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RESEARCH ARTICLE

Synthesis of copolymers based on divinylbenzene and dibenzocyclobutyldimethylsilane and a study of their functional characteristics

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Abstract

Objectives. To create new polymer materials based on organosilicon derivatives of benzocyclobutene and to study the possibility of their use as insulating dielectric layers in micro- and microwave electronics devices.

Methods. The synthesis of the dibenzocyclobutyldimethylsilane (diBCB-DMS) monomer was carried out from 4-brombenzocyclobutene through the production stage of the Grignard reagent. Copolymers based on divinylbenzene and dibenzocyclobutyldimethylsilane were obtained by means of thermal polymerization. The properties and structure of the copolymers thus obtained were studied using the following methods: thermogravimetric analysis, infrared spectroscopy, nuclear magnetic resonance (NMR), mass spectroscopy, and by means of high-frequency measurements of volt-ampere characteristics and volumetric resonator.

Results. diBCB-DMS was synthesized with a yield of 81.5%. The composition and structure were confirmed by ^{1}H and ^{13}C NMR spectroscopy. The dielectric constant of the diBCB-DMS homopolymer is ~2.6. The tangent of the dielectric loss angle at 1 GHz of the diBCB-DMS homopolymer is $2.3 \cdot 10^{-4}$. The tangent of the dielectric loss angle at 10 GHz of the diBCB-DMS homopolymer is $2.6 \cdot 10^{-4}$. The study of divinylbenzene and diBCB-DMS copolymers in different molar ratios on a thermogravimetric analyzer showed that the copolymers are able to withstand temperatures up to 470°C. The dielectric permittivity of diBCB-DMS and divinylbenzene copolymers in a molar ratio of 1 : 1 was 2.6. The values of the loss tangent at 1 and 10 GHz of copolymers in a molar ratio of 1 : 1 were $4.0 \cdot 10^{-4}$ and $5.6 \cdot 10^{-4}$, respectively.

Conclusion. Analysis of the obtained results shows that the samples of the diBCB-DMS homopolymer have the same dielectric characteristics as the samples based on diBCB-DMS and divinylbenzene, therefore, the introduction of divinylbenzene into the polymer structure does not worsen the dielectric parameters and such polimer materials can be used at high temperatures.

Keywords

benzocyclobutene, divinylbenzene, dibenzocyclobutyldimethylsilane, dielectric permittivity, loss tangent, TGA, materials for electronics, organosilicon polymers

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НАУЧНАЯ СТАТЬЯ

Синтез сополимеров на основе дивинилбензола и дибензоциклобутилдиметилсилана и исследование их функциональных характеристик

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Аннотация

Цели. Создание новых полимерных материалов на основе кремнийорганических производных бензоциклобутена и изучение возможности их использования в качестве изолирующих диэлектрических слоев в устройствах микро- и СВЧ-электроники.

Методы. Синтез мономера дибензоциклобутилдиметилсилана (diBCB-DMS) проводился из 4-бромбензоциклобутена через стадию получения реактива Гриньяра. Сополимеры на основе дивинилбензола и diBCB-DMS получали термополимеризацией. Исследование свойств и строение полученных сополимеров проводилось с помощью термогравиметрического анализа, инфракрасной спектроскопии, ядерного магнитного резонанса (ЯМР), масс-спектроскопии, а также методами высокочастотных измерений вольт-амперных характеристик и объемного резонатора.

Результаты. Синтезирован дибензоциклобутилдиметилсилан с выходом 81.5%, состав и строение которого подтверждены с помощью ^{1}H и ^{13}C ЯМР-спектроскопии. Диэлектрическая проницаемость гомополимера diBCB-DMS составила ~2.6. Тангенс угла диэлектрических потерь при 1 ГГц гомополимера diBCB-DMS равен $2.3\cdot10^{-4}$. Тангенс угла диэлектрических потерь при 10 ГГц гомополимера diBCB-DMS равен $2.6\cdot10^{-4}$. Исследование сополимеров дивинилбензола и diBCB-DMS в разном мольном соотношении на термогравиметрическом анализаторе показало, что сополимеры способны выдерживать температуру до 470°C. Диэлектрическая проницаемость сополимеров diBCB-DMS и дивинилбензола в мольном соотношении 1 : 1 составила 2.6. Значения тангенса угла диэлектрических потерь при 1 ГГц и 10 ГГц сополимеров в мольном соотношении 1 : 1 составили $4.0\cdot10^{-4}$ и $5.6\cdot10^{-4}$ соответственно.

