Synthesis and styrene copolymerization of novel dibromo and dichloro ring-disubstituted isobutyl phenylcyanoacrylates

Daniah H. Ibrahim, Chris J. Lee, Daniel N. Madock, Marcin Marciniak, Miguel A. Montero, Juan Orozco, Viany Ortiz, Mica C. Robles, 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 dibromo and dichloro ring-disubstituted isobutyl phenylcyanoacrylates, RPhCH=C(CN)$CO_2CH_2CH(CH_3)_2$ (where R is 2,5-dibromo, 3,5-dibromo, 2,3-dichloro, 2,4-dichloro, 2,5-dichloro, 2,6-dichloro, 3,4-dichloro, 3,5-dichloro) were synthesized by the piperidine catalyzed Knoevenagel condensation of ring-disubstituted benzaldehydes and isobutyl cyanoacetate and characterized by CHN analysis, IR, ^{1}H and ^{13}C NMR. The acrylates were copolymerized with styrene in solution with radical initiation at 70°C. The compositions of the copolymers were calculated from nitrogen analysis.

* Contact: gkharas@depaul.edu

1. Introduction

Dibromo ring-substituted phenylcyanoacrylates (PCA) were reported in a variety of applications. Thus, 3,5-dibromo ring-substituted PCA was mentioned in syntheses of (1) spiro[2.3]hexanes from methylenecyclopropane and cyanoalkenes catalyzed by a Tin-ate complex [1]; (2) phenylsuccinimide derivatives with anticonvulsant properties [2, 3]. 3,4-dichloro ring-substituted PCA was prepared by Knoevenagel condensation at room temperature using SeO_2/ZrO_2 catalyst in water-medium and solvent-free conditions [4]. It was used in a highly efficient protocol for the regio- and stereo-selective synthesis of spiro pyrrolidine and pyrrolizidine derivatives by multicomponent reaction [5] and in Knoevenagel condensation involving a PEG bridged tertiary amine functionalized ionic liquid that exhibited thermoregulated reversible biphasic behavior with cyclohexane /isopropanol mixtures [6], as well as in synthesis of 5,6-dichloroindan-1-acids and their tetrazolyl derivatives as analgesic and anti-inflammatory agents [7]. Other applications of this PCA include synthesis of 1,8-diazabicyclo[-5.4.0]-undec-7-ene by catalyzed Knoevenagel condensation of aromatic aldehydes with active methylene compounds under solvent-free conditions [8], preparation of pyrimidine derivatives as CXCR2 receptor antagonists [9], synthesis of 2-amino-4-aryl-5,6-dihydro-4H-pyrano[3,2-c]quinolin-5-one derivatives in water [10], synthesis of new pyridine, pyridone, pyrazole, thiophene, fused pyrimidine and triazine derivatives via β-amino-β-(pyrid-4-yl)acrylonitrile [11], synthesis of dibenzo[c,f]chromenes, dibenzo[c,h]chromenes and benzo[7,8]chromeno[3,4-f]isoindoles as antimicrobial agents [12], synthesis and studies of antimicrobial activity of substituted imidazolidinediones and thioxoimidazolidinones [13], in studies of neuroleptic activity and

dopamine-uptake inhibition in 1-piperazino-3-phenylindans [14], and in synthesis of 2-methoxy-5-chloro-, 3-chloro-4-methoxy-, and 3,4-dichlorophenylsuccinic acids [15].

Earlier we have reported synthesis and styrene copolymerization a number of dibromo and dichloro ring-substituted PCAs, such esters as methyl [16, 17], ethyl [18], propyl [19, 20], isopropyl [21], butyl [22], 2-methoxyethyl [23], and octyl [24].

In this work we have prepared novel dibromo and dichloro ring-disubstituted isobutyl PCA, $RPhCH=C(CN)CO_2CH_2CH(CH_3)_2$, where R is 2,5-dibromo, 3,5-dibromo, 2,3-dichloro, 2,4-dichloro, 2,5-dichloro, 2,6-dichloro, 3,4-dichloro, 3,5-dichloro, 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 [25].

