2CH_2O$); IR ($cm^{-1}$): 3034-2818 (m, C-H), 2222 (m, CN), 1728 (s, C=O), 1585 (C=C), 1256 (s, C-O-CH_3), 837 (s, C-H out of plane). Anal. Calcd. for $C_{18}H_{23}NO_3$: C, 71.73; H, 7.69; N, 4.65; Found: C, 70.59; H, 7.58; N, 4.75.

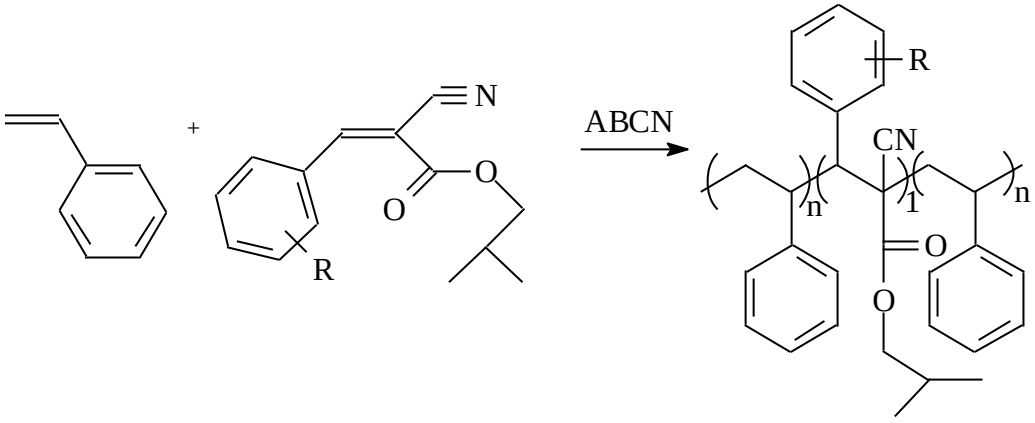
3.9. ***Isobutyl 4-hexyloxyphenylcyanoacrylate***

Yield 78.0%; mp 49.2°C; ^{1}H NMR δ8.2 (s, 1H, CH=), 8.0, 7.0 (m, 4H, Ph), 4.1 (m, 4H, $C_5H_{11}CH_2$ & CH_2O), 2.1 (m, 1H, CH), 1.8 (m, 2H, $C\underline{H}_2CH_2O$), 1.6 (m, 2H, $C\underline{H}_2CH_2CH_2O$), 1.3 (m, 4H, $C\underline{H}_2CH_2CH_2CH_2O$ & $C\underline{H}_2CH_2CH_2CH_2CH_2O$), 1.0 (d, 3H, CH_3 & t, 6H, $(CH_3)_2$); ^{13}C NMR δ 164 (C=O), 155 (HC=), 133, 124 (Ph), 115 (CN), 111 (C=), 73 ($C_5H_{11}CH_2O$), 69 ($\underline{C}H_2O$), 31-14 ($\underline{C}H_2CH_2CH_2CH_2O$ & $\underline{C}H_2CH_2O$ & $C\underline{H}_2CH_2CH_2O$ & ($CH_3\underline{C}H_2$) & $CH\underline{C}H_3$ & $\underline{C}H_3CH_2$ & $(CH_3)_3$; IR (cm^{-1}): 3063-2808 (m, C-H), 2222 (m, CN), 1724 (s, C=O), 1589 (C=C), 1266 (s, C-O-CH_3), 924 (s, C-H out of plane). Anal. Calcd. for $C_{20}H_{27}NO_3$: C, 72.92; H, 8.26; N, 4.25; Found: C, 71.93; H, 8.42; N, 4.30.

4. Copolymerization

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 composition of the copolymers was determined based on the nitrogen content. The copolymers' yield was kept low to minimize copolymer compositional drift at given conversion.



Scheme 2. ST-IPCA copolymer synthesis, where R is 2-methoxy, 3-methoxy, 4-methoxy, 2-ethoxy, 3-ethoxy, 4-ethoxy, 4-propoxy, 4-butoxy, 4-hexyloxy

Copolymerization (Scheme 2) of alkoxy ring-substituted IPCA with ST resulted in formation of copolymers (Table 1). 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.

The ST- IPCA copolymers are amorphous and show no crystalline DSC endotherm. Results of thermal analysis of ST- IPCA copolymers are presented in Table 2. 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 200-500ºC range with residue (1.8-3.3% wt.), which then decomposed in the 500-800ºC range.

Table 1. Copolymerization of isobutyl phenylcyanoacrylates with styrene.

R	Conversion %	Nitrogen wt%	% mole ST	% mole IPCA	M_W kD
2-CH_3O	12.1	2.06	80.2	19.8	57.2
3-CH_3O	14.2	2.74	70.9	29.1	55.1
4-CH_3O	12.8	2.09	79.8	20.2	57.2
2-C_2H_5O	12.7	1.98	80.7	19.3	55.4
3-C_2H_5O	11.2	2.20	77.7	22.3	58.5
4-C_2H_5O	13.4	2.06	79.6	20.4	55.3
4-C_3H_7O	15.1	2.03	79.5	20.5	52.5
4-C_4H_9O	14.1	1.95	80.0	20.0	52.5
4-$C_6H_{13}O$	12.7	1.86	80.3	19.7	54.3

Table 2. DSC and TGA data for isobutyl P(ST-*co*-IPCA) copolymers.

R	T_g ºC	Onset of decomp., ºC	10% wt loss, ºC	50% wt loss, ºC	Residue at 500 ºC, wt%
2-CH_3O	136	233	307	337	1.8
3-CH_3O	128	221	317	345	3.2
4-CH_3O	137	243	300	334	3.3
2-C_2H_5O	129	252	305	339	2.1
3-C_2H_5O	128	243	303	335	2.5
4-C_2H_5O	128	251	304	338	3.0
4-C_3H_7O	135	243	308	342	2.7
4-C_4H_9O	117	252	302	337	3.0
4-$C_6H_{13}O$	107	233	303	339	3.3

4. Conclusions

Novel alkoxy ring-substituted isobutyl cyanophenylacrylates were prepared and copolymerized with styrene. The compositions of novel 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 200-500°C range with a residue, which then decomposed in the 500-800ºC range.

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