Synthesis and characterization of a cross-linking monomer based on 1,3-diallyl-1,3-di[bicyclo[4.2.0]octa-1,3,5-trien-3-yl]-1,3-dimethyl-siloxane

K S Levchenko¹, E G Adamov¹, D U Demin², K A Chudov¹, A V Bulanova³, K A Lyssenko⁴, A Yu Kalashnikov⁵, P S Shmelin², E P Grebennikov²

¹RTU MIREA – Russian Technological University, 86 Vernadsky Avenue, Moscow, 119571, Russia
² JSC «Technomash», 4 Ivana Franko Str., Moscow 121108, Russian Federation
³ Nanotechnology Education and Research Center South Ural State University, 76 Lenina Avenue, Chelyabinsk, 454080, Russia
⁴ M.V. Lomonosov Moscow State University, Chemistry Department, 1 Leninskie Gory Str., Building 3, Moscow 119991, Russian Federation
⁵ JSC "Russian space systems", 53 Aviamotornaya Str., Moscow 111250, Russian Federation

Abstract. New cross-linking monomer based on 1,3-diallyl-1,3-di[bicyclo[4.2.0]octa-1,3,5-trien-3-yl]-1,3-dimethyl-siloxane (BCB-All) was synthesized and its physical properties were studied. BCB-All was incorporated into copolymer with TGM-3 and PFHDA by two stage thermal polymerization. The cross-linking of the copolymers occurs by thermo-initiated ring-opening reaction of BCB at 120-200°C. Resulting BCB-All homopolymer, BCB-All-TGM-3 (50:50), and BCB-All-PFHDA (50:50) copolymers have high thermal stability (T_d5%, =464°C, 322°C, 435°C respectively) and good dielectric properties (ε=2.34-2.48 at 10Hz).

1. Introduction
Benzocyclobutene (BCB) is an attractive compound, which has aroused extensive interests in developing cross-linked materials with exceptional properties [1]. The advantages of benzocyclobutene is in its ability to thermally isomerize with the formation of active o-xylylene, which is capable to enter into polymerization, dimerization[4+4] or [4+2] cycloaddition reactions. Depending on the environment, the active o-xylylene form of benzocyclobutene is able to interact either with active double bonds of alkenes, or in the absence of such, to form structures 4 or 5 (Scheme 1). [2]. The great advantage of such cross-linking is the absence of low molecular weight by-products capable of deteriorating the homogeneity, dielectric, mechanic and optical properties of the final polymers. In any case, benzocyclobutene-based polymers are usually characterized by high thermal stability (<550°C [3,4]) and excellent dielectric properties (ε=2.3-2.9 at 1MHz). Thuse benzocyclobutene is used as the starting compound for the synthesis of a number of monomeric and polymeric materials with photochemical and thermal curing, which are used in electronics [5-8] and photonics [9-10], as optical waveguides [11], dielectric in high-density electronic modules, photoresists [12-14] and etc. A series of reviews is devoted to BCB - based polymer materials where detailed aspects of their construction and properties are considered [2, 15-17].

In this paper, we consider a method for the synthesis and properties of a hybrid monomer molecule consisting of three functional fragments. The allyl and benzocyclobutene fragments provide cross-
linking of the resulting polymer. The siloxane fragment allows to obtain a monomer in the liquid state, which is convenient technologically.

\[
\begin{align*}
\text{Scheme 1.} & \quad \text{Scheme of dimerization and polymerization of BCB derivatives in the presence or absence of double bonds}
\end{align*}
\]

2. Results and discussion

2.1. Synthesis of BCB-All
The BCB-All monomer was synthesized from benzocyclobutene as a result of a three-step procedure (Scheme 2). In the first step, benzocyclobutene (1) was brominated with bromine in a two-phase aqueous system according to the known method with 70-72% yield [18]. Reaction 2 with Mg in THF at 30-40°C in presence of allyl-dichloro-methyl-silane give allyl-bicyclo [4.2.0] octa-1,3,5-trien-3-yl-chloro-methyl-silane (3) with 61% yield. Finally, chlorosilane 3 was converted into target monomer via addition of 1 eqv H2O in pyridine to toluene solution of 3. BCB-All was obtained in 80.8% yield as colorless liquid.