Выводы. Анализ полученных результатов показывает, что образцы гомополимера diBCB-DMS имеют такие же диэлектрические характеристики, как и образцы на основе diBCB-DMS и дивинилбензола, следовательно, введение дивинилбензола в структуру полимера не ухудшает диэлектрические показатели, и такие полимерные материалы можно использовать при высоких температурах.

Ключевые слова

бензоциклобутен, дивинилбензол, дибензоциклобутилдиметилсилан, диэлектрическая проницаемость, тангенс угла потерь, ТГА, материалы для электроники, кремнийорганические полимеры

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INTRODUCTION

The high level of interest in the creation of new polymer materials based on organosilicon derivatives of benzocyclobutene is due to the following reasons: its low dielectric constant (2.65); high breakdown voltage (5.3 MV/cm); high thermal stability (about 470°C); low moisture absorption; and good mechanical properties. These properties enable benzocyclobutene-based materials to be used as insulating dielectric layers, in order to create electronic and electro-optical components, including OLED devices [1], polymer waveguides [2], and others. Furthermore, micro- and microwave electronic devices, volumetric integrated circuits [3], bandpass filters [4], as well as devices using MEMS-on-CMOS technology [5] are manufactured on their basis. These devices are widely used in the military and space industries. The demand for such materials is increasing every year. Therefore, the development of and research into new polymer materials based on benzocyclobutene are still relevant to this day.

The synthesis of monomers of organosilicon derivatives of benzocyclobutene was carried out by several methods: the Heck reaction [6–8]; the Pierce–Rubinstein reaction [9–11]; hydrosilylation with the addition of a Karsted catalyst [12]; and through the stage of obtaining the Grignard reagent [13, 14]. The most convenient of these methods in laboratory conditions is synthesis through the stage of obtaining the Grignard reagent, since this does not require the use of expensive catalysts. For this reason, the dibenzocyclobutyldimethylsilane (diBCB-DMS) monomer was synthesized using the Grignard reagent in this study.

The objective of this study was to create new polymer materials based on organosilicon derivatives of benzocyclobutene and to examine the possibility of their use as insulating dielectric layers in micro- and microwave electronics devices.

EXPERIMENTAL

The diBCB-DMS monomer was synthesized according to the method described in [15]. All reagents were purchased from *Sigma-Aldrich* (USA). Dimethyldichlorosilane was purchased from *abcr GmbH* (Karlsruhe, Germany).

The synthesis of diBCB-DMS was carried out in two stages (Fig. 1).

In order to obtain the Grignard reagent, 4-brom obenzocyclobutene (0.9 mol) was added dropwise with vigorous stirring to a flask containing freshly distilled dry tetrahydrofuran (800 mL) and a mixture of magnesium powder (0.9 mol) and iodine (0.04 mol). The rate was such that the reaction temperature the mixture did not exceed 40°C. The resulting mixture was stirred for another 2 h at this temperature, and then the flask was placed in an ice bath and cooled to 0°C. After cooling the mixture, dimethyldichlorosilane (0.45 mol) was added dropwise at such a rate that the temperature of the reaction mixture did not exceed 10°C. The ice bath was then removed and the mixture was left at room temperature (20°C) overnight. The next day the mixture was diluted with hexane (100 mL). The resulting precipitate was filtered using a column filled with silica gel and washed with several portions of hexane. The filtrate was concentrated on a rotary evaporator. The remaining product was purified by means of vacuum distillation. All the reaction mixtures were analyzed by thin layer chromatography on Merck Silica gel 60 F254 UV-254 plates (*Merck*, Germany). The composition and structure of the resulting compound was confirmed by nuclear magnetic resonance (NMR) spectroscopy and infrared (IR) spectroscopy.

Figure 2 shows the first scheme for obtaining copolymers. According to this scheme, samples were prepared to study thermal stability with different molar ratios. The composition of the mixture was changed by adding diBCB-DMS, starting from 5 to 25 mol %.

