Synthesis and styrene copolymerization of novel alkyl ring-substituted *t*-butyl phenylcyanoacrylates

Daniah H. Ibrahim, Tarick Abu-Alrob, Maria Agoytia, John K. Butterfield, Maura K. Devine, Jennifer Y. Dinh, Angelo R. Donis, Kristen A. Folkes, Firyal M. Khan, Caroline J. Shishem, Sara M. Rocus, William S. Schjerven, and Gregory B. Kharas

DePaul University, Chemistry and Biochemistry Department, 1110 West Belden Avenue, Chicago, IL 60614-3214

Abstract

Novel alkyl ring-substituted *t*-butyl phenylcyanoacrylates, $RPhCH=C(CN)CO_2C(CH_3)_3$ (where R is H, 2-methyl, 3-methyl, 4-methyl, 2-ethyl, 4-ethyl, 4-propyl, 4-*i*-propyl, 4-butyl, 4-*i*-butyl) were prepared and copolymerized with styrene. The acrylates were synthesized by the piperidine catalyzed Knoevenagel condensation of ring-substituted benzaldehydes and *t*-butyl cyanoacetate, and characterized by CHN analysis, IR, ^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.

1. Introduction

t-Butyl phenylcyanoacrylate was synthesized by condensation catalyzed by porous silicate quaternary ammonium composite materials [1]. It was involved in studies of synthons for alkylation, alkenylation, and alkynylation reactions of acyl radicals from benzothiazolines [2].

> The acrylate was also reported in catalysis studies of bifunctional 2D Cd(II)-based metal-organic framework [3]. Conjugate addition of perfluoroarenes to *t*-butyl 4-methylphenylcyanoacrylate was enabled by an alkoxide-hydrosilane system [4]. *t*-Butyl cyanoacrylate polymers have found multiple applications like water-based ink compositions [5], preparation of polymer microspheres [6], and positive working radiation-sensitive composition [7].

Earlier we have reported synthesis and styrene copolymerization of a number of alkyl ring-substituted methyl [8, 9], ethyl [10, 11], propyl [12], isopropyl [13], butyl [14], isobutyl [15], methoxyethyl [16], and octyl [17] phenylcyanoacrylates.

In continuation of our investigation of novel phenylcyanoacrylate compounds we have prepared *t*-butyl phenylcyanoacrylates, $RPhCH=C(CN)CO_2C(CH_3)_3$, where R is H, 2-methyl, 3-methyl, 4-methyl, 2-ethyl, 4-ethyl, 4-propyl, 4-*i*-propyl, 4-butyl, 4-*i*-butyl, 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 [18].

2. Experimental

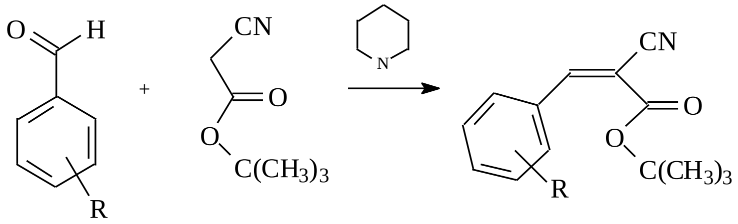
2.1. Materials

Benzaldehyde (≥99%), 2-methyl (≥96.5%), 3-methyl (97%), 4-methyl (97%), 4-ethyl (97%), 4-propyl (95%), 4-*i*-propyl (≥98%), 4-butyl (90%), 4-*i*-butyl (97%) benzaldehydes, *t*-butyl 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.

3. Results and discussion

3.1. Synthesis and characterization of t-butyl phenylcyanoacrylates

All *t*-butyl phenylcyanoacrylates (TBPCA) compounds were synthesized by Knoevenagel condensation [19] of appropriate benzaldehydes with *t*-butyl cyanoacetate, catalyzed by base, piperidine (Scheme 1).



Scheme 1. Synthesis of *t*-butyl phenylcyanoacrylates where R is H, 2-methyl, 3-methyl, 4-methyl, 4-ethyl, 4-propyl, 4-*i*-propyl, 4-butyl, 4-*i*-butyl.

The preparation procedure was essentially the same for all the monomers. In a typical synthesis, equimolar amounts of *t*-butyl 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 alkyl ring-substituted TBPCA was performed since no stereoisomers (*E* or/and *Z*) of known configuration were available.

