

Synthesis of photo and thermosetting monomers and polymers based on benzocyclobutene

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Modern approaches to the preparation of monomers and polymers based on benzocyclobutene are considered. The groups of polymers containing siloxane, silyl, polyfluorinated fragments, polyimides, polyamides, polyacrylates, polyolefins, and polyarylenes are distinguished among benzocyclobutene-containing polymers. The basic properties of these polymers (glass transition temperature, decomposition onset temperature, dielectric properties, moisture resistance) are described, and the possibility of their application in the creation of microelectronics devices is evaluated. It has been established that the dielectric constant of most known benzocyclobutene-based polymeric materials lies in the range from 2.3 to 3.07. Fluorine-containing and organosilicon derivatives show the best dielectric properties (2.3–2.38). Polysiloxanes possess the highest thermal stability between considered polymers, demonstrating stability up to 500–550 °C both in inert atmosphere and in air.

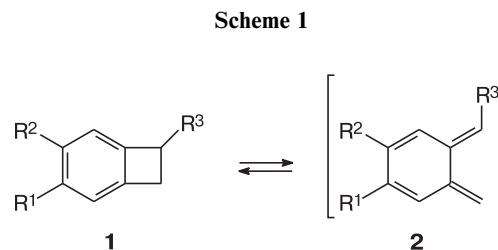
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The continuous evolution in the field of portable high-frequency microelectronic systems places high demands on the properties of polymeric materials (optical, dielectric, thermal, physico-chemical, adhesive, *etc.*) used in these applications.

An interest in benzocyclobutene-based polymeric materials has increased in recent years due to a number of unique properties of these polymers that makes it possible to use them in compact electronic microdevices capable of functioning also under extreme conditions.

Benzocyclobutene is the starting reagent for the synthesis of a number of monomers^{1,2} capable of thermal or photopolymerization. These polymers have found an application in electronics^{3–16} and photonics^{17–19} as optical waveguides,²⁰ matrices in high-density electronic modules,^{21,22} and photoresists.²³ They are also the raw materials for production of biologically active compounds.²⁴

Benzocyclobutene-based photo or thermosetting materials have an outstanding array of beneficial properties. The uniqueness of these materials is due to the possibility of thermally induced opening of the cyclobutene ring with the formation of active *o*-xylylenes. The latter are able to form polycyclic compounds by the Diels–Alder reaction with dienophiles (Scheme 1).



Most polymeric materials based on benzocyclobutene are characterized by low values of dielectric constant ($k = 2.3–2.8$), high values of electrical breakdown voltage $\sim (3–5) \cdot 10^6 \text{ V cm}^{-1}$, and stability at temperatures of 300–450 °C. At the same time, these materials are resistant to moisture (adsorb less than 0.14–1% of water at prolonged keeping in a humid atmosphere at high temperatures), and good mechanical properties. The combination of such characteristics in one material makes them more attractive than other known polymeric materials (polyacrylates, polyimides, phenol-formaldehyde and epoxy resins, *etc.*) for the application in various technological processes of electronics production.

Several reviews^{25–28} are devoted to materials based on benzocyclobutene. The methods for synthesis of mono-

mers, polymers, and copolymers based on them are discussed in these reviews. The analysis of these works allows to conclude that modern trends in the development of materials based on benzocyclobutene consist in the search and development of new hybrid molecules combining one or more functional benzocyclobutene fragments, one or more double bonds, and auxiliary connecting (bridge) fragments.