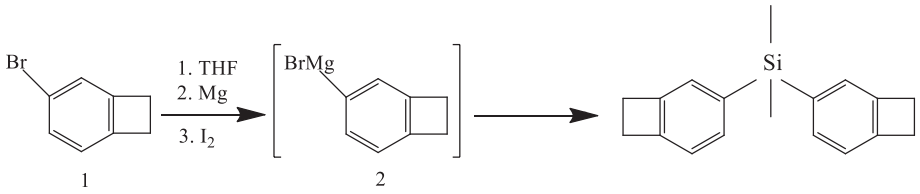

Fig. 1. Dibenzocyclobutyldimethylsilane (diBCB-DMS) synthesis scheme [15]

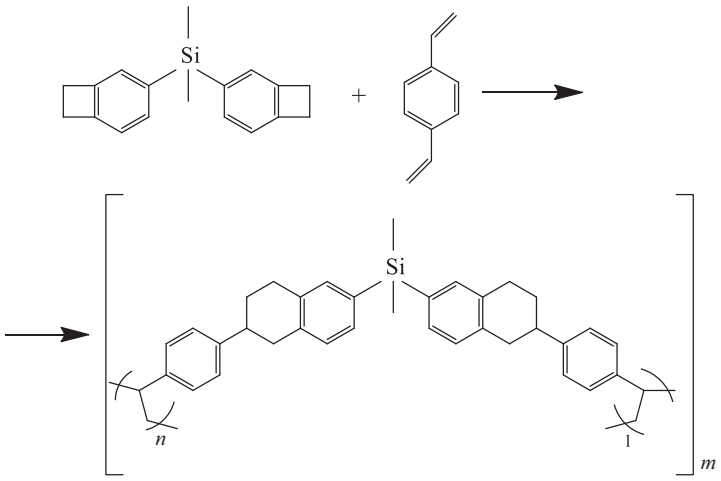

Fig. 2. Scheme for obtaining diBCB-DMS and divinylbenzene copolymers

In order to prepare samples, the mixture was placed in a crucible in an argon atmosphere. The crucibles were placed in an oven at 160–165°C for 30 min. Then the final heat treatment of the samples was carried out at a temperature of 250°C for 4 h.

Figure 3 shows the second production scheme. The addition of an inhibitor into the reaction is due to the fact that the different polymerization temperatures (220°C for diBCB-DMS and 80°C for divinylbenzene) make it difficult to obtain samples. Therefore, an inhibitor was used: 2-methylhydroquinone in an amount of 5% by weight of divinylbenzene.

In order to measure the dielectric constant and loss tangent, samples of 100% diBCB-DMS and a copolymer of diBCB-DMS and divinylbenzene in a 1 : 1 ratio were prepared using thermal polymerization. Samples of 5 × 5 cm in size and a thickness of about 2 mm were obtained. The samples were created using Teflon equipment specially made for this purpose.

Thermal polymerization of 100% diBCB-DMS was carried out in two steps. In the first stage, curing was carried out in a Teflon assembly, filled with ~6 mL of pure diBCB-DMS using a dispenser. The assembly was placed in an OFA-54-8 thermostat (*Esco*, Singapore) at a temperature of 160°C for 5 h, then at 220°C for 1.5 h. At the second stage, the sample was subjected to final heat treatment at a temperature of 250°C for 4 h.

A copolymer of diBCB-DMS and divinylbenzene was prepared in a similar manner. The reaction mixture consisting of diBCB-DMS (4.6 g), divinylbenzene (2.3 g) and 2-methylhydroquinone (0.115 g) was cured in two stages. Primary curing was carried out in a Teflon assembly, filled with ≥7 mL of a reaction mixture containing components in a given ratio using a dispenser. The assembly was placed in a Binder FD240 thermostat (*Binder*, Tuttlingen, Germany), at temperatures of 140°C for 1 h, 160°C for 2 h, 180°C for 1 h, 200°C for 1 h, and 220°C for 1 h. At the second stage, the sample was subjected to the final stage of heat treatment at a temperature of 250°C for 4 h.

Studies of the structure and functional properties of the diBCB-DMS homopolymer and copolymers of diBCB-DMS and divinylbenzene were carried out using the following methods: NMR spectroscopy; Fourier-transform IR spectroscopy; thermogravimetric analysis (TGA); high-frequency current-voltage measurement method (at 1 GHz); and a cavity resonator for measurements at 10 GHz.

