Synthesis and styrene copolymerization of novel alkoxy ring-substituted tert-butyl phenylcyanoacrylates

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Abstract

Novel alkoxy ring-substituted tert-butyl phenylcyanoacrylates, $RPhCH=C(CN)CO_2C(CH_3)_3$ (where R is 2-methoxy, 3-methoxy, 4-methoxy, 2-ethoxy, 3-ethoxy, 4-ethoxy, 4-propoxy, 4-butoxy) were prepared and copolymerized with styrene. The acrylates were synthesized by the piperidine catalyzed Knoevenagel condensation of ring-substituted benzaldehydes and tert-butyl cyanoacetate, and characterized by CHN analysis, IR, ^{1}H and ^{13}C NMR. All the acrylates were radically copolymerized with styrene in solution at 70°C. The compositions of the copolymers were calculated from nitrogen analysis.

1. Introduction

Methoxyphenylcyanoacrylates (MPCA) were reported in a number of studies [1-3]. Thus, methyl MPCA was involved in direct cyclopropanation of α-cyano β-aryl alkanes by light-mediated single electron transfer between donor-acceptor pairs [1]. Protic ionic liquid methylimidazolium thiocyanate was used as reagent, catalyst, and solvent in synthesis of MPCA [2]. The thiol addition to benzalcyanoacetate-based Michael-acceptors were utilized to access dynamic covalent network films [3]. Ethyl MPCA was synthesized by the Knoevenagel condensation catalyzed by imidazolium-based ionic liquids [4] and by ethylene glycol / urea / NH_4Cl low melting mixture-assisted reactions [5]. Novel synthesis of furancarboxylate derivatives was reported via cyclization reactions of ethyl MPCA and ethyl glycinate hydrochloride [6]. Propyl MPCA was prepared via cyanuric chloride-mediated three-component reactions involving Knoevenagel condensation/cyano hydration /esterification [7]. Several patents reported making of photographic materials involving propyl MPCA [8, 9]. Tert-butyl cyanoacrylate polymers are reported in [10-12].

Earlier we have reported synthesis and styrene copolymerization of a number of alkoxy ring-substituted methyl [13-15], ethyl [16, 17], propyl [18], isopropyl [19], butyl [20], isobutyl [21], 2-methoxyethyl [22], and octyl [23] phenylcyanoacrylates.

Thus, in continuation of our investigation of novel TSE compounds we have prepared tert-butyl alkoxyphenylcyanoacrylates (APCA), $RPhCH=C(CN)CO_2C(CH_3)_3$, where R is 2-methoxy, 3-methoxy, 4-methoxy, 2-ethoxy, 3-ethoxy, 4-ethoxy, 4-propoxy, 4-butoxy, 4-hexyloxy, and explored the feasibility of their copolymerization with styrene. To the best of our knowledge, except synthesis of tert-butyl 4-methoxyphenylcyanoacrylate [24], there have been no reports on either synthesis of these compounds, nor their copolymerization with styrene [25].

2. Experimental

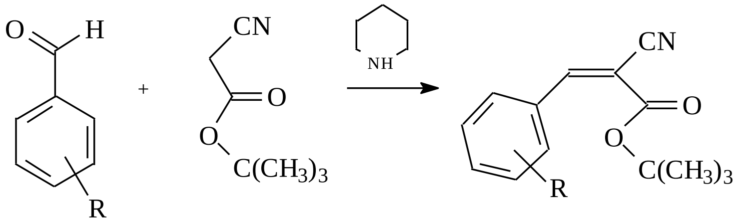
Materials

2-Methoxy, 3-methoxy, 4-methoxy, 2-ethoxy, 3-ethoxy, 4-ethoxy, 4-propoxy, 4-butoxybenzaldehydes, tert-butyl cyanoacetate (≥96.0%), 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 tert-butyl phenylcyanoacrylates

All tert-butyl phenylcyanoacrylates (APCA) compounds were synthesized by Knoevenagel condensation [26] of appropriate benzaldehydes with tert-butyl cyanoacetate, catalyzed by base, piperidine (Scheme 1).