\[
\begin{align*}
\text{Scheme 2. a) Scheme of Synthesis 1,3-diallyl-1,3-di[bicyclo[4.2.0]octa-1,3,5-trien-3-yl]-1,3-dimethyl-siloxane (BCB-All).} & \quad \text{(i) Br2, H2O, 0-25°C overnight (ii) Mg, THF, allylmethyl dichlorosilane, 25-32 °C; (iii) Py, H2O, Tol, THF; b) TGM-3 and PFHDA monomers}
\end{align*}
\]
2.2. Synthesis of BCB-All polymers and copolymers with TGM-3 and PFHDA

The BCB-All homopolymer and its copolymers with triethylene glycol dimethacrylic ester (TGM-3) and 1H, 1H, 6H, 6H-perfluorohexyl diacrylate (PFHDA) (P & M Invest, Russia) were obtained and studied with different contents of components (100% and 50:50).

A thermopolymerizable composition was prepared by mixing appropriate amounts of monomers with 3% (wt.) of benzoyl peroxide as thermal initiator. The mixtures were then placed by a microdoser in the air atmosphere between two glass substrates pretreated with a dimethyldichlorosilane and trimethylchlorosilane containing anti-adhesive composition. The distance between the substrates was about 480 μm. The polymerization process was carried out with sequential heating at 120°C and 200°C: Low temperature BCB-All oligomerization was initiated, presumably due to allyl substituents of BCB-All and acrylic and methacrylic fragments TGM-3 and PFHDA. In this case, a significant increase in the viscosity of the polymerizable composite is culminating in substantially partial or complete solidification. Further heating at 200 °C leads to cross-linking by opening of cyclobutene rings of BCB-All. As a result, yellow or pale yellow transparent polymer films were formed (Figure 1).

![Figure 1. Photo of the obtained polymer films](image)

The completeness of polymerization was monitored by FTIR spectroscopy. The figure 2 shows the data obtained for the homopolymer from BCB-All at various temperature and time conditions of polymerization.

According to the literature [19], the band at 1462 cm⁻¹ characterizes the vibrations of the CH₂ groups of the cyclobutene ring, and the band at 1491 cm⁻¹ characterizes the vibrations in the crosslinked polymer. This is confirmed by our results: during polymerization, the band at 1462 cm⁻¹ gradually decreases, while the intensity of the band at 1491 cm⁻¹ increases. We also observed an increase in the band intensity at cm⁻¹, which characterizes plane vibrations of the C – H bond at the sp³ hybridized carbon atom [20]. These vibrations are nonspecific; therefore, they are present in the initial monomer (allyl substituent, methyl group, and cyclobutene ring). During polymerization, the number of sp³-hybridized carbon atoms increases; therefore, the intensity of this band increases. Also, a band at 1452 cm⁻¹ appears in the spectrum of the crosslinked polymer. It characterizes the C – C bond of the sp³-hybridized tertiary carbon atom [19], which is not in the initial monomer but arising as a result of the [4 + 2] cycloaddition between the allyl group and an open cyclobutene ring. The band at 1418 cm⁻¹ characterizes the vibrations of the C – H bond at the sp² hybridized carbon atom of the allyl fragment [21]. Its monotonic decrease during polymerization indicates that it participates in the formation of the polymer chain and cyclization processes according to the [4 + 2] type of attachment with a cyclobutene ring.
2.3. Thermal stability of BCB-All polymers and copolymers with TGM-3 and PFHDA

The thermal behavior of the polymers was studied by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). Figure 3 shows the TGA data of BCB-All, TGM-3, PFHDA homopolymers and copolymers. The highest thermal stability was found for homopolymer BCB-All ($T_{d5\%} = 464^\circ C$) that show less than 0.5% weight loss up to 370$^\circ$C. The lowest value was for TGA-3 homopolymer ($T_{d5\%} = 276^\circ$C). $T_{d5\%}$ for PFHDA homopolymer was 324$^\circ$C. It was found that addition of BCB-All to TGM-3 and PFHDA significantly increases the thermal stability of copolymers. For BCB-All : TGM-3 (50:50) copolymer an increase in degradation temperature was observed up to 322$^\circ$C. For BCB-All: PFHDA (50:50) copolymer an increasing of degradation temperature was more significant ($T_{d5\%} = 435^\circ$C).

