Novel styrene copolymers with some ethyl phenylcyanoacrylates

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Abstract

Novel styrene copolymers with ring-substituted ethyl phenylcyanoacrylates, $RPhCH=C(CN)CO_2C_2H_5$ (where R is 2-ethyl, 2-ethoxy, 4-benzyloxy, 2,3-dimethyl) were prepared in solution with radical initiation (ABCN) at 70°C. The compositions of the copolymers were calculated from nitrogen analysis, being between 18.3 and 42.3 mol% of the acrylate monomer units.

1. Introduction

Ethyl phenylcyanoacrylates were noted in variety of reports [1-7]. Thus, liquid compositions containing cyanoacrylates were investigated for endovascular embolization in treating aneurysm, artery and venous malformation [1] and in synthesis of heteroaryl compounds as sodium channel blockers [2]. Cadmium and mercury complexes with ethyl 3-phenyl-2-cyanoacrylate were studied [3]. Synthetic applications include use of zirconium potassium phosphate and methyl phosphonatesas heterogeneous catalysts in synthesis of the acrylates

via Knoevenagel condensation under solvent free conditions [4], direct access to multifunctionalized norcamphor scaffolds by asymmetric organocatalytic Diels-Alder reactions [5], strongly basic polymer-supported catalyst with guanidine groups [6], silica grafted polyethylenimine as heterogeneous catalyst for condensation reactions [7]. Of interest is also study of neuroleptic activity and dopamine-uptake inhibition in 1-piperazino-3-phenylindans [8].

In regard to polymerization reactivity, our studies showed very low reactivity in radical homopolymerization of ethyl cyanophenylacrylates [9, 10] similarly to all trisubstituted monomers containing double bond substituents larger than fluorine apparently due to polar and steric reasons [11]. Thus, in continuation of our investigation of phenylcyanoacrylates, we have prepared ring-substituted ethyl phenylcyanoacrylates (EPCA), $RPhCH=C(CN)CO_2C_2H_5$, where R is 2-ethyl, 2-ethoxy, 4-benzyloxy, 2,3-dimethyl, and explored the feasibility of their copolymerization with styrene. To the best of our knowledge, except 4-benzyloxy [12] and 2,3-dimethyl [13] ring substituted ethyl cyanoacrylates, there have been no reports on either synthesis of these compounds, nor their copolymerization with styrene [14].

2. Experimental

2.1. Materials

2-Ethyl, 2-ethoxy, 4-benzyloxy, 2,3-dimethylbenzaldehydes, ethyl cyanoacetate (≥98.0%), piperidine (99%), styrene (≥99%), 1,1'-azobis(cyclohexanecarbonitrile) (98%), (ABCN), and toluene (98%) supplied from Sigma-Aldrich Co., were used as received.

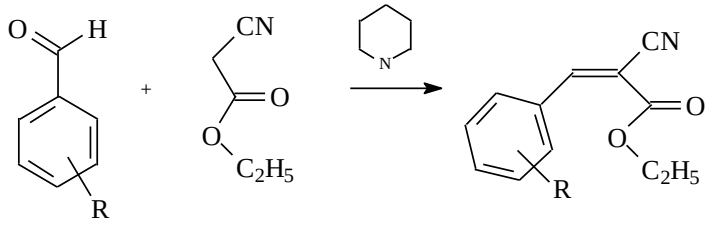
2.2. Instrumentation

Infrared spectra of the EPCA compounds and polymers (NaCl plates) were determined with an ABB FTLA 2000 FT-IR spectrometer. The melting points of the EPCA compounds were measured with TA (Thermal Analysis, Inc.) Model Q10 differential scanning calorimeter (DSC). ^{1}H and ^{13}C NMR spectra were obtained on 10-25% (w/v) EPCA solutions in $CDCl_3$ at ambient temperature using Avance 300 MHz spectrometer. CHN-elemental analyses of EPCA compounds and nitrogen analysis of the copolymers were performed by Midwest Microlab, LLC (IN).

3. Results and discussion

3.1. Synthesis and characterization of ethyl phenylcyanoacrylates

All ethyl phenylcyanoacrylates (EPCA) compounds were synthesized by Knoevenagel condensation [15] of appropriate benzaldehydes with ethyl cyanoacetate, catalyzed by base, piperidine (Scheme 1).