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

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

3.1.1. ***Tert-butyl 2-methoxyphenylcyanoacrylate***

Yield 84%; mp 129°C; ^{1}H NMR δ 8.7 (s, 1H, CH=), 8.4-6.9 (m, 4H, Ph), 3.9 (s, 3H, OCH_3), 1.7 (s, 9H, CH_3); ^{13}C NMR δ 162 (C=O), 150 (HC=), 148-111 (Ph), 116 (CN), 104 (C=), 83 (OC), 56 ($PhOCH_3$), 27 (CH_3); IR (cm^{-1}): 2928 (m, C-H), 2223 (m, CN), 1710 (s, C=O), 1598 (s, C=C), 1267 (s, C-O-CH_3), 752 (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, 68.99; H, 6.53; N, 5.47.

3.1.2. ***Tert-butyl 3-methoxyphenylcyanoacrylate***.

Yield 91%; ^{1}H NMR δ 8.1 (s, 1H, CH=), 7.7-7.0 (m, 4H, Ph), 3.9 (s, 3H, OCH_3), 1.6 (s, 9H, CH_3); ^{13}C NMR δ 161 (C=O), 154 (HC=), 160, 132, 130, 126, 124, 116 (Ph), 115 (CN), 105 (C=), 84 (OC), 55 (PhOC), 28 (CH_3); IR (cm^{-1}): 3120-2820 (m, C-H), 2223 (m, CN), 1725 (s, C=O), 1602 (m, C=C), 1278 (s, C-O-CH_3), 765 (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, 66.95; H, 6.56; N, 5.31.

3.1.3. ***Tert-butyl 4-methoxyphenylcyanoacrylate***.

Yield 88%; mp 110°C; ^{1}H NMR δ 8.1 (s, 1H, CH=), 8.0-6.9 (m, 4H, Ph), 3.9 (s, 3H, OCH_3), 1.6 (s, 9H, CH_3); ^{13}C NMR δ 164 (C=O), 154 (HC=), 161, 134, 125, 117 (Ph), 116 (CN), 101 (C=), 83 (OC), 56 ($PhOCH_3$), 23 (CH_3); IR (cm^{-1}): 3100-2800 (m, C-H), 2213 (m, CN), 1711 (s, C=O), 1592 (s, C=C), 1263 (s, C-O-CH_3), 762 (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, 68.13; H, 6.46; N, 5.33.

3.1.4. ***Tert-butyl 2-ethoxyphenylcyanoacrylate*.**

Yield 73%; mp 55.8°C; ^{1}H NMR δ 8.7 (s, 1H, CH=), 8.4-6.9 (m, 4H, Ph), 4.1 (t, 2H, $PhOCH_2$), 1.6 (s, 9H, CH_3), 1.3 (t, 3H, $PhCH_2C\underline{H}_3$); ^{13}C NMR δ 162 (C=O), 150 (HC=), 158, 135, 130, 121, 112 (Ph), 116 (CN), 103 (C=), 84 (OC), 64 ($PhOCH_2$), 27 (CH_3), 14 ($PhOCH_2\underline{C}H_3$); IR (cm^{-1}): 2957 (m, C-H), 2220 (m, CN), 1717 (s, C=O), 1598 (s, C=C),1240 (s, C-O-CH_3), 817 (s, C-H out of plane). Anal. Calcd. for $C_{19}H_{16}NO_3$: C, 70.31; H, 7.01; N, 5.12; Found: C, 69.13; H, 6.89; N, 5.28.

3.1.5. ***Tert-butyl 3-ethoxyphenylcyanoacrylate*.**

Yield 86%; ^{1}H NMR δ 8.1 (s, 1H, CH=), 7.6-7.0 (m, 4H, Ph), 4.1 (t, 2H, $PhOCH_2$), 1.4 (s, 9H, CH_3), 1.3 (t, 3H, $PhOCH_2C\underline{H}_3$); ^{13}C NMR δ 161 (C=O), 154 (HC=), 159, 130, 123, 125, 113 (Ph), 116 (CN), 105 (C=), 84 (OC), 28 $(CH_3)_3$, 15 ($PhOCH_2\underline{C}H_3$); IR (cm^{-1}): 3000-2780 (m, C-H), 2225 (m, CN), 1726 (s, C=O), 1606 (s, C-O-CH_3), 827, 787, 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, 68.76; H, 7.11; N, 5.01.

