

<http://doi.org/10.32864/polymmattech-2023-9-3-47-54>

УДК 542.06:541.64:547.1:546.273

МЕХАНОХИМИЧЕСКИЙ СИНТЕЗ ПОЛИ(ФЕНИЛБОРДИФЕНИЛСИЛОКСАНОВ)

В. В. ЛИБАНОВ⁺, А. А. КАПУСТИНА, Н. П. ШАПКИН

Департамент химии и материалов, Институт наукоемких технологий и передовых материалов, Дальневосточный федеральный университет, о. Русский, п. Аякс, 10, Лабораторный корпус, 690922, г. Владивосток, Россия

Поскольку соединения бора (в том числе фенилбороновая кислота) обладают биологической активностью, их введение в полимерную цепь позволит получить материалы с полезными свойствами. Например, борсодержащие полимеры можно использовать в качестве покрытий для защиты от насекомых-переносчиков различных заболеваний. Поэтому целью нашей работы было введение фрагментов фенилбороновой кислоты в полимерную силсесквиоксановую цепь.

В работе впервые изучено механохимическое взаимодействие фенилбороновой кислоты с дифенилсиландиолом. Методом механохимической активации синтезированы олигомерные фенилбордифенилсилоксаны. Показано, что в результате механохимической активации основными побочными процессами являются отрыв фенильного заместителя от атома бора, образование 1,1'-бифенила и тримеризация фенилбороновой кислоты. Дифенилдигидроксисилан в условиях механохимической активации также частично тримеризуется. Установлено, что введение фенилбороновой кислоты с небольшим количеством ацетилацетона приводит к получению олигомерного фенилбордифенилсилоксана с соотношением Si/B примерно равным 1. При этом ацетилацетон взаимодействует с гидроксильными группами фенилбороновой кислоты, защищая исходные соединения от тримеризации. Нагревание полученного преполимера приводит к дальнейшей конденсации с увеличением молекулярно-массового распределения и молекулярной массы.

Показано, что механохимическая активация исходных соединений отдельно друг от друга приводит к их тримеризации. В случае фенилбороновой кислоты происходит отрыв фенильного заместителя с образованием метаборной кислоты и 1,1'-бифенила, что подтверждает радикальный и ион-радикальный механизмы механохимической активации.

Ключевые слова: дифенилсиландиол, фенилбороновая кислота, механохимический синтез, борсилоксаны, механохимия полимеров.

MECHANOCHEMICAL SYNTHESIS OF POLY(PHENYLBORONDIPHENYLSILOXANES)

V. V. LIBANOV⁺, A. A. KAPUSTINA, N. P. SHAPKIN

Department of Chemistry and Materials, Institute of High Technologies and Advanced Materials, Far Eastern Federal University, Russky Island, Ajax Bay, 10, Laboratory Building, 690922, Vladivostok, Russia

Since boron compounds (including phenylboronic acid) are biologically active, their introduction into the polymer chain will make it possible to obtain materials with useful properties. For example, boron-containing polymers can be used as coatings to protect against insect vectors of various diseases. Therefore, the aim of our work was to introduce phenylboronic acid fragments into the polymeric silsesquioxane chain.

In this work, the mechanochemical interaction of phenylboronic acid with diphenylsilanediol was studied for the first time. Oligomeric phenylborondiphenylsiloxanes have been synthesized by mechanochemical

⁺ Автор, с которым следует вести переписку. E-mail: libanov.vv@dvfu.ru

activation. It has been shown that, as a result of mechanochemical activation, the main side processes are abstraction of the phenyl substituent from the boron atom, formation of 1,1'-biphenyl, and trimerization of phenylboronic acid. Diphenyldihydroxysilane under the conditions of mechanochemical activation is also partially trimerized. It has been established that the introduction of phenylboronic acid with a small amount of acetylacetone leads to the production of oligomeric phenylborondiphenylsiloxane with a Si/B ratio of about 1. In this case, acetylacetone interacts with the hydroxyl groups of phenylboronic acid, protecting the starting compounds from trimerization. Heating the resulting prepolymer leads to further condensation with an increase in molecular weight distribution and molecular weight.

It has been shown that mechanochemical activation of the starting compounds separately from each other leads to their trimerization. In the case of phenylboronic acid, the abstraction of the phenyl substituent occurs with the formation of metaboric acid and 1,1'-biphenyl, which confirms the radical and radical ion mechanisms of mechanochemical activation.