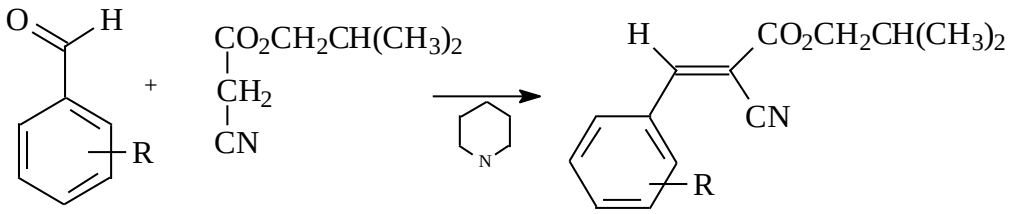
2. Experimental

2,5-Dibromo, 3,5-dibromo, 2,3-dichloro, 2,4-dichloro, 2,5-dichloro, 2,6-dichloro, 3,4-dichloro, 3,5-dichloro benzaldehydes, isobutyl cyanoacetate, piperidine, styrene, 1,1'-azobis(cyclohexanecarbonitrile) (ABCN), and toluene supplied from Sigma-Aldrich Co., were used as received. Instrumentation is reported in [26].

3. Results and discussion

3.1. Synthesis and characterization of isobutyl phenylcyanoacrylates

All isobutyl phenylcyanoacrylates (IPCA) compounds were synthesized by Knoevenagel condensation [27] of appropriate benzaldehydes with isobutyl cyanoacetate, catalyzed by base, piperidine (Scheme 1).



Scheme 1. Synthesis of isobutyl R-phenylcyanoacrylates, where R is 2,5-dibromo, 3,5-dibromo, 2,3-dichloro, 2,4-dichloro, 2,5-dichloro, 2,6-dichloro, 3,4-dichloro, 3,5-dichloro.

The preparation procedure was essentially the same for all the monomers. In a typical synthesis, equimolar amounts of isobutyl 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 reactions was allowed to proceed 48 hrs at r.t. 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. Melting points of the compounds in crystalline state were measured by DSC. The compounds were characterized by IR, ^{1}H and ^{13}C NMR spectroscopies. No stereochemical analysis of the novel ring-substituted IPCA was performed since no stereoisomers (*E* or/and *Z*) of known configuration were available.

3.1.1. ***Isobutyl 2,5-dibromophenylcyanoacrylate***

Yield: 70.3%; mp 86.4°C; ^{1}H NMR: δ 8.5 (s, 1H, CH=), 7.9-7.2 (m, 3H, Ph), 4.1 (d, 2H, CH_2), 2.0 (m, 1H, CH), 1.0 (d, 6H, CH_3); ^{13}C NMR: δ 162 (C=O), 151 (HC=), 137, 134,

131, 124, 120 (Ph), 116 (CN), 101 (C=), 72 (CH_2), 28 (CH), 17 (CH_3); IR: (cm^{-1}) 2873 (m, C-H), 2232 (m, CN), 1734 (s, C=O), 1686 (s, C=C), 1248 (s, C-O-CH_3), 824 (s, C-H out of plane). Anal. calcd. for $C_{14}H_{13}Br_2NO_2$: C, 43.44; H, 3.39; N, 3.62; Found: C, 45.12; H, 3.26; N, 3.66.

3.1.2. ***Isobutyl 3,5-dibromophenylcyanoacrylate***

Yield 71.4%; mp 122.9°C; ^{1}H NMR: δ8.2 (s, 1H, CH=), 8.1-7.6 (m, 3H, Ph), 4.1 (d, 2H, CH_2), 2.1 (m, 1H, CH), 1.0 (d, 6H, CH_3); ^{13}C NMR: δ162 (C=O), 151 (HC=), 136, 134, 132, 128 (Ph), 115 (CN), 108 (C=), 73 (CH_2), 28 (CH), 19 $(CH_3)_2$; IR: (cm^{-1}) 3147-2868 (m, C-H), 2224 (m, CN), 1718 (s, C=O), 1612 (s, C=C), 1271 (s, C-O-CH_3), 883 (s, C-H out of plane). Anal. calcd. for $C_{14}H_{13}Br_2NO_2$: C, 43.44; H, 3.39; N, 3.62; Found: C, 40.91; H, 3.13; N, 2.84.