Scheme 1. Synthesis of ethyl phenylcyanoacrylates where R is 2-ethyl, 2-ethoxy, 4-benzyloxy, 2,3-dimethyl.

The preparation procedure was essentially the same for all the monomers. In a typical synthesis, equimolar amounts of ethyl cyanoacetate and an appropriate 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. The compounds were characterized by IR, ^{1}H and ^{13}C NMR spectroscopies. No stereochemical analysis of the novel ring-monosubstituted EPCA was performed since no stereoisomers (*E* or/and *Z*) of known configuration were available.

3.1.1. Ethyl 2-ethylphenylcyanoacrylate

Yield 83%; ^{1}H NMR δ 8.6 (s, 1H, CH=), 7.9-7.1 (m, 4H, Ph), 4.3 (t, 2H, CO_2CH_2), 2.9 (q, 2H, $PhCH_2$), 1.3 (t, 3H, $OCH_2C\underline{H}_3$, 1.2 (t, 3H, $PhCH_2C\underline{H}_3$); ^{13}C NMR δ 163 (C=O), 153 (HC=), 140-126 (Ph), 116 (CN), 105 (C=), 61 (OCH_2), 27 ($PhCH_2$), 15 ($PhCH_2\underline{C}H_3$), 14 ($OCH_2\underline{C}H_3$); IR (cm^{-1}): 2938 (m, C-H), 2226 (m, CN), 1749 (s, C=O), 1596 (s, C=C), 1266 (s, C-O-CH_3), 763 (s, C-H out of plane). Anal. Calcd. for $C_{14}H_{15}NO_2$: C, 73.34; H, 6.59; N, 6.11; Found: C, 72.06; H, 6.41; N, 6.52.

3.1.2. *Ethyl 2-ethoxyphenylcyanoacrylate*.

Yield 72%; mp 82.0°C; ^{1}H NMR δ 8.2 (s, 1H, CH=), 7.7-6.8 (m, 4H, Ph), 4.3 (t, 2H, CO_2CH_2), 4.1 (q, 2H, $PhOCH_2$), 1.3 (t, 3H, $PhOCH_2C\underline{H}_3$), 1.3 (t, 3H, $OCH_2C\underline{H}_3$); ^{13}C NMR δ 163 (C=O), 149 (HC=), 158, 134, 129, 122, 121, 112 (Ph), 116, (CN), 103 (C=), 64 ($PhOCH_2$), 61 (OCH_2), 15 ($PhOCH_2\underline{C}H_3$), 14 ($OCH_2\underline{C}H_3$); IR (cm^{-1}): 2986 (m, C-H), 2222 (m, CN), 1709 (s, C=O), 1594 (C=C), 1268 (s, C-O-CH_3), 941 (s, C-H out of plane). Anal. Calcd. for $C_{14}H_{15}NO_3$: C, 68.56; H, 6.16; N, 5.71; Found: C, 68.60; H, 6.23; N, 5.87.

3.1.3. ***Ethyl 4-benzyloxyphenylcyanoacrylate***.

Yield 81%; mp 95.9°C; ^{1}H NMR δ8.2 (s, 1H, CH=), 7.5-6.8 (m, 4H, Ph), 5.1 (s, $PhOCH_2$), 4.3 (t, 2H, CO_2CH_2), 1.3 (t, 3H, $OCH_2C\underline{H}_3$); ^{13}C NMR δ163 (C=O), 153 (HC=), 162-115 (Ph), 116, (CN), 100 (C=), 70 (OCH_2Ph), 61 ($OC\underline{H}_2CH_3$), 14 ($OCH_2\underline{C}H_3$); IR (cm^{-1}): 2928 (m, C-H), 2219 (m, CN), 1717 (s, C=O), 1585 (C=C), 1267 (s, C-O-CH_3), 893 (s, C-H out of plane). Anal. Calcd. for $C_{19}H_{17}NO_3$: C, 74.25; H, 5.58; N, 4.56; Found: C, 73.95; H, 5.55; N, 4.52.

3.1.4. ***Ethyl 2,3-dimethylphenylcyanoacrylate***.

