Brief Communications

Novel cross-linking monomer based on benzocyclobutene for an application in microelectronics

K. S. Levchenko,^{a*} G. E. Adamov,^b K. A. Chudov,^b P. S. Shmelin,^b A. Yu. Kalashnikov,^c and E. P. Grebennikov^b

^aN. S. Enikolopov Institute of Synthetic Polymer Materials of Russian Academy of Sciences,

 70 ul. Profsoyuznaya, 117393 Moscow, Russian Federation ^bCentral Technological Research Institute "Technomash", 4 ul. Ivana Franko, 121108 Moscow, Russian Federation ^cState Space Corporation ROSCOSMOS, 53 ul. Aviamotornaya, 111250 Moscow, Russian Federation. E-mail: k.s.levchenko@gmail.com

A new cross-linking monomer, allyl-bis(benzocyclobuten-4-yl)methylsilane (ABCBMS), was synthesized and its physical properties were investigated. Copolymers of ABCBMS with triethylene glycol dimethacrylate (TGM-3) and bis(methacryloylethylene glycol) carbonate (BMCC-2) were obtained by photo- and thermal polymerization. The final cross-linking of the copolymers took place at 200 °C. Homo- and copolymers of ABCBMS, ABCBMS—TGM-3 (50 : 50) and ABCBMS— BMCC-2 (50 : 50) exhibit high thermal stability ($T_{d5\%} = 460, 359, and 352$ °C, respectively) and good dielectric properties ($\varepsilon = 2.7-2.8$ and tg $\delta = (3.7-6.7) \cdot 10^{-4}$ at 10 GHz).

Key words: benzocyclobutene, polymers, oligomers, monomers, dielectric materials, insulating materials, thermal polymerization, photopolymers, silanes, acrylates.

Polymers based on benzocyclobutene (BCB, 1) exhibit exceptional properties and can be used in microelectronics as dielectric materials.¹ Fragments of BCB can be thermally isomerized to form *o*-xylylene derivatives (2). The latter, in turn, can react with active double bonds or dimerize in the absence of such with the formation of structures 3, 4, or 5, respectively (Scheme 1).² This affords BCB-based polymers unique properties, namely, thermal stability (up to 550 °C),^{3,4} low dielectric constant ($\varepsilon = 2.3-2.9$ at 1 MHz), high chemical resistance, and low moisture absorption.

The properties and options for the practical use of materials based on BCB are described in a number of publications.^{2,5–10} The BCB-based polymers are used in electronics and photonics^{5–7} as dielectric layers in high-density electronic modules.

The method of synthesis and properties of allylbis(benzocyclobuten-4-yl)methylsilane (ABCBMS), a new

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Scheme 1

monomer containing two benzocyclobutene and one allyl fragment capable of polymerization, are described in this work.

Results and Discussion

Synthesis of ABCBMS. Monomer ABCBMS was synthesized from BCB in two steps (Scheme 2). First, BCB (1) was brominated using molecular bromine in a twophase aqueous system according to a known method¹¹ in 70–72% yield. Then, the target product **9** was obtained in the form of a colorless liquid as a result of the reaction of 4-bromobenzocyclobutene (**6**) with Mg in THF proceeding at 30–40 °C in the presence of allyldichloromethyl-silane **7**. Two fractions were isolated after purification by column chromatography. The main product is allyl-bis-(benzocyclobuten-4-yl)methylsilane (**9**) (48% yield). In addition, siloxane **10** was present in an insignificant amount (5–10%). The compound **10** was synthesized by us earlier by the reaction of allylbicyclo-[4.2.0]octa-1,3,5-trien-3-ylchloromethylsilane (8) with water in the presence of pyridine.¹² The formation of product 10 may indicate an incomplete reaction between intermediate 8 and Grignard's reagent. Siloxane 10 is formed during purification of the reaction product, including aqueous extraction. An increase in the reaction time and temperature (up to 65 °C) upon addition of an excess of compound 6 and Mg led to the disappearance of the siloxane in the reaction mixture. However, the yield of the target product did not increase, which is obviously due to the accumulation of the by-products.

Synthesis of polymers and copolymers based on ABCBMS with triethylene glycol dimethacrylate (TGM-3) and bis-(methacryloylethylene glycol) carbonate (BMCC-2). ABCBMS homopolymers were obtained by heating the monomer at 200 °C. Copolymers with TGM-3 and BMCC-2 were synthesized in two steps using photo- and thermal polymerization and compositions with different monomer ratios (25 : 75, 50 : 50).

In the first step, photopolymerizable compositions were prepared by mixing appropriate amounts of mono-



Scheme 2

Reagents and conditions: i. Br₂, H₂O, -10-25 °C, 24 h; ii-iv. Mg, THF, 30-40 °C, 12 h.