3.1.3. ***Isobutyl 2,3-dichlorophenylcyanoacrylate***

Yield 82.8%; mp 37.2°C; ^{1}H NMR: δ8.8 (s, 1H, CH=), 8.1-7.1 (m, 3H, Ph), 4.2 (d, 2H, CH_2), 2.1 (m, 1H, CH), 1.0 (d, 6H, CH_3); ^{13}C NMR: δ162 (C=O), 151 (HC=), 136, 134, 132, 128 (Ph), 115 (CN), 108 (C=), 73 (CH_2), 28 (CH), 19 $(CH_3)_2$; IR: (cm^{-1}) 2962 (m, C-H), 2230 (m, CN), 1730 (s, C=O), 1638 (s, C=C), 1281 (s, C-O-CH_3), 822, 751 (s, C-H out of plane). Anal. calcd. for $C_{14}H_{13}Cl_2NO_2$: C, 56.40; H, 4.39; N, 4.70; Found: C, 55.59; H, 4.42; N, 4.47.

3.1.4. ***Isobutyl 2,4-dichlorophenylcyanoacrylate***

Yield 88%; mp 83.1°C; ^{1}H NMR δ8.7 (s, 1H, CH=), 8.2-7.2 (m, 3H, Ph), 4.1 (d, 2H, CH_2), 2.0 (m, 1H, CH), 1.0 (d, 6H, CH_3); ^{13}C NMR δ 162 (C=O), 149 (HC=), 140, 138,

131, 128 (Ph), 115 (CN), 107 (C=), 73 (CH_2), 28 (CH), 19 (CH_3); IR (cm^{-1}): 2961 (m, C-H), 2225 (m, CN), 1728 (s, C=O), 1612 (s, C=C), 1286 (s, C-O-CH_3), 782, 755 (s, C-H out of plane). Anal. Calcd. for $C_{14}H_{13}Cl_2NO_2$: C, 56.40; H, 4.39; N, 4.70; Found: C, 56.32; H, 4.39; N, 4.78.

3.1.5. ***Isobutyl 2,5-dichlorophenylcyanoacrylate***

Yield 70.5%; mp 46.7°C; ^{1}H NMR: δ8.5 (s, 1H, CH=), 8.2-7.2 (m, 3H, Ph), 4.1 (d, 2H, CH_2), 2.1 (m, 1H, CH), 1.0 (d, 6H, CH_3); ^{13}C NMR: δ 162 (C=O), 149 (HC=), 134, 132, 130, 114 (Ph), 114 (CN), 107 (C=), 73 (CH_2), 28 (CH), 19 (CH_3); IR: (cm^{-1}) 2966 (m, C-H), 2220 (m, CN), 1728 (s, C=O), 1587 (s, C=C), 1271 (s, C-O-CH_3), 821, 758 (s, C-H out of plane). Anal. calcd. for $C_{14}H_{13}Cl_2NO_2$: C, 56.40; H, 4.39; N, 4.70; Found: C, 56.40; H, 4.44; N, 4.82.

3.1.6. ***Isobutyl 2,6-dichlorophenylcyanoacrylate***

Yield 72.7%; mp 65.5°C; ^{1}H NMR: δ8.3 (s, 1H, CH=), 7.2 (s, 3H, Ph), 4.1 (d, 2H, CH_2), 2.1 (m, 1H, CH), 1.0 (d, 6H, CH_3); ^{13}C NMR: δ 161 (C=O), 151 (HC=), 134, 134, 131, 129 (Ph), 116 (CN), 103 (C=), 73 (CH_2), 27 (CH), 19 $(CH_3)_2$; IR: (cm^{-1}) 2967 (m, C-H), 2233 (m, CN), 1732 (s, C=O), 1614 (s, C=C), 1232 (s, C-O-CH_3), 781 (s, C-H out of plane). Anal. calcd. for $C_{14}H_{13}Cl_2NO_2$: C, 56.40; H, 4.39; N, 4.70; Found: C, 56.87; H, 4.51; N, 4.74.