Keywords: diphenylsilanediol, phenylboronic acid, mechanochemical synthesis, borosiloxanes, mechanochemistry of polymers.

Поступила в редакцию 03.08.2023

© В. В. Либанов, А. А. Капустина, Н. П. Шапкин, 2023

Для приобретения полного текста статьи, обращайтесь в [редакцию журнала](#)
Full text of articles can be purchased from the editorial office

Адрес редакции: ул. Кирова, 32а, 246050, г. Гомель, Беларусь
Телефон/факс: +375 (232) 34 06 36 / 34 17 11

Address: Kirov St., 32a, 246050, Gomel, Belarus
Phone: +375 (232) 34 06 36. Fax: +375 (232) 34 17 11

E-mail: polmatte@gmail.com
Web: <http://mpri.org.by/izdaniya/pmt/>

Образец цитирования:

Либанов В. В., Капустина А. А., Шапкин Н. П. Механохимический синтез поли(фенилбордифенилсилоксанов) // Полимерные материалы и технологии. 2023. Т. 9, № 3. С. 47–54. <http://doi.org/10.32864/polymmattech-2023-9-3-47-54>

Citation sample:

Libanov V. V., Kapustina A. A., Shapkin N. P. Mekhanokhimicheskiy sintez poli(fenilbordifenilsiloksanov) [Mechanochemical synthesis of poly(phenylborondiphenylsiloxanes)]. *Polimernye materialy i tekhnologii* [Polymer Materials and Technologies], 2023, vol. 9, no. 3, pp. 47–54. <http://doi.org/10.32864/polymmattech-2023-9-3-47-54>

Литература

1. Carneiro R. L., de Melo C. C., de Alvarenga B. R., Dayo Owoyemi B. C., Ellena J., da Silva C. C. P. Mechanochemical synthesis and characterization of a novel AAs–Flucytosine drug–drug cocrystal: A versatile model system for green approaches // *Journal of Molecular Structure*, 2022, vol. 1251. doi: 10.1016/j.molstruc.2021.132052
2. Korchagin M. A., Dudina D. V., Gavrillov A. I., Bokhonov B. B., Bulina N. V., Panin A. V., Lyakhov N. Z. Combustion of titanium-carbon black high-energy ball-milled mixtures in nitrogen: Formation of titanium carbonitrides at atmospheric pressure // *Materials*, 2020, vol. 13. doi: 10.3390/ma13081810
3. Andreichikova M. P., Udalova T. A. Mechanochemical synthesis of highly dispersed molybdenum from magnesium molybdate. *Materials Today: Proceedings*, 2020, vol. 31, pp. 526–528. doi: 10.1016/j.matpr.2020.06.086
4. Kiseleva T. Y., Lazareva E. V., Zholudev S. I., Grigoreva T. F., Devyatkina E. T., Ivanenko I. P., Yakuta E. V., Ilyushin A. S., Lyakhov N. Z. Synthesis and study of perspective composite material based on mechanochemically synthesized magnesium ferrite and ultra-high molecular weight polyethylene // *Materials Today: Proceedings*, 2020, vol. 25, pp. 513–516. doi: 10.1016/j.matpr.2020.01.264
5. Vakili M., Qin R., Cagnetta G., Huang J., Wang B., Yu G. Improved fractal kinetic model to predict mechanochemical destruction rate of organic pollutants // *Chemosphere*, 2021, vol. 284. doi: 10.1016/j.chemosphere.2021.131307
6. Lou Z., Song L., Liu W., Wu Sh., He F., Yu J. Deciphering CaO-induced peroxydisulfate activation for destruction of halogenated organic pollutants in a low energy vibrational mill // *Chemical Engineering Journal*, 2022, vol. 431, is. 2. doi: 10.1016/j.cej.2021.134090