Fig. 1. Photos of the obtained polymer samples.

mers with 3 wt.% of DarocurTM 4265 photoinitiator. The compositions were then placed using a microdispenser between two glass substrates pretreated with a dimethyl-dichlorosilane/trimethylchlorosilane release agent (1 : 1). The distance between the substrates was about 480 μ m. The polymerization process was carried out under irradiation with a UV lamp (395 nm) for 1 h. At the second step, the sample was heated at 200 °C for 2–3 h. As a result, yellow or pale-yellow polymer films were obtained (Fig. 1).

The completeness of polymerization was monitored by FTIR spectroscopy. Figure 2 shows the data obtained for the ABCBMS homopolymer at various temperature and various time conditions of the polymerization.

According to the data, ¹³ the bands at 1462 cm^{-1} and 1491 cm⁻¹ belong to the vibrations of the CH₂ groups of the cyclobutene ring in the initial state and after thermal ring opening in the cross-linked polymer, respectively. This is also confirmed by our results, namely, in the course of 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 intensity of the band at 1431-1433 cm⁻¹, which characterizes the vibrations of the C-H bond on the hybridized carbon atom sp³.¹³ These vibrations are nonspecific and they are also present in the spectrum of the starting monomer (allyl substituent, methyl group, and cyclobutene ring). In the course of polymerization, the number of sp³-hybridized carbon atoms increases. Therefore, the intensity of this band increases. The band at 1418 cm⁻¹ characterizes the vibrations of the C-H bond on the hybridized carbon atom of the sp²-allyl fragment.¹⁴ Its monotonic decrease in the course of polymerization indicates that this atom is involved in the formation of a cross-linking polymer chain. The band at 1452 cm^{-1} , characteristic of the [4+2]-cycloaddition products, was not clearly manifested in the spectrum of the cross-linked ABCBMS polymer in contrast to compound **10** with a similar structure described earlier.¹² This is due to the fact that in the ABCBMS molecule, there are two BCB fragments per allyl substituent. As a result, transverse [4+2]-polymerization competes with the mechanism of [4+4]-cycloaddition and the mechanisms leading to the appearance of structures **3** and **4** (see Scheme 1).

Thermal stability of ABCBMS and its copolymers with TGM-3 and BMCC-2. The thermal behavior of polymers



Fig. 2. Fourier transform infrared spectroscopy data for the ABCBMS homopolymer at various temperatures and duration of thermal polymerization: the initial monomer (1), after thermal polymerization at 200 °C for 30 min (oligomer) (2) and for 2.5 h (polymer) (3).



Fig. 3. TGA thermograms of ABCBMS (1), TGM-3 (2), BMCC-2 (3) and their copolymers ABCBMS—TGM-3 (50 : 50) (4), ABCBMS—BMCC-2 (5).

was studied by thermogravimetric analysis (TGA) carried out in a dynamic mode in the range of 50–700 °C using a TG50 M3 instrument (Mettler Toledo) with an accuracy of determining the sample weight of up to 1 μ g. The heating rate was 10 °C min⁻¹.

The measurements were carried out under nitrogen flow (200 mL min⁻¹). Figure 3 shows the TGA data for homopolymers and copolymers of ABCBMS, TGM-3, and BMCC-2.

The highest thermal stability was found for the ABCBMS homopolymer ($T_{d5}\% = 460 \text{ °C}$); the weight loss upon heating to 358 °C was 0.5%. The lowest values were determined for homopolymers TGM-3 ($T_{d5\%} = 276 \text{ °C}$) and BMCC-2 ($T_{d5\%} = 295 \text{ °C}$). It was found that the addition of ABCBMS to TGM-3 and BMCC-2 significantly increases the thermal stability of the copolymers. An increase in the degradation temperature to 359 °C was ob-

served for the copolymer ABCBMS—TGM-3 (50 : 50) and up to 352 °C for the copolymer ABCBMS—BMCC-2 (50 : 50).

Dielectric properties of ABCBMS polymers. Dielectric characteristics were measured at a frequency of 10 GHz using the volume resonance method. For this purpose, a measuring stand consisting of a G 4-83 high-frequency generator, a DK 565 resonator, a V8-7 voltage ratio meter, and an S1-76 oscilloscope, was used. We used a cylindrical cavity resonator with vibration of the H_{01p} type (where *p* is the number of half-waves that fit along the length of the resonator) for measurements. The inner diameter of the resonator was 50 mm, and the length of the resonance cavity was 80 mm. The relative dielectric constant ε was determined from the difference between the resonant length of the resonator without a sample and after placing a sample in it at a fixed resonance frequency.