3.1.7**.** ***Isobutyl 3,4-dichlorophenylcyanoacrylate***

Yield 74%; mp 157.2°C; ^{1}H NMR δ8.3 (s, 1H, CH=), 8.1-7.2 (m, 3H, Ph), 4.2 (d, 2H, CH_2), 2.1 (m, 1H, CH), 1.0 (d, 6H, CH_3) ; ^{13}C NMR δ 162 (C=O), 152 (HC=), 137, 134,

133, 132, 130 (Ph), 115 (CN), 105 (C=), 73 (CH_2), 28 (CH), 19 $(CH_3)_2$; IR (cm^{-1}): 3532-2873 (m, C-H), 2221 (m, CN), 1718 (s, C=O), 1614 (s, C=C), 1227 (s, C-O-CH_3), 811, 743 (s, C-H out of plane). Anal. Calcd. for $C_{14}H_{13}Cl_2NO_2$: C, 56.40; H, 4.39; N, 4.70; Found: C, 56.27; H, 4.39; N, 4.73.

3.1.8. ***Isobutyl 3,5-dichlorophenylcyanoacrylate***

Yield 81%; mp 117.1°C; ^{1}H NMR δ 8.1 (s, 1H, CH=), 8.0-7.2 (s, 3H, Ph), 4.1 (s, 2H, CH_2), 2.0 (m, 1H, CH), 1.0 (d, 6H, $(CH_3)_2$; ^{13}C NMR δ 162 (C=O), 152 (HC=), 136, 134, 133, 129 (Ph), 114 (CN), 106 (C=), 73 (CH_2), 28 (CH), 19 $(CH_3)_2$; IR (cm^{-1}): 2972 (m, C-H), 2228 (m, CN), 1720 (s, C=O), 1574 (s, C=C), 1271 (s, C-O-CH_3), 841, 759 (s, C-H out of plane). Anal. Calcd. for $C_{14}H_{13}Cl_2NO_2$: C, 56.40; H, 4.39; N, 4.70; Found: C, 56.19; H, 4.46; N, 5.13.

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

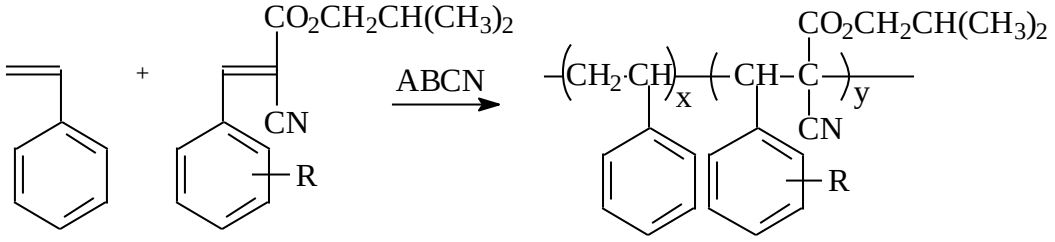
Copolymers of the styrene (ST) and the IPCA compounds, P(ST-co-IPCA) were prepared in 25-mL glass screw cap vials at ST/IPCA = 3 (mol) the monomer feed using 0.12 mol/L of ABCN at an overall monomer concentration 2.44 mol/L in 10 mL of toluene. The copolymerization was conducted at 70ºC. After a predetermined 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 novel synthesized IPCA 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).

Table 1. Copolymerization of isobutyl phenylcyanoacrylates with styrene.