3.1.6. ***Tert-butyl 4-ethoxyphenylcyanoacrylate*.**

Yield 87%; mp 117°C; ^{1}H NMR δ 8.1 (s, 1H, CH=), 8.0-6.8 (m, 4H, Ph), 4.1 (t, 2H, $PhOCH_2$), 1.5 (s, 9H, CH_3), 1.4 (t, 3H, $PhOCH_2C\underline{H}_3$); ^{13}C NMR δ 163 (C=O), 153 (HC=), 160, 134, 130, 124, 115 (Ph), 116 (CN), 102 (C=), 84 (OC), 70 ($PhOCH_2$), 28 $(CH_3)_3$, 10 ($PhOCH_2\underline{C}H_3$); IR (cm^{-1}): 3023-2828 (m, C-H), 2220 (m, CN), 1724 (s, C=O), 1261 (s, C-O-CH_3), 862 (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, 69.23; H, 7.13; N, 5.22.

3.1.7. *Tert-butyl 4-propoxyphenylcyanoacrylate.*

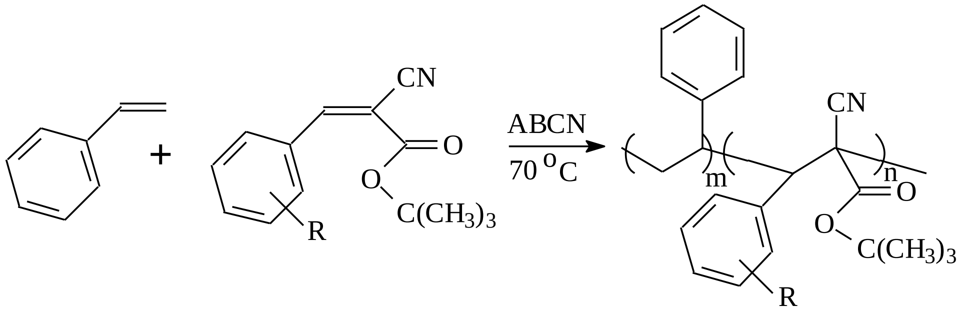
Yield 84%; ^{1}H NMR δ 8.1 (s, 1H, CH=), 7.9, 6.9 (m, 4H, Ph), 4.0 (t, 2H, $PhOCH_2$), 1.8-1.7 (m, 2H, $PhOCH_2C\underline{H}_2$), 1.4 (s, 9H, $(CH_3)_3$, 1.0 (t, 3H, $PhO(CH_2)_2C\underline{H}_3$); ^{13}C NMR δ 163 (C=O), 154 (HC=), 160, 133, 125, 115 (Ph), 116 (CN), 100 (C=), 84 (OC), 70 (OCH_2), 27 $(CH_3)_3$, 23 ($PhOCH_2\underline{C}H_2$), 10 ($PhOCH_2CH_2\underline{C}H_3$); IR (cm^{-1}): 3012-2822 (m, C-H), 2218 (m, CN), 1716 (s, C=O), 1590 (s, C=C), 1269 (s, C-O-CH_3), 847 (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, 65.98; H, 7.77; N, 6.77.

3.1.8. *Tert-butyl 4-butoxyphenylcyanoacrylate*.

Yield 79%; mp 91°C; ^{1}H NMR δ 8.1 (s, 1H, CH=), 8.0, 6.9 (m, 4H, Ph), 4.0 (t, 2H, $PhOCH_2$), 1.8 (m, 2H, $PhOCH_2C\underline{H}_2$), 1.6 (s, 9H, CH_3), 1.4 (t, 3H, $PhO(CH_2)_2C\underline{H}_2$), 0.9 (t, 3H, $PhO(CH_2)_3CH_3$); ^{13}C NMR δ 163 (C=O), 154 (HC=), 162, 134, 124, 115 (Ph), 116 (CN), 100 (C=), 84 (OC), 68 ($PhOCH_2$), 31 ($PhOCH_2\underline{C}H_2$), 27 $(CH_3)_3$, 19 ($PhO(CH_2)_3\underline{C}H_2$), 14 ($PhO(CH_2)_3\underline{C}H_3$); IR (cm^{-1}): 3008-2816 (m, C-H), 2216 (m, CN), 1709 (s, C=O), 1587 (s, C=C), 1184 (s, C-O-CH_3), 836 (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, 69.98; H, 7.53; N, 4.89.