To determine the optimal conditions for cross-linking, several types of samples were used in DSC studies that differ in heating time and temperature. Figure 4 show the DSC data of the BCB-All homopolymer. DSC curves demonstrate the absence of peaks characterizing allyl group polymerization processes on samples curried at 200 $^\circ$C for 2h. This suggests that double bonds of allyl- groups effectively polymerize at temperatures 120-200 $^\circ$C.

In the case of short time of heating (< 4h at 200$^\circ$C) polymer contains unopened cyclobutene rings that give a signal on the DSC curve. According to DSC data, the temperature of the beginning of cyclobutene ring opening is above 200 $^\circ$C with a maximum at 250 $^\circ$C. These results are in good agreement with those previously reported for other BCB derivatives in the literature. [22].

No signals was recorded on the DSC curve after step heating at 120 $^\circ$C for 2 h, 200 $^\circ$C for 2 h and 300$^\circ$C for 1 h. This indicates the complete occurrence of the crosslinking processes based benzocyclobutene ring opening.
The determination of the relative permittivity $\varepsilon$ consisted in measuring the difference in the resonance length of the resonator without a sample and the resonance length after placing the sample in it at a fixed resonant frequency. The dielectric loss tangent $\tan\delta$ was determined by measuring the intrinsic $Q$ factor of the resonator with the sample and comparing it with the intrinsic $Q$ factor of the resonator without the sample, taking into account changes in the field distribution and ohmic losses in the cavity walls after the sample was placed. The results are given in Table 1.

### Table 1. Dielectric parameters BCB-All homopolymer and copolymers at a frequency of 10 GHz.

| №  | Sample                        | $\varepsilon$, $T=25^\circ$C | $\tan\delta$, $T=25^\circ$C |
|----|--------------------------------|-------------------------------|-------------------------------|
| 1  | BCB-All, (homopolymer)         | 2.34                          | 4.4$\cdot$10$^{-4}$           |
| 2  | BCB-All/TGM-3 (50/50)          | 2.46                          | -                             |
| 3  | BCB-All/TGM-3 (75/25)          | 2.48                          | -                             |
| 4  | BCB-All/PFHDA (50/50)          | 2.45                          | 6.6$\cdot$10$^{-4}$           |
| 5  | BCB-All/PFHDA (75/25)          | 2.37                          | 1.3$\cdot$10$^{-3}$           |
| 6  | BCB-All/PFHDA (25/75)          | 2.41                          | -                             |

The obtained dielectric parameters for the BCB-All homopolymer and its PFHDA copolymers demonstrate a high prospect of using the synthesized benzocyclobutene derivative and copolymers based on it as insulating materials, including for microwave technology.