DiBCB-DMS NMR spectra were recorded using a Bruker AM-300 spectrometer (*Bruker Corporation*, USA) in $CDCl_3$. Mass spectra were obtained on a Varian MAT CH-6 instrument (*Varian*, USA) using a direct input system. The ionization energy was 70 eV, and the acceleration voltage was 1.75 kV.

In order to obtain IR spectra of materials, an FSM2201 IR Fourier spectrometer (*Infraspec*, Russia) was used. To study polymer samples, they were first ground into powder, then KBr was added and the powder pressed into a tablet. The measurements were carried out in the range of 400–4000 cm^{-1}.

The thermal stability of the copolymer samples was measured by simultaneous TGA using a Shimadzu DTG-60 instrument (*Shimadzu Corporation*, Kyoto, Japan) in dynamic mode in the range of 20–700°C with heating rate of 10°C/min. The measurements were carried out in an argon/air flow at a rate of 50/100 mL/min.

The samples were studied by methods of high-frequency measurements of current-voltage characteristics and a cavity resonator consisting of an Agilent E4991A RF material properties and impedance analyzer. This enabled the dielectric characteristics to be measured at 1 GHz. The Agilent PNA E8361C network analyzer + 85072A 10-GHz cylindrical split resonator (*Agilent Technologies*, Santa Clara, California, USA), enabled dielectric measurements at 10 GHz.

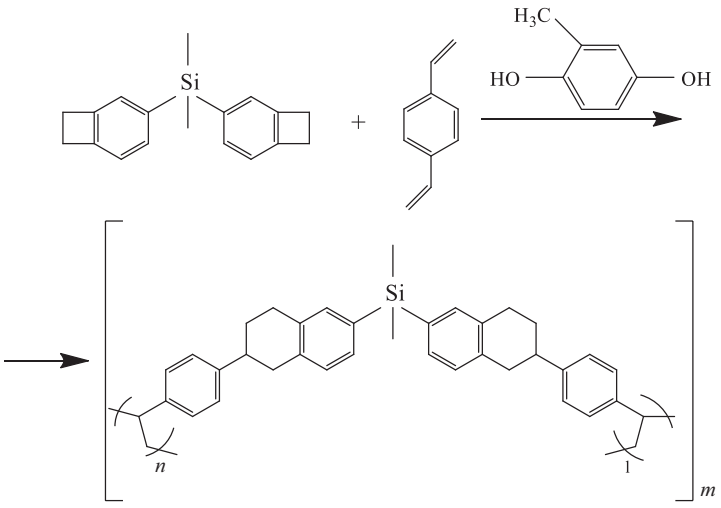

Fig. 3. Scheme for the production of diBCB-DMS and divinylbenzene in the presence of 2-methylhydroquinone

RESULTS AND DISCUSSION

As a result of synthesizing diBCB-DMS through the stage of obtaining the Grignard reagent, the product yield was 95.12 g (81.5%). The compound is a colorless liquid which hardens easily in the refrigerator. ^{1}H NMR spectrum (300 MHz, $CDCl_3$, δ, ppm): 7.62 (d, J = 7.3 Hz, 2H), 7.47 (s, 2H), 7.28 (d, J = 7.3 Hz, 2H), 3.40 (s, J = 3.4 Hz, 8H), 0.76 (s, 6H). ^{13}C NMR spectrum (76 MHz, $CDCl_3$, δ, ppm): 147.30, 145.75, 136.85, 132.73, 128.16, 122.13, 30.14, 30.01, −1.67. Mass spectrum, found: 265.1414; calculated: 265.1407.

Figure 4 shows the IR spectrum of diBCB-DMS. The band at 1463 cm^{-1} is characteristic of the CH_2 group of cyclobutene. The band at 1255 cm^{-1} indicates the presence of a Si–CH_3 bond in the monomer. The band at 1107 cm^{-1} is characteristic of the Si–C_6H_5 bond. Thus, IR spectroscopy data makes it possible to confirm the structure of the synthesized diBCB-DMS monomer.