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

Copolymers of the ST and the APCA compounds, P(ST-co-APCA) were prepared in 25-mL glass screw cap vials at ST/APCA = 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 APCA). The novel synthesized APCA 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 tert-butyl phenylcyanoacrylates, where R is 2-methoxy, 3-methoxy, 4-methoxy, 2-ethoxy, 3-ethoxy, 4-ethoxy, 4-propoxy, 4-butoxy.

Table 1. Copolymerization of styrene and tert-butyl phenylcyanoacrylates.

R	Yield[a] (wt%)	N (wt%)	ST in copol. (mol%)	APCA in copol. (mol%)
2-Methoxy	11.4	2.62	72.6	27.4
3-Methoxy	12.5	2.87	68.8	31.2
4-Methoxy	13.3	2.66	72.0	28.0
2-Ethoxy	14.7	2.65	71.1	28.9
3-Ethoxy	12.4	2.82	87.4	12.6
4-Ethoxy	12.4	2.6	88.5	11.5
4-Propoxy	15.2	2.41	89.4	10.6
4-Butoxy	12.2	2.63	88.0	12.0

Nitrogen elemental analysis showed that between 10.6 and 31.2 mol% of APCA is present in the copolymers prepared at ST/ APCA = 3 (mol), which is indicative of relatively high reactivity of the APCA monomers towards ST radical which is typical of alkoxy ring-substituted APCA [13-23]. Since APCA monomers do not homopolymerize, the most likely structure of the copolymers would be isolated APCA 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, tert-butyl alkoxyphenylcyanoacrylates, $RPhCH=C(CN)CO_2C(CH_3)_3$ (where R is 2-methoxy, 3-methoxy, 4-methoxy, 2-ethoxy, 3-ethoxy, 4-ethoxy, 4-propoxy, 4-butoxy) were prepared and copolymerized with styrene.

Acknowledgments

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References

[1] Direct Cyclopropanation of α-Cyano β-Aryl Alkanes by Light-Mediated Single Electron Transfer Between Donor-Acceptor Pairs. Li, Jing; Lear, Martin J.; Hayashi, Yujiro. Chemistry - European Journal (2021), 27(19), 5901-5905.

[2] Protic Ionic Liquid as Reagent, Catalyst, and Solvent: 1-Methylimidazolium Thiocyanate. Andreev, Ivan A.; Ratmanova, Nina K.; Augustin, Andre U.; Ivanova, Olga A.; Levina, Irina I.; Khrustalev, Victor N.; Werz, Daniel B.; Trushkov, Igor V. Angewandte Chemie, International Edition (2021), 60(14), 7927-7934.

[3] Dynamic reaction-induced phase separation in tunable, adaptive covalent networks. Herbert, Katie M.; Getty, Patrick T.; Dolinski, Neil D.; Hertzog, Jerald E.; de Jong, Derek; Lettow, James H.; Romulus, Joy; Onorato, Jonathan W.; Foster, Elizabeth M.; Rowan, Stuart J. Chemical Science (2020), 11(19), 5028-5036.

[4] The Knoevenagel condensation catalysed by ionic liquids: a mass spectrometric insight into the reaction mechanism. Salvitti, Chiara; Bortolami, Martina; Chiarotto, Isabella; Troiani, Anna; de Petris, Giulia. New Journal of Chemistry (2021), 45(38), 17787-17795.

[5] Ethylene Glycol: Urea: NH4Cl Low Melting Mixture-Assisted Reactions between Aromatic Aldehydes and Active Methylene Compounds. Theresa, Letcy V.;

Ponmalakunnu, Saranya; Baby, Anju M.; Sreekumar, Krishnapillai. ChemistrySelect (2021), 6(28), 7150-7157.