The presence of a benzocyclobutene fragment allows thermal and photopolymerization processes to be used separately, which is important when combining technologies for design of integrated circuits. Cross-linking of individual linear fragments with each other occurs as a result of the final thermal treatment of such polymers. This ensures an increase in such operational characteristics as glass transition temperature, decomposition temperature, resistance to solvents, chemical stability, *etc.* Thermal opening of the cyclobutene ring is attractive from the point of view of the purity of the process, since it does not require the presence of a catalyst or a process initiator contaminating the final polymer. It is also important that the polymerization proceeds without evolution of by-products and that the products of thermal polymerization do not contain polar groups, and therefore do not impair the dielectric properties of the polymer as a whole.^{29–34}

Most of the monomers containing benzocyclobutene includes in its structure also double bonds. Their presence in the monomer or oligomer determines the ability of both photo and thermal polymerization. The possibility of photopolymerization ensures the applicability of such materials in technologies involving photolithographic processes. In addition, the presence of additional active double bonds in the monomer or composite material containing benzocyclobutene fragment leads to a decrease in the temperature of the opening of cyclobutene ring, an increase in the efficiency and completeness of polymerization³⁵ and provides for a different direction of the polymerization of the cyclobutene fragment (Scheme 2, path *A*).

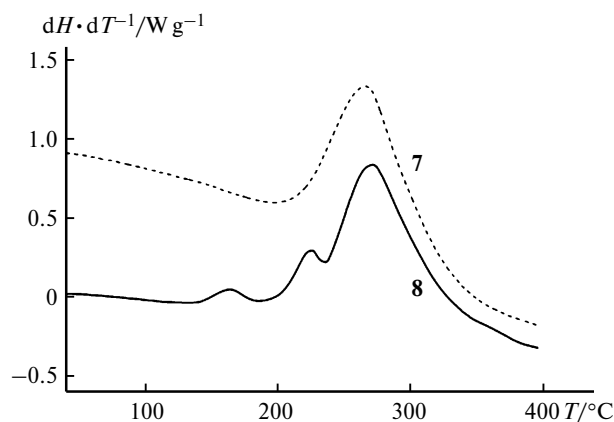
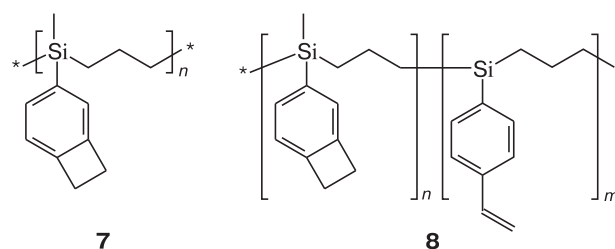


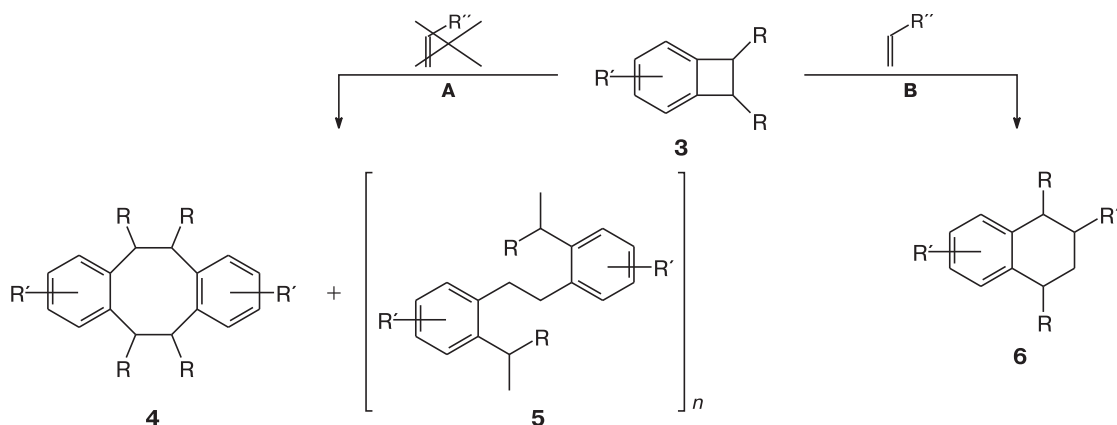
Fig. 1. DSC curves of polymers 7 and 8.

Thus, two types of polymers were synthesized.³⁵ One of them contains only the benzocyclobutene fragment (7), while another contains benzocyclobutene alternating with styrene fragments (8).