3.1.1. *t-Butyl phenylcyanoacrylate*

Yield 72%; ^{1}H NMR δ 8.2 (s, 1H, CH=), 7.8-7.2 (m, 5H, Ph), 1.6 (s, 9H, CH_3); ^{13}C NMR δ 161 (C=O), 154 (HC=), 134-128 (Ph), 116 (CN), 105 (C=), 85 (OC), 28 (CH_3); IR (cm^{-1}): 2924 (m, C-H), 2245 (m, CN), 1726 (s, C=O), 1263 (s, C-O-CH_3), 778 (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, 70.65; H, 6.69; N, 6.49.

3.1.2. *t-Butyl 2-methylphenylcyanoacrylate*.

Yield 86%; ^{1}H NMR δ 8.5(s, 1H, CH=), 8.2-7.1 (m, 4H, Ph), 2.4 (s, 3H, $PhCH_3$), 1.4 (s, 9H, CH_3); ^{13}C NMR δ 161 (C=O), 152 (HC=), 140-127 (Ph), 116 (CN), 106 (C=), 84 (OC), 28 (CH_3), 20 ($PhCH_3$); IR (cm^{-1}): 2926 (m, C-H), 2226 (m, CN), 1725 (s, C=O), 1593 (m, C=C), 1263 (s, C-O-CH_3), 813 (s, C-H out of plane). Anal. Calcd. for $C_{15}H_{17}NO_2$: C, 74.05; H, 7.04; N, 5.76; Found: C, 72.57; H, 7.29; N, 5.89.

3.1.3. *t-Butyl 3-methylphenylcyanoacrylate*.

Yield 89%; ^{1}H NMR δ 8.1 (s, 1H, CH=), 7.9-7.0 (m, 4H, Ph), 2.4 ($PhCH_3$), 1.4 (s, 9H, CH_3); ^{13}C NMR δ 162 (C=O), 153 (HC=), 138-124 (Ph), 116 (CN), 104 (C=), 28 (CH_3), 21 ($PhCH_3$); IR (cm^{-1}): 2928 (m, C-H), 2224 (m, CN), 1729 (s, C=O), 1612 (m, C=C), 1234 (s, C-O-CH_3), 888, 762 (s, C-H out of plane). Anal. Calcd. for $C_{15}H_{17}NO_2$: C, 74.05; H, 7.04; N, 5.76; Found: C, 72.33; H, 7.41; N, 5.93.

3.1.4. *t-Butyl 4-methylphenylcyanoacrylate*.

Yield 91%; ^{1}H NMR δ 8.2 (s, 1H, CH=), 7.9, 7.3 (d, 4H, Ph), 2.4 ($PhCH_3$), 1.5 (s, 9H, CH_3); ^{13}C NMR δ 162 (C=O), 154 (HC=), 144, 131, 130, 129 (Ph), 116 (CN), 103 (C=), 84 (OC), 28 (CH_3), 21 ($PhCH_3$); IR (cm^{-1}): 2929 (m, C-H), 2223 (m, CN), 1729 (s, C=O), 1614 (m, C=C), 1222 (s, C-O-CH_3), 826 (s, C-H out of plane). Anal. Calcd. for $C_{15}H_{17}NO_2$: C, 74.05; H, 7.04; N, 5.76; Found: C, 72.55; H, 7.39; N, 5.93.

3.1.5. *t-Butyl 2-ethylphenylcyanoacrylate*.

Yield 81%; ^{1}H NMR δ 8.5 (s, 1H, CH=), 8.2-7.0 (m, 4H, Ph), 2.8 ($PhC\underline{H}_2CH_3$), 1.4 (s, 9H, CH_3), 1.3 (t, 3H, $PhCH_2C\underline{H}_3$); ^{13}C NMR δ 161 (C=O), 153 (HC=), 147-125 (Ph), 116 (CN), 106 (C=), 83 (OC), 28 (CH_3), 27 ($Ph\underline{C}H_2$), 16 ($PhCH_2C\underline{H}_3$); IR (cm^{-1}): 2928 (m, C-H), 2227 (m, CN), 1726 (s, C=O), 1606 (C=C), 1232 (s, C-O-CH_3), 817 (s, C-H out of plane). Anal. Calcd. for $C_{16}H_{19}NO_2$: C, 74.68; H, 7.44; N, 5.44; Found: C, 73.39; H, 7.64; N, 5.47.