[6] Novel synthesis of furancarboxylate derivatives via cyclization reactions of (E)-ethyl 3-aryl-2-cyanoacrylates and ethyl glycinate hydrochloride. Luo, Naili; Wang, Shan; Su, Zhenjie; Wang, Cunde. Journal of Chemical Research (2021), 45(5-6), 476-481.

[7] Metal-free synthesis of cyano acrylates via cyanuric chloride-mediated three-component reactions involving a cascade consists of Knoevenagel condensation/cyano hydration/esterification. Wan, Jie-Ping; Jing, Yanfeng; Liu, Yunyun; Sheng, Shouri. RSC Advances (2014), 4(109), 63997-64000.

[8] UV absorbing polymer particle for use in photoimaging elements. Wang, Yongcai; Smith, Dennis E.; Schroeder, Kurt M. U.S. (1999), US 5919850 A 19990706.

[9] Photographic material having a blue sensitive coupler starved unit. Rieger, John Brian; Friday, James Anthony. U.S. (2000), US 6159672 A 20001212.

[10] Influence of surface and cohesion parameters of adhesives on the metal adhesive joints strength (α-cyanoacrylates). Pritykin, L. M.; Lukienko, T. V.; Lyubchenko, A. N. Adhesion '99, International Conference on Adhesion and Adhesives, 7th, Cambridge, United Kingdom, Sept. 15-17, 1999 (1999), 363-368.

[11] Effect of the electronic structure of α-cyanoacrylates on the surface energy of their polymers. Pritykin, L. M.; Lyubchenko, A. N.; Selyutin, O. B.; Bol'shakov, V. I. Ukrainskii Khimicheskii Zhurnal (Russian Edition) (1998), 64(11-12), 57-64. Database: CAPLUS.

[12] . Determination of the adhesion characteristics of α-cyanoacrylate adhesives. Pritykin, L. M.; Novikova, R. G.; Danilov, D. M. Plasticheskie Massy (1993), (3), 37-42. Database: CAPLUS.

[13] Novel Copolymers of Trisubstituted Ethylenes with Styrene: 1. Alkyl and Alkoxy Phenyl Substituted Methyl 2-Cyano-3-phenyl-2-propenoates. G.B. Kharas, Eaker, J.M., Dian, B.C., Elenteny, M.E., Kamenetsky, M., Provenza, L.M., Quinting, G.R., Macromolecular Reports, A32, 13-23 (1995).

[14] Synthesis and Copolymerization of Trisubstituted Ethylenes with Styrene - 6. Alkoxy, Phenoxy, and Cyano ring-substituted methyl 2-cyano-3-phenyl-2-propenoates. K. Kim, D.A. Blaine, L.M. Brtek, R.M. Flood, C.G. Krubert, A.M.T. Rizzo, E.A. Sterner, S. De Armas, G.B. Kharas and K. Watson. J. Macromol. Sci., A37, 841-854 (2000).

[15] Novel Copolymers of Styrene. 13. Oxy Ring-substituted Methyl 2-Cyano-3-phenyl-2-propenates. G.B. Kharas, E.E. Pierce, K.C. Aguirre, R.O. Anyaeche, C.L. Arrieta, N.L. Falk, H. In't Veld, M. Klipinitser, R.A. Lach, M. Mclaughlin, M. D. Murillo, J. Pacheco, G.M. Van Metre, and Z. Wahrenburg. J. Macromol. Sci. A51(6) 465 - 469 (2014).

[16] Novel copolymers of Alkyl and Alkoxy Ring-substituted 2-Cyano-3-phenyl-2-propenoates and Styrene. G.B. Kharas, C.A. Diener, H.A. Barbarawi, N.D. Beavers, M. Borovilos, J. Carney, A.A. Fox, K.M. McClelland, J. Yedlinski, and K. Watson. J. Macromol. Sci., A41 (8), 889-896 (2004)

[17] Novel Copolymers of Styrene. 5. Oxy Ring-substituted Ethyl 2-Cyano-3-Phenyl-2-propenoates. G.B. Kharas, A.A. Delgado, N. Gange, M.C. Hattzell, N.W. Hawley, K.A. Kupczyk, E.K. Lam, S.S. Lyngaas, F.B. Mohammad, M.E. Montgomery, A.J. Ryan, and V.M. Wright. J. Macromol. Sci. A50 (3) 271-275 (2013).