A comparison of the properties of the polymers obtained using the differential scanning calorimetry (DSC) makes it possible to identify various directions of polymerization processes. Thus, the peaks on the DSC curve of compound 8 (Fig. 1) correspond to three variants of cross-linking, namely, reactions of vinylbenzene fragments (extremum at 164 °C), [4+2]-cycloaddition of benzocyclobutene and vinylbenzene-containing fragments

Scheme 2



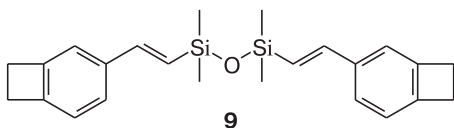
(exotherm with a maximum at 225 °C), and the reactions of *o*-xylenes, which are formed during the process, with each other (exotherm with maxima at 269 °C).

A peculiarity of the modern design of benzocyclobutene-based monomers is the presence of several functional fragments (active double bonds), which provide a greater degree of cross-linking and significantly improve the thermal and mechanical properties of the final polymer.

At present, the known benzocyclobutene-based monomers can be divided into following groups, namely, siloxane and silyl derivatives containing vinyl fragment, compounds with perfluorinated fragments, compounds containing ether (including acrylate), amide, imide groups; polyolefins or polyaromatics. The most common are siloxane- and silyl-containing compounds.

Siloxane compounds

Commercially available monomer bis(cyclobutenylvinyl)siloxane (**9**) should be first noted between the compounds of this group.



Polymer based on **9** has low dielectric constant value ($k = 2.65$) in the frequency range of 1 kHz–20 GHz²³ and insignificant dispersion in a wider range of 100 Hz–60 GHz,³⁶ excellent planarization ability, low moisture absorption, capability for photo and thermally induced curing without evolution of the by-products.

Composition based on compound **9** was developed in the 1980s by The Dow Chemical Co. (Midland, MI, USA). The company produces until now various material varia-

tions under CYCLOTENE brand name. The production of integrated circuits, GaAs chips on their basis started in the 1990s (TriQuint Semiconductors, Hillsboro, OR, USA, Nortel Networks, Brampton, ON, Canada). The materials are also used as insulating materials in the manufacture of flat-panel displays.^{37–39} These coatings are used in Japan to insulate copper conductors when creating a new generation of printed circuit boards for communication devices.⁴⁰

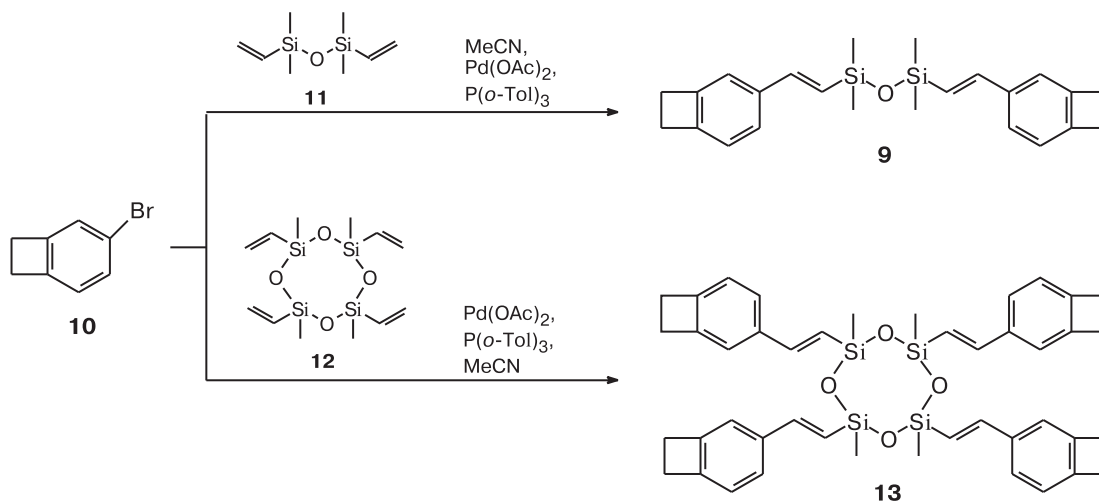
By 2017, The Dow Chemical Co. proposed a series of commercial composite materials based on compound **9**, which are adapted to different technological tasks and allow to create dielectric layers of a given thickness using a variety of curing technologies.