7. Santiago A., González J., Iruin J., Fernández-Berridi M. J., Muñoz M. E., Irusta L. Urethane/siloxane copolymers with hydrophobic properties // *Macromolecular Symposia*, 2012, vol. 321–322, pp. 150–154. doi: 10.1002/masy.201251126
8. Im H., Kim J. Enhancement of the thermal conductivity of aluminum oxide-epoxy terminated poly(dimethyl siloxane) with a metal oxide containing polysiloxane // *Journal of Materials Science*, 2011, vol. 46, pp. 6571–6580. doi: 10.1007/s10853-011-5604-7
9. Hao Y., Gao Y., Fan Y., Zhang C., Zhan M., Cao X., Shi X., Guo R. A tumor microenvironment-responsive poly(amidoamine) dendrimer nanoplatfor for hypoxia-responsive chemo/chemodynamic therapy // *J. Nanobiotechnol.*, 2022, vol. 20. doi: 10.1186/s12951-022-01247-6
10. Hu J., Ding L., Chen J., Fu J., Zhu K., Guo Q., Huang X., Xiong Y. Ultrasensitive dynamic light scattering immunosensing platform for NT-proBNP detection using boronate affinity amplification // *J. Nanobiotechnol.*, 2022, vol. 20. doi: 10.1186/s12951-021-01224-5
11. Huang D., Gao S., Luo Y., Zhou X., Lu Z., Zou L., Hu K., Zhao Z., Zhang Y. Glucose-sensitive membrane with phenylboronic acid-based contraction-type microgels as chemical valves // *J. Membrane Sci.*, 2022, vol. 650. doi: 10.1016/j.memsci.2022.120406
12. Liu N., Xiang X., Sun M., Li P., Qin H., Liu H., Zhou Y., Wang L., Wu L., Zhu J. Flexible hydrogel non-enzymatic QCM sensor for continuous glucose monitoring // *Biosensors and Bioelectronics: X*, 2022, vol. 10. doi: 10.1016/j.biosx.2022.100110
13. Liu B., Li J., Zhang Z., Roland J.D., Lee B.P. pH responsive antibacterial hydrogel utilizing catechol–boronate complexation chemistry // *Chem. Engin. J.*, 2022, vol. 441. doi: 10.1016/j.cej.2022.135808
14. Zhou Y., Chu F., Yang W., Qiu S., Hu Y. Innovative design of hierarchical cobalt-based borate functionalized black phosphorus structure with petal-like wrinkle: Enhancing the fire safety and mechanical properties of epoxy resin // *Composites Part B: Engineering*, 2022, vol. 238. doi: 10.1016/j.compositesb.2022.109886
15. Hsu C., Hwang P. The water uptake, thermal and mechanical properties, and aging resistance to thermo-oxidation of phenylboronic acid-modified benzoxazine-glass fiber composites // *J. Appl. Polymer Science*, 2022, vol. 139. doi: 10.1002/app.52135
16. Bugday N., Altin S., Bulut F., Altin E., Yaşar S. Boron-doped porous carbon material derived from ZIF-11: Investigation of cotton fabric supercapacitor and Li-ion battery performances // *International Journal of Energy Research*, 2022, vol. 46, pp. 7732–7748. doi: 10.1002/er.7676
17. Карякин Ю. В., Ангелов И. И. Чистые химические вещества. Изд. 4-е, доп. и пер. М.: Химия, 1974. 408 с.
18. де Векки Д. А., Москвин А. В., Петров М. Л., Резников А. Н., Скворцов Н. К., Тришин Ю. Г. Новый справочник химика и технолога. Основные свойства неорганических, органических и элементоорганических соединений. СПб.: Мир и Семья, 2002. 1280 с.
19. Lappert M. F. Organic Compounds of Boron // *Chem. Rev.*, 1956, vol. 56, pp. 959–1064. doi: 10.1021/cr50011a002
20. Bykova L. N., Kreshkov A. P., Kazaryan N. A., Pevzner I. D. Progress in the Analytical Chemistry of Non-aqueous Solutions // *Russ. Chem. Rev.*, 1968, vol. 37, pp. 278–297. doi: 10.1070/RC1968v037n04ABEH001634
21. Newstead E. G., Gulbierz J. E. Determination of Boron in Titanium Alloys by Ion Exchange Method // *Anal. Chem.*, 1957, vol. 29, pp. 1673–1674. doi: 10.1021/ac60131a033
22. Zhou X., Lai R., Li H., Stains C. I. The 8-Silyloxyquinoline Scaffold as a Versatile Platform for the Sensitive Detection of Aqueous Fluoride // *Analytical Chemistry*, 2015, vol. 87, pp. 4081–4086. doi: 10.1021/acs.analchem.5b00430
23. Bellamy L. J., Gerrard W., Lappert M. F., Williams R. L. Infrared spectra of boron compounds // *J. Chem. Soc.*, 1958, pp. 2412–2415. doi: 10.1039/JR9580002412
24. Nahm F. C., Rothery E. F., Niedenzu K. A Spectroscopic study of phenylboron halides // *J. Organometallic Chem.*, 1972, vol. 35, is. 1, pp. 9–17. doi: 10.1016/S0022-328X(00)86878-3
25. Smith A. L. Infrared spectra-structure correlations for organosilicon compounds // *Spectrochimica Acta.*, 1960, vol. 16, pp. 87–105. doi: 10.1016/0371-1951(60)80074-4
26. Chukin G. D., Ignat'eva L. A. A study of the active centers of silica gel by IR spectroscopy. I // *J. Appl. Spectrosc.*, 1968, vol. 8, pp. 527–529. doi: 10.1007/BF01103250