### 3. Experimental part

#### 3.1. 3-Bromobenzocyclobutene synthesis
Benzocyclobutene (23.7 g, 22.8 mmol) was dispersed in 240 ml of water at room temperature. After cooling with ice water, 11.7 ml of bromine (-10-5°C) was added dropwise. After complete of addition, the ice and water bath was removed and the reaction mixture was warmed to room temperature and stirred overnight (24 hours). The reaction was monitored by TLC until the starting benzocyclobutene disappeared. The mixture was diluted with 50 ml of n-hexane and sodium sulfite (3 g, 23.8 mmol) was added. Upon completion of the addition, the mixture was stirred at room temperature for 30 minutes. In this case, the mixture is discolored. Then, the separated organic layer was dried over anhydrous sodium sulfate, filtered to remove a drying agent, and concentrated under reduced pressure to obtain 3-bromobicyclo [4.2.0] octa-1 (6), 2,4-triene. After distillation at 110-114 °C, 28-30 g was obtained as a colorless liquid.$^1$H NMR (300 MHz, CDCl3) $\delta$ 7.40 (d, $J = 7.8$ Hz, 1H), 7.26 (s, $J = 7.0$ Hz, 1H), 6.99 (d, $J = 7.8$ Hz, 1H), 3.31 – 3.10 (m, 4H).
3.2. Synthesis of allyl-bicyclo [4.2.0] octa-1,3,5-trien-3-yl-chloro-methyl-silane
To a mixture of 1.3 g of magnesium shavings and 7.3 g of allyl-methyl-dichlorosilane in 10 ml of THF, 9.15 g of 3-bromobenzocyclobutene was added at a temperature of 25-40 °C at such a rate that the temperature does not fall outside the specified temperature range. (at a temperature of <25 °C, the reaction stops, above 40 °C the reaction proceeds violently). In order to ensure a stable course of the reaction, it is sufficient to use a water bath with a temperature of 20-25 °C. After complete addition of entire amount, the reaction mass continues to stirred overnight. The heterogeneous solution was evaporated in the absence of moisture, and the solid white residue was washed with dry hexane. Hexane extracts were combined and evaporated. The residue was distilled under vacuum at a temperature of 92-105 °C (3.5-5 mbar). 5.39 g of a colorless liquid are obtained. Yield 61%. 1H NMR (300 MHz, CDCl3) δ 7.51 (d, J = 7.3 Hz, 1H), 7.36 (s, 1H), 7.15 (d, J = 7.3 Hz, 1H), 5.93 – 5.75 (m, 1H), 5.05 (d, J = 5.2 Hz, 1H), 5.00 (s, 1H), 3.25 (s, J = 8.5 Hz, 4H), 2.13 – 2.05 (m, 2H), 0.70 (s, 3H). 13C NMR (75 MHz, CDCl3) δ 148.88, 145.90, 132.72, 131.92, 131.87, 127.19, 126.67, 122.22, 115.78, 77.46, 77.04, 76.61, 29.95, 29.71, 25.77, -0.22.

3.3. Synthesis of 1,3-Diallyl-1-bicyclo [4.2.0] octa-1,3,5-trien-3-yl-3-bicyclo [4.2.0] octa-1 (6), 2,4- triene 3-y1-1,3-dimethyl-disiloxane
Under argon atmosphere, 22 ml of toluene was added to 4.5 g of the starting chlorosilane and heated to 80 °C. To this solution a mixture of 183 mg of H2O and 1.65g of pyridine was added dropwise. The mixture was stirred at a predetermined temperature for 2 hours, then cooled to room temperature and poured into 10 hydrochloric acid. The heterogeneous solution was extracted with ethyl acetate. The extracts were combined and dried over anhydrous sodium sulfate. After evaporation of the solvent, the residue was purified by column chromatography. Obtain 3.193 g of pure product (80.8%). 1H NMR (300 MHz, CDCl3) δ 7.42 (d, J = 7.3 Hz, 1H), 7.26 (s, 1H), 7.08 (d, J = 7.2 Hz, 1H), 5.80 (td, J = 17.6, 8.1 Hz, 1H), 4.92 (d, J = 9.0 Hz, 1H), 4.87 (s, 1H), 3.22 (s, 4H), 1.83 (d, J = 7.9 Hz, 2H), 0.37 (s, 3H). 13C NMR (75 MHz, CDCl3) δ 209.79, 147.59, 145.42, 136.23, 133.93, 131.70, 127.11, 114.01, 77.43, 77.01, 76.58, 29.94, 29.83, 25.63, -1.21, -1.24.

3.4. FTIR spectra registration
FTIR spectra of polymer films were recorded on a Nicolet iS10 IR Fourier spectrometer (Thermo Scientific, United States) with a prefixed Smart iTR total reflection with a Ge crystal in the middle infrared region of 4000-400 cm⁻¹ with a spectral resolution of 8 cm⁻¹. To take the spectrum, the sample was placed on a crystal and fixed with a clamping element. The accumulation time was 14 s for each spectrum. Data recording and processing was performed using OMNIC Thermo Scientific software.

3.5. Thermogravimetric analysis (TGA)
TGA studies were carried out in dynamic mode in the range of 50-700°C using the TG50 M3 system manufactured by Mettler Toledo with an accuracy of determining the weight of the sample up to 1 μg. The heating rate was 10°C/min. The measurements were carried out in an inert gas (nitrogen) stream of 200 ml / min.