R	Yield[a] (wt%)	N (wt%)	ST in copol. (mol%)	IPCA in copol. (mol%)
2,5-Dibromo	13.6	1.20	88.2	11.8
3,5-Dibromo	10.8	1.76	79.7	20.3
2,3-Dichloro	11.5	2.54	70.9	29.1
2,4-Dichloro	13.8	2.81	65.8	34.2
2,5-Dichloro	14.5	2.55	70.7	29.3
2,6-Dichloro	11.9	1.44	86.6	13.4
3,4-Dichloro	12.5	2.46	72.3	27.7
3,5-Dichloro	11.6	2.61	69.6	30.4

Nitrogen elemental analysis showed that between 11.8 and 30.4 mol% of IPCA is present in the copolymers, which is indicative of relatively high reactivity of the IPCA monomers towards ST radical which is typical of different esters of PCA. Since IPCA monomers do not homopolymerize, the most likely structure of the copolymers would be isolated IPCA monomer (y = 1) units alternating with short ST sequences (x > 1) (Scheme 2).



Scheme 2. Copolymerization of ST and the ring-substituted isobutyl phenylcyanoacrylates, RPhCH = $C(CN)CO_2CH_2CH(CH_3)_2$, R = 2,5-dibromo, 3,5-dibromo, 2,3-dichloro, 2,4-dichloro, 2,5-dichloro, 2,6-dichloro, 3,4-dichloro, 3,5-dichloro.

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 dibromo and dichloro and ring-disubstituted isobutyl phenylcyanoacrylates, $RPhCH=C(CN)CO_2CH_2CH(CH_3)_2$ (where R is 2,5-dibromo, 3,5-dibromo, 2,3-dichloro, 2,4-dichloro, 2,5-dichloro, 2,6-dichloro, 3,4-dichloro, 3,5-dichloro) were synthesized and copolymerized with styrene. The compositions of the copolymers were calculated from nitrogen analysis.

Acknowledgments

The authors are grateful to acknowledge that the project was partly supported by Chicago Society of Coating Technology (CSCT).

References

1. Diastereoselective Synthesis of Spiro[2.3]hexanes from Methylenecyclopropane and Cyanoalkenes Catalyzed by a Tin-Ate Complex. Suzuki, Itaru; Shimazu, Jun-ya; Tsunoi, Shinji; Shibata, Ikuya. European Journal of Organic Chemistry (2019), 2019(22), 3658-3661.

2. Synthesis and properties of cyclic derivatives of phenylsuccinic acid. VII. New phenylsuccinimide derivatives with anticonvulsant properties. Lange, Jerzy; Lapszewicz, Jacek. Acta Poloniae Pharmaceutica (1978), 35(3), 289-94.

3. Synthesis and properties of new cyclic derivatives of succinic acid with anticonvulsant activity. Lange, J.; Rump, S.; Galecka, E.; Ilczuk, I.; Lechowska-Postek, M.; Rabsztyn, T.; Szymanska, T.; Walczyna, K. Pharmazie (1977), 32(2), 82-4.

4. Knoevenagel condensation at room temperature using SeO2/ZrO2 catalyst in water-medium and solvent-free conditions. Banothu, Vijaya; Basude, Manohar; Battu, Satyanarayana. Journal of Chemical and Pharmaceutical Research (2013), 5(10), 97-101.

5. A highly efficient protocol for the regio- and stereo-selective synthesis of spiro pyrrolidine and pyrrolizidine derivatives by multicomponent reaction. Dandia, Anshu; Jain, Anuj K.; Laxkar, Ashok K.; Bhati, Dharmendra S. Tetrahedron Letters (2013), 54(24), 3180-3184.

6. A PEG bridged tertiary amine functionalized ionic liquid exhibiting thermoregulated reversible biphasic behavior with cyclohexane/isopropanol: synthesis and application in Knoevenagel condensation. Luo, Jun; Xin, Tantan; Wang, Yinglei. New Journal of Chemistry (2013), 37(2), 269-273.

7. Synthesis of 5,6-dichloroindan-1-acids and their tetrazolyl derivatives as analgesic and anti-inflammatory agents. Pal, Rajib Kumar; Yasmin, Hasina; Nahar, Lutfun; Datta, Bidyut Kanti; Chowdhury, Abul Kalam Azad; Kundu, Joydeb Kumar; Bachar, Sitesh Chandra; Sarker, Satyajit Dey. Medicinal Chemistry (2012), 8(5), 874-882.