References

1. Carneiro R. L., de Melo C. C., de Alvarenga B. R., Dayo Owoyemi B. C., Ellena J., da Silva C. C. P. Mechanochemical synthesis and characterization of a novel AAs–Flucytosine drug–drug cocrystal: A versatile model system for green approaches. *Journal of Molecular Structure*, 2022, vol. 1251. doi: 10.1016/j.molstruc.2021.132052
2. Korchagin M. A., Dudina D. V., Gavrilov A. I., Bokhonov B. B., Bulina N. V., Panin A. V., Lyakhov N. Z. Combustion of titanium-carbon black high-energy ball-milled mixtures in nitrogen: Formation of titanium carbonitrides at atmospheric pressure. *Materials*, 2020, vol. 13. doi: 10.3390/ma13081810
3. Andreichikova M. P., Udalova T. A. Mechanochemical synthesis of highly dispersed molybdenum from magnesium molybdate. *Materials Today: Proceedings*, 2020, vol. 31, pp. 526–528. doi: 10.1016/j.matpr.2020.06.086
4. Kiseleva T. Y., Lazareva E. V., Zholudev S. I., Grigoreva T. F., Devyatkina E. T., Ivanenko I. P., Yakuta E. V., Ilyushin A. S., Lyakhov N. Z. Synthesis and study of perspective composite material based on mechanochemically synthesized magnesium ferrite and ultra-high molecular weight polyethylene. *Materials Today: Proceedings*, 2020, vol. 25, pp. 513–516. doi: 10.1016/j.matpr.2020.01.264
5. Vakili M., Qin R., Cagnetta G., Huang J., Wang B., Yu G. Improved fractal kinetic model to predict mechanochemical destruction rate of organic pollutants. *Chemosphere*, 2021, vol. 284. doi: 10.1016/j.chemosphere.2021.131307
6. Lou Z., Song L., Liu W., Wu Sh., He F., Yu J. Deciphering CaO-induced peroxydisulfate activation for destruction of halogenated organic pollutants in a low energy vibrational mill. *Chemical Engineering Journal*, 2022, vol. 431, is. 2. doi: 10.1016/j.cej.2021.134090
7. Santiago A., González J., Iruin J., Fernández-Berridi M. J., Muñoz M. E., Irusta L. Urethane/siloxane copolymers with hydrophobic properties. *Macromolecular Symposia*, 2012, vol. 321–322, pp. 150–154. doi: 10.1002/masy.201251126
8. Im H., Kim J. Enhancement of the thermal conductivity of aluminum oxide-epoxy terminated poly(dimethyl siloxane) with a metal oxide containing polysiloxane. *Journal of Materials Science*, 2011, vol. 46, pp. 6571–6580. doi: 10.1007/s10853-011-5604-7
9. Hao Y., Gao Y., Fan Y., Zhang C., Zhan M., Cao X., Shi X., Guo R. A tumor microenvironment-responsive poly(amidoamine) dendrimer nanoplatfor for hypoxia-responsive chemo/chemodynamic therapy. *J. Nanobiotechnol.*, 2022, vol. 20. doi: 10.1186/s12951-022-01247-6
10. Hu J., Ding L., Chen J., Fu J., Zhu K., Guo Q., Huang X., Xiong Y. Ultrasensitive dynamic light scattering immunosensing platform for NT-proBNP detection using boronate affinity amplification. *J. Nanobiotechnol.*, 2022, vol. 20. doi: 10.1186/s12951-021-01224-5
11. Huang D., Gao S., Luo Y., Zhou X., Lu Z., Zou L., Hu K., Zhao Z., Zhang Y. Glucose-sensitive membrane with phenylboronic acid-based contraction-type microgels as chemical valves. *J. Membrane Sci.*, 2022, vol. 650. doi: 10.1016/j.memsci.2022.120406
12. Liu N., Xiang X., Sun M., Li P., Qin H., Liu H., Zhou Y., Wang L., Wu L., Zhu J. Flexible hydrogel non-enzymatic QCM sensor for continuous glucose monitoring. *Biosensors and Bioelectronics: X*, 2022, vol. 10. doi: 10.1016/j.biosx.2022.100110
13. Liu B., Li J., Zhang Z., Roland J.D., Lee B.P. pH responsive antibacterial hydrogel utilizing catechol–boronate complexation chemistry. *Chem. Engin. J.*, 2022, vol. 441. doi: 10.1016/j.cej.2022.135808
14. Zhou Y., Chu F., Yang W., Qiu S., Hu Y. Innovative design of hierarchical cobalt-based borate functionalized black phosphorus structure with petal-like wrinkle: Enhancing the fire safety and mechanical properties of epoxy resin. *Composites Part B: Engineering*, 2022, vol.