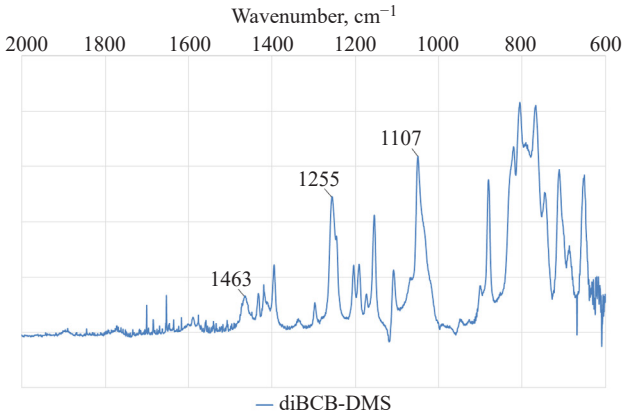

Fig. 4. IR spectrum of diBCB-DMS

Copolymers of diBCB-DMS and divinylbenzene prepared using the first method in different molar ratios were studied by means of TGA. The results of the study are presented in Fig. 5 and in Table 1. Figure 5 shows that polymer samples can withstand temperatures up to 470°C before thermal decomposition.

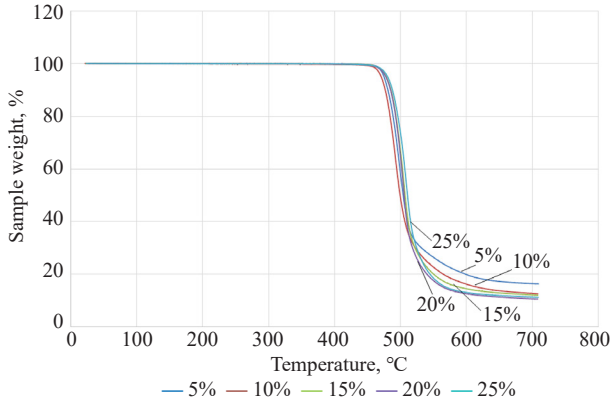

Fig. 5. Curves of polymerized samples with ratios from 5 to 25 mol % diBCB-DMS obtained by the TGA method

Table 1. The initial decomposition temperature of the samples

Ratio of components in the sample	Decomposition temperature, °C
5% diBCB-DMS and 95% divinylbenzene	474.9
10% diBCB-DMS and 90% divinylbenzene	470.7
15% diBCB-DMS and 85% divinylbenzene	478.4
20% diBCB-DMS and 80% divinylbenzene	477.7
25% diBCB-DMS and 75% divinylbenzene	480.4

A sample was obtained as a result of thermal polymerization of the 100% poly-diBCB-DMS monomer. A photograph is shown in Fig. 6. The sample was solid, transparent and had a yellowish tint. After secondary heat treatment, the appearance of the sample did not change.

Fig. 6. 100% diBCB-DMS sample after primary heat treatment: 160°C — 5 h, 220°C — 1.5 h

In the IR spectrum of diBCB-DMS (Fig. 7), a shift of the band 1463 cm^{-1} to 1490 cm^{-1} was observed. This characterizes the process of polymerization of the cyclobutene fragment [4+2]- or [4+4]-cycloaddition (Diels–Alder reaction), with the formation of a six- or eight-membered ring, respectively, containing methylene groups [17].

As a result of copolymerization of diBCB-DMS and divinylbenzene in the presence of an inhibitor in a 1 : 1 molar ratio, a solid, transparent sample with a yellowish tint was obtained (Figs. 8a and 8b). After the second stage of preparation, the sample retained its shape and remained transparent.

The IR spectrum of the resulting copolymer (Fig. 9) showed that during copolymerization, the band at 1630 cm^{-1}, characteristic for C=C vibrations in