3.1.6. ***t-Butyl 4-ethylphenylcyanoacrylate*.**

Yield 77%; ^{1}H NMR $\delta\,\delta$ 8.1 (s, 1H, CH=), 7.9, 7.3 (m, 4H, Ph), 2.8 ($PhC\underline{H}_2CH_3$), 1.6 (s, 9H, CH_3), 1.4 (t, 3H, $PhCH_2C\underline{H}_3$); ^{13}C NMR δ 162 (C=O), 154 (HC=), 150-128 (Ph), 116 (CN), 103 (C=), 84 (OC), 29 ($Ph\underline{C}H_2$), 28 (CH_3), 15 ($PhCH_2C\underline{H}_3$); IR (cm^{-1}): 2928 (m, C-H), 2226 (m, CN), 1716 (s, C=O), 1606 (C=C), 1235 (s, C-O-CH_3), 823 (s, C-H out of plane). Anal. Calcd. for $C_{16}H_{19}NO_2$: C, 74.68; H, 7.44; N, 5.44; Found: C, 72.43; H, 7.37; N, 5.63.

3.1.7. ***Octyl 4-propylphenylcyanoacrylate.***

Yield 84%; ^{1}H NMR δ 8.1 (s, 1H, CH=), 8.0-7.1 (m, 4H, Ph), 2.6 (t, 2H, $CH_3CH_2C\underline{H}_2Ph$), 1.8 (m, 2H, $CH_3C\underline{H}_2CH_2Ph$), 1.6 (s, 9H, CH_3), 0.9 (t, 3H, $C\underline{H}_3CH_2CH_2Ph$); ^{13}C NMR δ 162 (C=O), 154 (HC=), 148-127 (Ph), 116 (CN), 103 (C=), 84 (OC), 38 ($CH_3CH_2\underline{C}H_2Ph$), 27 ($CH_3$), 24 ($CH_3\underline{C}H_2CH_2Ph$), 13.8 (Ph-$CH_2CH_2\underline{C}H_3$); IR (cm^{-1}): 2943 (m, C-H), 2226 (m, CN), 1724 (s, C=O), 1583 (C=C), 1264 (s, C-O-CH_3), 844 (s, C-H out of plane). Anal. Calcd. for $C_{17}H_{21}NO_2$: C, 75.25; H, 7.80; N, 5.16; Found: C, 72.52; H, 7.64; N, 5.46.

3.1.8. ***t-Butyl 4-i-propylphenylcyanoacrylate*.**

Yield 76%; ^{1}H NMR δ 8.1 (s, 1H, CH=), 8.0-7.2 (m, 4H, Ph), 3.1 (m, 1H, CHPh), 1.4 (s, 9H, CH_3), 1.3 (d, 6H, $(C\underline{H}_3)_2CH$); ^{13}C NMR δ 162 (C=O), 154 (HC=), 132-126 (Ph), 116 (CN), 103 (C=), 84 (OC), 34 (PhCH), 27 (CH_3), 23 ($CH(\underline{C}H_3)_2$); IR (cm^{-1}): 2912 (m, C-H), 2224 (m, CN), 1719 (s, C=O), 1623 (C=C), 1254 (s, C-O-CH_3), 823 (s, C-H out of plane). Anal. Calcd. for $C_{17}H_{21}NO_2$: C, 75.25; H, 7.80; N, 5.16; Found: C, 71.33; H, 7.11; N, 5.25.