8. 1,8-Diazabicyclo[-5.4.0]-undec-7-ene catalyzed Knoevenagel condensation of aromatic aldehydes with active methylene compounds under solvent-free conditions. Wang, Li-min; Hu, Wen-ji; Pi, Chun-yan; Ying, An-guo. Jingxi Yu Zhuanyong Huaxuepin (2011), 19(7), 16-21.

9. Pyrimidine derivatives as CXCR2 receptor antagonists and their preparation, pharmaceutical compositions and use in the treatment of diseases. Press, Neil John; Hunt, Peter; Porter, David; Janus, Diana. PCT Int. Appl. (2008), WO 2008061740 A1 20080529.

10. Synthesis of 2-amino-4-aryl-5,6-dihydro-4H-pyrano[3,2-c]quinolin-5-one derivatives in water. Wang, Xiang-Shan; Zeng, Zhao-Sen; Li, Yu-Ling; Shi, Da-Qing; Tu, Shu-Jiang; Wei, Xian-Yong; Zong, Zhi-Min. Youji Huaxue (2006), 26(2), 228-232.

11. β-Amino-β-(pyrid-4-yl)acrylonitrile in heterocyclic synthesis: synthesis of some new pyridine, pyridone, pyrazole, thiophene, fused pyrimidine and triazine derivatives. Ghozlan, Said A. S.; Hassanien, Abu Zeid A. Tetrahedron (2002), 58(46), 9423-9429.

12. A novel synthesis of dibenzo[c,f]chromenes, dibenzo[c,h]chromenes and benzo[7,8] chromeno[3,4-f]isoindoles as antimicrobial agents. El-Gaby, Mohamed S. A.; Zahran, Medhat A.; Ismail, Magda M. F.; Ammar, Yousry A. Farmaco (2000), 55(3), 227-232.

13. Synthesis and antimicrobial activity of substituted imidazolidinediones and thioxoimidazolidinones. Albuquerque, J. F. C.; Rocha Filho, J. A.; Brandao, S. S. F.; Lima, M. C. A.; Ximenes, E. A.; Galdino, S. L.; Pitta, I. R.; Chantegrel, J.; Perrissin, M.; Luu-Duc, C. Farmaco (1999), 54(1-2), 77-82.

14. Neuroleptic activity and dopamine-uptake inhibition in 1-piperazino-3-phenylindans. Boegesoe, Klaus P. Journal of Medicinal Chemistry (1983), 26(7), 935-47.

15. Substituted dicarboxylic acids. I. Synthesis of 2-methoxy-5-chloro-, 3-chloro-4-methoxy-, and 3,4-dichlorophenylsuccinic acids. Genge, D. K.; Trivedi, J. J. Journal of the Indian Chemical Society (1957), 34, 915-16.

16. Novel Copolymers of Styrene. 11. Some Ring-Substituted Methyl 2-Cyano-3-phenyl-2-propenates. G.B. Kharas, S.E. Chavez, A.N. Luna, E.E. Lusk, D.P. Mendez, D.S. O'Rourke, C.S. Roat, S.G. Robinson, G.S. Stamelos, J.D. Schoenburg, D.H. Vinanzaca, S. Zermeno, M.P. O'Mara. J. Macromol. Sci. A51 (1), 1-5 (2014).

17. Novel Copolymers of Trisubstituted Ethylenes and Styrene – 5. Ring-disubstituted Methyl 2-Cyano-3-phenyl-2-propenoates. K.Kim, M. Morales, M.J. Scully, C.D. Seitz, A.-M. Sikora, A.M. Spaulding, R.Sudman, A.C. Sullivan, G.B. Kharas, K.Watson. Designed Monomers and Polymers, 2, 333 (1999).

18. Novel Copolymers of Styrene. 7. Dihalogen Ring-substituted Ethyl 2-Cyano-3-phenyl-2-propenoates and Styrene. G.B. Kharas, A.A. Delgado, K. Aco, L.M. Cardenas, M.L. Lopez, A.D. Mazerat, P.D. Merageas, D.M. Perone, M.D. Pickering, C.S. Samuelson, C.L. Shelly. J. Macromol. Sci. A50 (4) 365-369 (2013).