[18] Novel Copolymers of Styrene. 2. Oxy Ring-Substituted Propyl 2-Cyano-3-Phenyl-2-Propenoates G.B. Kharas, C.F. Dos Santos, Y. Gao, R. Godina, P. John, C. Kent, M. Konopka, A.M. Malinovski, A.J. Mlotkowski, J.M. Olsen, C.A. Ovies, S.B. Scheinman, and J.Z. Smith. J. Macromol. Sci. A53 (10) 600-604 (2016).

[19] Synthesis and styrene copolymerization of novel trisubstituted ethylenes: 3. Alkoxy ring-sabstituted isopropyl 2-cyano-3-phenyl-2-propenoates. N. Shinde, J.K. Jody, E.K. Mosher, N. Kaur, A.A.R. Oriol, D.M. Perez, R. Ranganathan, A. Renteria, T.A. Rydbom, C. Yeager, W.S. Schjerven and G.B. Kharas. Designed Monomers and Polymers, 21 (1) 163-171 (2018).

[20] Novel Copolymers of Styrene. 2. Alkoxy Ring-Substituted Butyl 2-Cyano-3-Phenyl-2-Propenoates. G.B. Kharas, H. Feng, C. Aranda, M.E. Navarro, S. Pacheco, Q. Pazderka, P. Rebollar, T. Reynolds, M.E. Sanchez, J.L. Sichory, A. Susol, and N. Ziemianska. J. Macromol. Sci. A52(7) 504-509 (2015).

[21] Synthesis and styrene copolymerization of novel ring-substituted isopropyl and isobutyl phenylcyanoacrylates. C.A. Savittieri, A. Cimino, A.M. Johnson, C.M. Myslicki, M.R. Nealon, D.J. O'Neill, A. Patel, K. Quebral, A.S. Seng, K.N. Shishido, J. Stamos, A.A. Shinde, S.M. Rocus, W.S. Schjerven, and G.B. Kharas. ChemRxiv (27.07.2020). https://doi.org/10.26434/chemrxiv.11401347.v2

[22] Synthesis and styrene copolymerization of novel trisubstituted ethylenes: 2. Alkoxy ring-substituted 2-methoxyethyl 2-cyano-3-phenyl-2-propenoates. Christian Lopez, Monica A. Martinez, Emma L. Melendez-Scherer, Alyssa Nunez, Kyle J. Ochwat, Presley O'Neil, Michal P. Papierz, Limariz Rebolledo, Alyssa D. Spires, Sara M. Rocus, William S. Schjerven, and Gregory B. Kharas. ChemRxiv. Preprint. (12.23.2020). https://doi.org/10.26434/chemrxiv.13262660.v2

[23] Synthesis and styrene copolymerization of novel trisubstituted ethylenes: 2. Alkoxy ring-substituted octyl phenylcyanoacrylates. David R. Graykowski, Marlena D. Hadas, Marianna C. Haddad, Jacqueline Jimenez, Marcelina A. Skowronski, Jade D. Smith, Brendan S. Van Voorhis, Zoe M. Varsbergs, Sara M. Rocus, William S. Schjerven, Gregory B. Kharas. ChemRxiv. Preprint. (16.03.2021). https://doi.org/10.26434/chemrxiv.13262660.v13

[24] Conjugate Addition of Perfluoroarenes to α,β-Unsaturated Carbonyls Enabled by an Alkoxide-Hydrosilane System: Implication of a Radical Pathway. Xie, Weilong; Park, Sung-Woo; Jung, Hoimin; Kim, Dongwook; Baik, Mu-Hyun; Chang, Sukbok. JACS (2018), 140(30), 9659-9668.

[25] SciFinder; Chemical Abstracts Service: Columbus, OH; https://scifinder.cas.org (Accessed November 14, 2021).

[26] Smith, M. B.; March, J. *Addition to Carbon-Hetero Multiple Bonds*, In March's Advanced Organic Chemistry, J. Wiley & Sons: New York, Ch.16, 1225, **2001**.