The tangent of dielectric losses $tg\delta$ was determined by measuring the intrinsic *Q*-factor of the resonator with and without sample, taking into account the change in the field distribution and ohmic losses in the resonator walls when the sample was placed. The obtained dielectric characteristics for the ABCBMS homopolymer and copolymers with BMCC-2 and TGM-3 indicate a high perspective of using the synthesized benzocyclobutene derivative and copolymers based on it as insulating materials, including microwave technology.

Thus, we have successfully synthesized a new monomer, allyl-bis(benzocyclobuten-3-yl)methylsilane (ABCBMS) and a series of polymers based on it. The obtained polymers are characterized by high thermal stability (>350 °C), low dielectric constants ($\epsilon = 2.68$ at 10 GHz), and good filmforming ability. They can find application as dielectrics in the microelectronic industry.

Experimental

NMR spectra of the samples were recorded using a Bruker Avance 600 spectrometer in CDCl₃ (¹H, 500 MHz; ¹³C, 125 MHz). High resolution mass spectra were obtained using a BrukermicrOTOF II spectrometer with electrospray ionization (ESI).

Table 1. Thermal and dielectric characteristics of ABCBMS homopolymer and copolymers at a frequency of 10 GHz at 25 $^{\circ}$ C

Sample	$\varepsilon (T = 25 \circ C)$	tgδ	$T_{5\%}/^{\circ}\mathrm{C}$
ABCBMS (homopolymer)	2.68	$3.7 \cdot 10^{-4}$	460
ABCBMS—TGM-3 (50 : 50)	2.81	$1.3 \cdot 10^{-3}$	359
ABCBMS—TGM-3 (25 : 75)	2.86	_	_
ABCBMS-BMCC-2 (50 : 50)	2.66	$5.7 \cdot 10^{-4}$	352
ABCBMS-BMCC-2 (25 : 75)	2.80	$6.7 \cdot 10^{-4}$	_
BMCC-2	3.186	$1.54 \cdot 10^{-2}$	295
TGM-3	3.324	$3.64 \cdot 10^{-2}$	276

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Analysis of the reaction mixtures to confirm the purity of all products was carried out using thin layer chromatography on Merck Silicagel 60 F254 UV-254 plates.

4-Bromocyclobutene (6). Benzocyclobutene (23.7 g, 22.8 mmol) was emulsified in water (240 mL) and cooled in an ice bath. Bromine (11.7 mL) was added to the resulting mixture in small portions at a temperature of 0-5 °C. The reaction mixture was allowed to warm to 20 °C and then stirred for 24 h. The reaction was monitored by thin layer chromatography. Then *n*-hexane (50 mL) and sodium sulfite were added to the mixture. The mixture was stirred at 20 °C for 30 min until complete discoloration. The organic layer was separated, washed with water, and dried over sodium sulfate. After distillation at 110–114 °C and reduced pressure, 30 g of a colorless liquid were obtained. ¹H NMR (300 MHz, CDCl₃) δ : 7.40 (d, 1 H, *J* = 7.8 Hz); 7.26 (s, 1 H, *J* = 7.0), 6.99 (d, 1 H, *J* = 7.8 Hz); 3.31–3.10 (m, 4 H).

Allyl-bis(benzocyclobuten-4-yl)methylsilane (9). 4-Bromobenzocyclobutene (6.1 g, 33.3 mmol) was added dropwise to a mixture of magnesium (900 mg, 37.5 mmol) and allylmethyl-dichlorosilane (2.62 g, 16.9 mmol) in THF (30 mL) at a temperature of 30-40 °C. Thereafter, the mixture was kept for 12 h, and then water (10 mL) was added thereto and the product was extracted with ethyl acetate. The product was purified by column chromatography. Yield 2.4 g. ¹H NMR (500 MHz, CDCl₃) δ : 7.40 (d, 2 H, J = 7.2 Hz); 7.24 (s, 2 H); 7.09 (d, 2 H, J = 7.2 Hz); 5.91-5.71 (m, 1 H); 4.95 (d, 1 H, J = 17.0 Hz); 4.90 (d, 1 H, J = 11.0 Hz); 3.22 (s, 8 H); 2.09 (d, 2 H, J = 8.0 Hz); 0.55 (s, 3 H). ¹³C NMR (75 MHz, CDCl₃) δ : 147.33, 145.58, 134.99, 134.51, 132.90, 128.63, 122.25, 113.97, 29.96, 29.83, 22.61, -4.32. Found: m/z 313.1373 [M + Na]. Calculated: 313.1383 [M + Na].

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