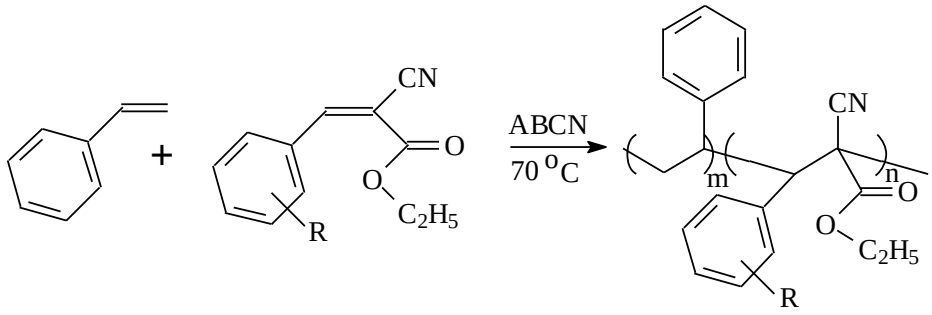
Yield 78%; mp 65.0°C; ^{1}H NMR δ8.6 (s, 1H, CH=), 7.9-7.0 (m, 3H, Ph), 4.3 (q, 2H, CO_2CH_2), 2.3 (s, 6H, $PhCH_3$), 1.3 (t, 3H, $OCH_2C\underline{H}_3$); ^{13}C NMR δ163 (C=O), 153 (HC=), 140-126 (Ph), 116 (CN), 105 (C=), 68 (OCH_2), 20, 16 ($PhCH_3$), 14 ($OCH_2\underline{C}H_3$); IR (cm^{-1}): 2957 (m, C-H), 2218 (m, CN), 1722 (s, C=O), 1605 (C=C), 1223 (s, C-O-CH_3), 941 (s, C-H out of plane). Anal. Calcd. for $C_{14}H_{15}NO_2$: C, 73.34; H, 6.59; N, 6.11; Found: C, 72.95; H, 6.46; N, 5.98.

3.2. ***Homopolymerization***

An attempted homopolymerization of the EPCA compounds in the presence of ABCN did not produce any polymer as indicated by the lack of a precipitate in methanol. The inability of the monomers to polymerize is associated with steric difficulties encountered in homopolymerization of 1,1- and 1,2-disubstituted ethylenes [11]. Homopolymerization of ST under conditions identical to those in copolymerization experiments yielded 18.3% of polystyrene, when polymerized for 30 min.

3.3. *Synthesis and characterization of styrene – EPCA copolymers*

Copolymers of the ST and the EPCA compounds, P(ST-co-EPCA) were prepared in 25-mL glass screw cap vials at ST/ EPCA = 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 (cyano group in EPCA). The novel synthesized EPCA compounds copolymerized readily with ST under free-radical conditions (Scheme 2) forming white flaky precipitates when their solutions were poured into methanol. The conversion of the copolymers was kept between 10 and 20% to minimize compositional drift (Table 1).



Scheme 2. Copolymerization of ST and the ethyl phenylcyanoacrylates, where R is 2-ethyl, 2-ethoxy, 4-benzyloxy, 2,3-dimethyl.

Table 1. Copolymerization of styrene and ethyl phenylcyanoacrylates.

R	Yield[a] (wt%)	N (wt%)	ST in copol. (mol%)	EPCA in copol. (mol%)
2-Ethyl	13.4	2.02	81.7	18.3
2-Ethoxy	12.7	3.62	57.7	42.3
4-Benzyloxy	13.6	2.52	70.5	29.5
2,3-Dimethyl	11.5	2.86	71.5	28.5

Nitrogen elemental analysis showed that between 18.3 and 42.3 mol% of EPCA is present in the copolymers prepared at ST/ EPCA = 3 (mol), which is indicative of relatively high reactivity of the EPCA monomers towards ST radical which is typical of ring-substituted EPCA [18-26]. Since EPCA monomers do not homopolymerize, the most likely structure of the copolymers would be isolated EPCA 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.

4 Conclusions

Novel trisubstituted ethylenes, ethyl phenylcyanoacrylates, $RPhCH=C(CN)CO_2CH_2CH_3$ (where R is 2-ethyl, 2-ethoxy, 4-benzyloxy, 2,3-dimethyl were prepared and copolymerized with styrene.

Acknowledgments

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