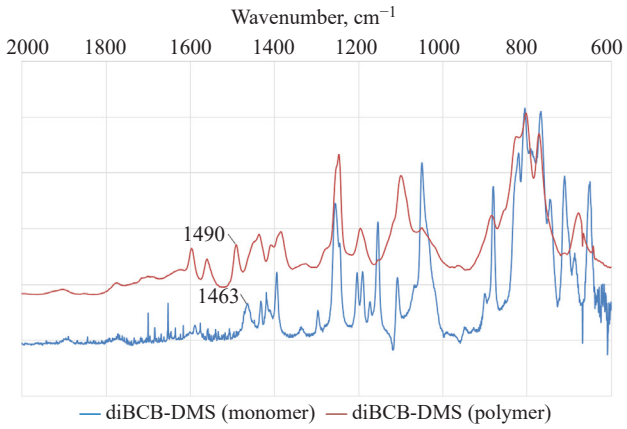

Fig. 7. IR spectrum of diBCB-DMS polymer

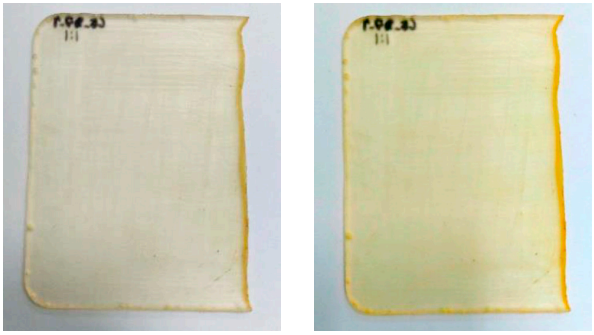

Fig. 8. Photograph of a sample of a diBCB-DMS and divinylbenzene mixture in a molar ratio of 1 : 1. (a) After primary heat treatment at temperature modes: 140°C — 1 h, 160°C — 2 h, 180°C — 1 h, 200°C — 1 h, and 220°C — 1 h; (b) after secondary temperature treatment at 250°C

divinylbenzene, decreases. The band at 985 cm^{-1}, characteristic of the bond of the aromatic ring with the vinyl group in divinylbenzene, also decreases. The band at 1463 cm^{-1}, characteristic of the CH_2 group of cyclobutene, shifts to 1490 cm^{-1}. The presence of changes and the formation of new bands indicates that cyclobutene opens, forming reactive double bonds (Fig. 10). These bonds enter into a [4+2] cycloaddition reaction with vinyl moieties of divinylbenzene. As a result, a copolymer based on diBCB-DMS and divinylbenzene is formed.

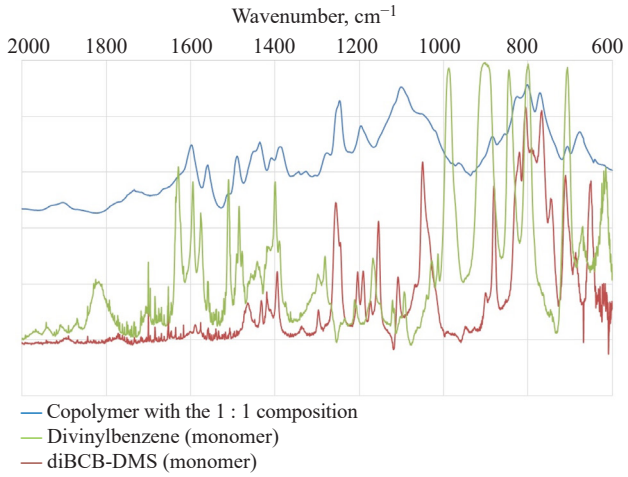

Fig. 9. IR spectrum of diBCB-DMS copolymer and divinylbenzene

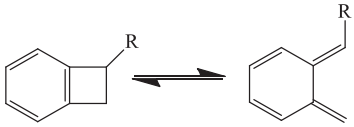

Fig. 10. Process of cyclobutene disclosure in benzocyclobutene

The dielectric characteristics of the samples of 100% diBCB-DMS thus obtained and copolymers of diBCB-DMS and divinylbenzene in a molar ratio of 1 : 1 are presented in Table 2. It can be seen that polymer samples made from a mixture of diBCB-DMS and divinylbenzene monomers in a 1 : 1 molar ratio have a similar dielectric constant and loss tangent when compared to a sample from 100% diBCB-DMS monomer. When divinylbenzene is added to the samples, the dielectric characteristics do not deteriorate. The alues obtained at 1 GHz and 10 GHz remain almost unchanged, allowing the material to be used at higher frequencies.