19. Novel Copolymers of Styrene. 9. Chloro and Fluoro Ring-Disubstituted Propyl 2-Cyano-3-Phenyl-2-Propenoates. G.B. Kharas, W.S. Schjerven, F.A.S. Aldakheel, E.J. Crespo, Z.M. Gaskell, K.J.M. Jordan, J.D. Knight, A.R. Moses, and A.H.A. Niyazi. J. Macromol. Sci. A54(2) 67-70 (2017).

20. Novel Copolymers of Styrene. 10. Bromo and Chloro Ring-Disubstituted Propyl 2-Cyano-3-Phenyl-2-Propenoates. G.B. Kharas, J. Bates, A.T. Boyd, J.N. Burke, J.L. Crosby, S.B. Sundquist, C.C. Zoleta, A.K. Zurek, and P.L. Bromby II. J. Macromol. Sci. A54(6) 372-375 (2017).

21. Synthesis and Styrene Copolymerization of Novel Dihalogen Ring-Substituted Isopropyl Cyanophenylacrylates. S. Flieger, P.M. McCaw, S. Mouradkhanian, B.

Pedroza, M.M. Peffley, R.L. Pride, P.R. Ramirez, M.S. Rogers, B. Romanov, M. Saleh, C. Soler, L.D. Warnick, and G.B. Kharas. (2019) ChemRxiv Preprint. https://doi.org/10.26434/chemrxiv.11336852.v1

22. Novel Copolymers of Styrene. 10. Halogen Ring-substituted Butyl 2-Cyano-3-Phenyl-2-Propenoates. G.B. Kharas, H. Feng, S.G. Robinson, A. Eduardo, K.M.A. Carlson, V. Djordjevic, E. Dominguez, K.M. English, R.J. Hudson, and D.B. Kennedy. J. Macromol. Sci. A53(5) 253-257 (2016).
23. Synthesis and styrene copolymerization of novel trisubstituted ethylenes: 9. Ring-disubstituted 2-methoxyethyl 2-cyano-3-phenyl-2-propenoates. Ehab Abdelhamid, Hussein Abourahma, Julia Bellino, Joshua S.M. Bowser, Lourdes De Anda, Richard E. DeMaria, Erika Galeczka, Madeline Martin, Abdulrafey Nasir, Alexis Pawlak, Ashley Pezza, Rachel Quade, Anna Schell, Valerie Tafoya, Bhavi D. Vashi, Sabah I. Vikaruddin, Sophia L. Zygowski, Sara M. Rocus, William S. Schjerven, and Gregory B. Kharas. ChemRxiv. Preprint. (10.02.2021). https://doi.org/10.26434/chemrxiv.13262660.v9
24. Synthesis and styrene copolymerization of novel trisubstituted ethylenes: 8. Dichloro and difluoro ring-substituted octyl phenylcyanoacrylates. Christian Ibarra, Andy N. La, Victoria Orban, Taha Raziuddin, Amir Sedighzadeh, Amina Torlo, Ania Tyrawa, Peter A. Wild Crea, Jessica E. Youngs, Stephanie Block, David C. Dainko, Sara M. Rocus, William S. Schjerven, and Gregory B. Kharas. ChemRxiv. Cambridge Open Engage Version 19 Jul 15, 2021. https://doi.org/10.33774/chemrxiv-2021-k812v-v19
25. SciFinder structure search Mar 4, 2022.

26. Synthesis and styrene copolymerization of novel alkyl ring-substituted isobutyl 2-cyano-3-phenyl-2-propenoates. Schjerven, William S.; Groy, Randi; Antonishina, Yekaterina S.; Black, Claire I.; Bolin, Madysen P.; Caniglia, John; Daroach, Deepak P.; Farooqui, Farah T.; Feiz, Yalda; Garcia, Sam; Gasparini, Gabriella; Kharas, Gregory B. Abstracts of Papers, 259th ACS National Meeting & Exposition, Philadelphia, PA, United States, March 22-26, (2020), POLY-0388.

27. 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).