3.6. Differential scanning calorimetry (DSC)
DSC analysis of the samples was carried out on a Netzsch STA 449F1 synchronous thermal analyzer. The analysis proceeded in open corundum crucibles in an argon atmosphere with a constant gas flow rate of 40 ml / min. The heating rate was 10 degrees / min. Heating temperature from 25°C to 400°C. The weight of the samples ranged from 5 mg to 8 mg.

3.7. Measurement of dielectric parameters
The dielectric parameters were measured at a frequency of 10 GHz using the volume resonance method. For this, a measuring stand was used, which includes the HF Generator G 4-83, Resonator DK 565, Voltage Ratio Meter B8-7 and Oscilloscope S1-76. For measurements, a cylindrical volume resonator
with $H_{01p}$-type oscillation was used (where $p$ is the number of half-waves that fit along the length of the resonator). The internal diameter of the resonator was 50 mm, the length of the resonance cavity was 80 mm.

4. Conclusions
In summary, we have successfully synthesized new cross-linking monomer based on 1,3-diallyl-1,3-di[bicyclo[4.2.0]octa-1,3,5-trien-3-yl]-1,3-dimethyl-siloxane (BCB-All). The formed polymers exhibited good properties including high thermal stability, low dielectric constants and good film-forming ability. Obtained materials have a potential application as dielectrics in microelectronic industry.

Acknowledgements
The work was financially supported by a grant from the Ministry of Science and Higher Education of the Russian Federation (Agreement on granting a subsidy from the Ministry of Science and Higher Education of the Russian Federation dated June 14, 2019, № 075-15-2019-1273 (inner № 14.577.21.0273), Unique identifier -RFMEFI57717X0273.

References
[1] Yang J, Xie L, Zhu F, Sui H, Li H, Huang Y 2011 *J. Macromol. Sci., Phys. B* 50 2129-2139
[2] Levchenko K S, Chudov K A, Adamov G E, Poroshin N O, Shmelin P S, Grebennikov E P, Parshikov Yu G 2018 *Russ. J. Gen. Chem.* 88 2793–2812
[3] Zuo X, Chen J, Zhao X, Yang S, Fan L 2008 *J. Polym. Sci., Part A: Polym. Chem.* 46 7868
[4] Fang Q, Chen X, Wang J, Sun J 2018 *Mater. Chem. Front.* 2 1397-1402
[5] US Patent 20170358682 A1 2017
[6] US Patent 9490317 B1 2016
[7] JP Patent 2016212155 A 2016
[8] KR Patent 2014028450 A 2014
[9] Zhong H, Wang R, Li L, Yang H 2012 *Bandaoti Jishu* 37 197
[10] Kim B J, Jung H, Shin J, Mastro M A, Eddy C R, Hite J K, Kim S H, Bang J, Kim J 2009 *Thin Solid Films* 517 2742
[11] Kane C F, Krchnavek R R 1995 *IEEE Photonics Technology Letters* 7 535
[12] WO Patent 2013081698 A1 2013
[13] US Patent 4831172 A 1989
[14] http://www.dow.com/cyclotene
[15] Levchenko K S, Chudov K A, Demin D Yu, Adamov G E, Poroshin N O, Shmelin P S, Grebennikov E P, Chvalun S N, Zubov V P 2019 *Russ. Chem. Bull.* 68 1321-1342
[16] Yang J, Huang Y, Cao K 2012 *Recent Progress in Benzocyclobutene Related Polymers* Ed Ailton De Souza Gomes (IntechOpen)
[17] Mehta G, Kotha S 2001 *Tetrahedron* 57 625-659
[18] EP Patent EP2236500 2010
[19] Yang J, Xie L, Zhu F, Sui H, Li H, Huang Y 2011 *J. Macromol. Sci. B.* 50 2129-2139
[20] Dechant J 1972 *Ultrarotspektroskopische Untersuchungen an Polymeren* (Akademie-Verlag, Berlin) p 516
[21] Kazicina L A, Kupletskaya N B *Primenenie UF-, IK- i YaMR-spektroskopii v organicheskoy khimii* (MSU, Moscow) p 208
[22] Zuo X, Yu R, Shi S, Feng Z, Li Z, Yang S, Fan L 2009 *J. Polym. Sci. A* 47 6246-6258