238. doi: 10.1016/j.compositesb.2022.109886
15. Hsu C., Hwang P. The water uptake, thermal and mechanical properties, and aging resistance to thermo-oxidation of phenylboronic acid-modified benzoxazine-glass fiber composites. *J. Appl. Polymer Science*, 2022, vol. 139. doi: 10.1002/app.52135
16. Bugday N., Altin S., Bulut F., Altin E., Yaşar S. Boron-doped porous carbon material derived from ZIF-11: Investigation of cotton fabric supercapacitor and Li-ion battery performances. *International Journal of Energy Research*, 2022, vol. 46, pp. 7732–7748. doi: 10.1002/er.7676
17. Karyakin Yu. V., Angelov I. I. *Chistye khimicheskie veshche-stva* [Pure Chemicals]. Moscow : Khimiya Publ., 1974. 408 p.
18. de Vekki D. A., Moskvina A. V., Petrov M. L., Reznikov A. N., Skvortsov N. K., Trishin Yu. G. *Novyy spravochnik khimika i tekhnologa. Osnovnye svoystva neorganicheskikh, organicheskikh i elementoorganicheskikh soedineniy* [New handbook for chemist and technologist. Basic properties of inorganic, organic and organoelement compounds]. Saint-Petersburg : Mir i Sem'ya Publ., 2002. 1280 p.
19. Lippert M. F. Organic Compounds of Boron. *Chem. Rev.*, 1956, vol. 56, pp. 959–1064. doi: 10.1021/cr50011a002
20. Bykova L. N., Kreshkov A. P., Kazaryan N. A., Pevzner I. D. Progress in the Analytical Chemistry of Non-aqueous Solutions. *Russ. Chem. Rev.*, 1968, vol. 37, pp. 278–297. doi: 10.1070/RC1968v037n04ABEH001634
21. Newstead E. G., Gulbierz J. E. Determination of Boron in Titanium Alloys by Ion Exchange Method. *Anal. Chem.*, 1957, vol. 29, pp. 1673–1674. doi: 10.1021/ac60131a033
22. Zhou X., Lai R., Li H., Stains C. I. The 8-Silyloxyquinoline Scaffold as a Versatile Platform for the Sensitive Detection of Aqueous Fluoride. *Analytical Chemistry*, 2015, vol. 87, pp. 4081–4086. doi: 10.1021/acs.analchem.5b00430
23. Bellamy L. J., Gerrard W., Lippert M. F., Williams R. L. Infrared spectra of boron compounds. *J. Chem. Soc.*, 1958, pp. 2412–2415. doi: 10.1039/JR9580002412
24. Nahm F. C., Rothergy E. F., Niedenzu K. A Spectroscopic study of phenylboron halides. *J. Organometallic Chem.*, 1972, vol. 35, is. 1, pp. 9–17. doi: 10.1016/S0022-328X(00)86878-3
25. Smith A. L. Infrared spectra-structure correlations for organosilicon compounds. *Spectrochimica Acta.*, 1960, vol. 16, pp. 87–105. doi: 10.1016/0371-1951(60)80074-4
26. Chukin G. D., Ignat'eva L. A. A study of the active centers of silica gel by IR spectroscopy. I. *J. Appl. Spectrosc.*, 1968, vol. 8, pp. 527–529. doi: 10.1007/BF01103250
-