3.1.9. ***t-Butyl 4-butylphenylcyanoacrylate*.**

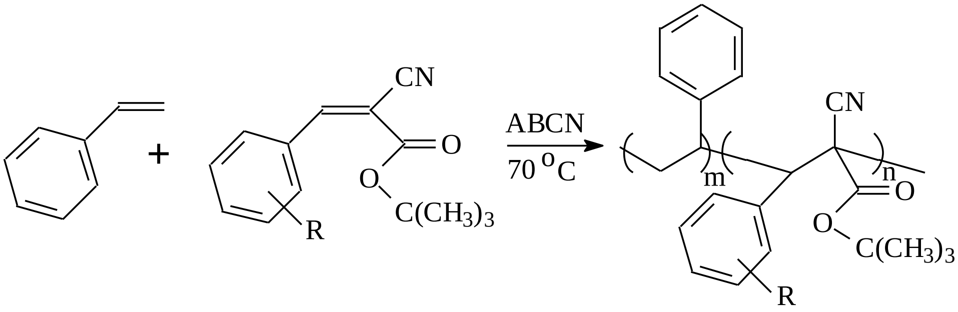
Yield 72%; ^{1}H NMR δ 8.1 (s, 1H, CH=), 7.9-7.2 (m, 4H, Ph), 2.7 (t, 2H, $C_3H_7C\underline{H}_2Ph$), 1.7-1.6 (m, 2H, $C_2H_5C\underline{H}_2CH_2Ph$), 1.4 (s, 9H, CH_3), 0.9 (t, 3H, $C\underline{H}_3(CH_2)_3Ph$); ^{13}C NMR δ 163 (C=O), 154 (HC=), 135-129 (Ph), 116 (CN), 102 (C=), 83 (OC), 36 ($\underline{C}H_2Ph$), 33 ($\underline{C}H_2CH_2Ph$), 27 $(CH_3)_3$, 22 ($\underline{C}H_2C_2H_4Ph$), 13.9 ($Ph\text{-}C_3H_6\underline{C}H_3$); IR (cm^{-1}): 3038 (m, C-H), 2223 (m, CN), 1725 (s, C=O), 1593 (C=C), 1266 (s, $C\text{-}O\text{-}CH_3$), 882 (s, C-H out of plane). Anal. Calcd. for $C_{18}H_{23}NO_2$: C, 75.76; H, 8.12; N, 4.91; Found: C, 77.79; H, 8.39; N, 3.61.

3.1.10. *t-Butyl 4-i-butylphenylcyanoacrylate.*

Yield 94%; ^{1}H NMR δ 8.1 (s, 1H, CH=), 8.0-7.2 (m, 4H, Ph), 2.6 (d, 2H, $PhCH_2$), 1.8 (m, 1H, $PhCH_2CH$), 1.4 (s, 9H, OC), 0.9 (d, 6H, $CHC\underline{H}_3$); ^{13}C NMR δ 162 (C=O), 155 (HC=), 149-128 (Ph), 117 (CN), 103 (C=), 84 (OC), 43 ($PhCH_2$), 30 ($PhCH_2CH$), 27 (CH_3), 22 $(CH_3)_2CH$); IR (cm^{-1}): 2924 (m, C-H), 2224 (m, CN), 1724 (s, C=O), 1593 (C=C), 1292 (s, $C\text{-}O\text{-}CH_3$), 847 (s, C-H out of plane). Anal. Calcd. for $C_{18}H_{23}NO_2$: C, 75.76; H, 8.12; N, 4.91; Found: C, 74.65; H, 8.18; N, 3.86.

3.2. *Synthesis and characterization of styrene – TBPCA copolymers*

Copolymers of the ST and the TBPCA compounds, P(ST-co-TBPCA) were prepared in 25-mL glass screw cap vials at ST/TBPCA = 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 TBPCA). The novel synthesized TBPCA 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 ring-substituted *t*-butyl phenylcyanoacrylates, where R is H, 2-methyl, 3-methyl, 4-methyl, 4-ethyl, 4-propyl, 4-*i*-propyl, 4-butyl, 4-*i*-butyl.

Table 1. Copolymerization of styrene and *t*-butyl phenylcyanoacrylates.

R	Yield[a] (wt%)	N (wt%)	ST in copol. (mol%)	TBPCA in copol. (mol%)
H	14.2	2.86	71.5	28.5
2-Methyl	13.1	2.71	72.5	27.5
3-Methyl	12.1	2.8	71.2	28.8
4-Methyl	15.6	2.55	74.6	25.4
2-Ethyl	12.3	2.66	88.4	11.6
4-Ethyl	11.4	2.79	87.8	12.2
4-Propyl	15.8	2.53	88.9	11.1
4-Isopropyl	16.4	2.61	88.5	11.5
4-Butyl	13.2	2.38	74.5	25.5
4-i-Butyl	13.6	2.64	70.2	29.8

Nitrogen elemental analysis showed that between 11.1 and 29.8 mol% of TBPCA is present in the copolymers prepared at ST/TBPCA = 3 (mol), which is indicative of relatively high reactivity of the TBPCA monomers towards ST radical which is typical of alkyl ring-substituted TBPCA [8-17]. Since TBPCA monomers do not homopolymerize, the most likely structure of the copolymers would be isolated TBPCA 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, alkyl ring-substituted *t*-butyl phenylcyanoacrylates, $RPhCH{=}C(CN)CO_2C(CH_3)_3$ (where R is H, 2-methyl, 3-methyl, 4-methyl, 4-ethyl, 4-propyl, 4-i-propyl, 4-butyl, 4-i-butyl) were prepared and copolymerized with styrene.

Acknowledgments

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