Table 2. Dielectric characteristics of a 100% diBCB-DMS monomer and a mixture of diBCB-DMS monomers and divinylbenzene

Sample	Dielectric Permittivity at 1 GHz, ε	Loss tangent at 1 GHz, α	Dielectric permittivity at 10 GHz, ε	Loss tangent at 10 GHz, α
Sample of 100% diBCB-DMS before thermal polymerization	2.653	$4.4 \cdot 10^{-4}$	2.730	$4.4 \cdot 10^{-4}$
Sample of 100% diBCB-DMS after thermal polymerization	2.671	$2.3 \cdot 10^{-4}$	2.711	$2.6 \cdot 10^{-4}$
5 cm × 5 cm sample from a monomer mixture before thermal polymerization	2.605	$3.8 \cdot 10^{-4}$	2.674	$7.0 \cdot 10^{-3}$
5 cm × 5 cm sample from a monomer mixture after thermal polymerization	2.619	$4.0 \cdot 10^{-4}$	2.616	$5.6 \cdot 10^{-4}$

CONCLUSIONS

The study shows that, based on organosilicon derivatives of benzocyclobutene, it is possible to obtain polymer materials and use them as insulating dielectric layers in micro- and microwave electronics devices. New thermal polymerizable materials based on diBCB-DMS and divinylbenzene in different molar ratios were obtained for the first time and their functional characteristics were studied. Thus, diBCB-DMS was obtained by a two-stage synthesis method with a yield of 81.5%. Also, the possibility of obtaining copolymers of divinylbenzene and diBCB-DMS was studied. DiBCB-DMS copolymers with divinylbenzene were obtained in the molar ratios: 1 : 1, 1 : 20, 1 : 10, 1 : 6.7, 1 : 5, 1 : 4.

It was established that when producing materials based on copolymers of diBCB-DMS and divinylbenzene, there is no deterioration in dielectric constant and loss tangent relative to the results obtained based on material from 100% diBCB-DMS. The resulting materials have been shown to be capable of withstanding temperatures up to 470°C.

Authors' contribution

All authors equally contributed to the research work.

The authors declare no conflicts of interest.

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RESEARCH ARTICLE

New approaches to the synthesis of substituted derivatives of the $[B_3H_8]^-$ anion

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Abstract

Objectives. To develop methods for the synthesis of substituted derivatives of the octahydrotriborate anion. Such compounds can be considered as hydrogen storage, components of ionic liquids, precursors for the production of boride coatings using the traditional chemical vapor deposition method, and also as a building material for the production of higher boron hydrogen clusters.

Methods. Since substitution reactions are sensitive to moisture and atmospheric oxygen, the syntheses were carried out in a direct flow of argon or in a dry, sealed SPEKS GB02M glove box with a double gas purification unit and two airlocks. The reaction was initiated by cooling to 0°C, in order to avoid the formation of by-products. All the results were characterized using infrared (IR) and nuclear magnetic resonance (NMR) spectroscopies.

Results. The study presents a detailed study of the known methods for preparing substituted derivatives of the octahydrotriborate(1−) anion using dry hydrogen chloride as an electrophilic inductor and makes recommendations for improvement. In this method it is advisable to use cesium octahydrotriborate which facilitates the yield of the target product. New methods were proposed to initiate the substitution reaction in the $[B_3H_8]^-$-anion using *N*-chlorosuccinimide and bromine. Using these inductors, new substituted derivatives of the octahydrotriborate anion with *N*-nucleophiles were obtained and defined by means of IR and NMR spectroscopies: $[B_3H_7NCR]$, (R = Et, *i*-Pr, Ph) and $[B_3H_7NH_2R]$, (R = C_9H_{19} (INA), Bn), $[B_3H_7NHEt_2]$, as well as $Bu_4N[B_3H_7Hal]$, $Bu_4N[B_3H_6Hal_2]$, where Hal = Cl, Br. It was also established that hydrogen bromide is released during the reaction with bromine and amines. This immediately protonates the amine which requires additional heating of the reaction mixture. The study also established that the reaction mechanism with *N*-chlorosuccinimide is not radical.

Conclusions. The main factors influencing the course of the substitution reaction are the possible occurrence of side interactions between the nucleophile and the inducer, steric possibilities, and subsequent isolation of the reactive reaction products.

Keywords

boron, borohydrides, octahydrotriborate(1−) anion, Lewis acids, nucleophilic substitution, succinimide, halogens

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