The synthesis of compound **9** and its analogues is described in many publications. For example, in work⁴¹ monomers **9** and **13**, polymers and copolymers based on them were prepared and studied (Scheme 3). The starting compound for the synthesis of these monomers is 3-bromobenzocyclobutene (**10**), which is obtained by direct bromination of benzocyclobutene under various conditions.^{26,42–50}

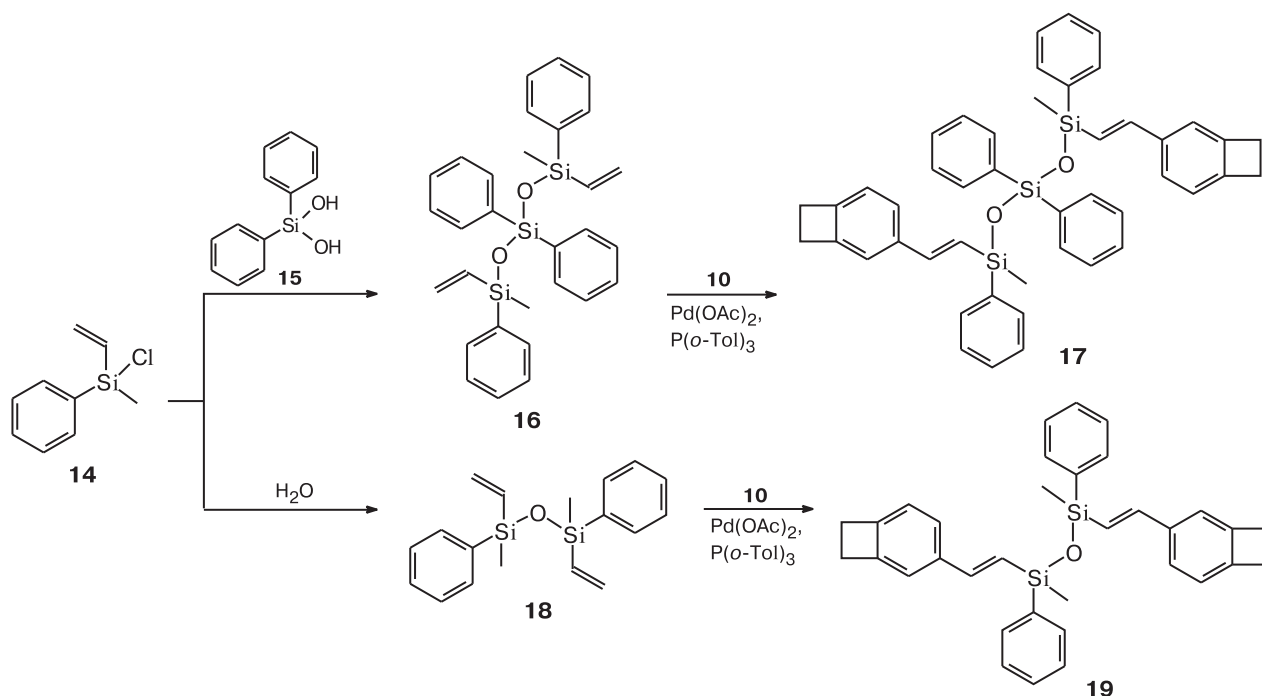
Polymeric materials based on bis(cyclobutenylvinyl)siloxane have a low dielectric constant (2.65 (**9**), 2.77 (**13**) at 1 MHz) and high thermal stability (T_d (**9**) = 456 °C, T_d (**13**) = 487 °C). High glass transition temperature (>400 °C) is also noted for materials based on compound **13**. This is obviously associated with a denser cross-linking in the structure of such polymer. These polymers are characterized by low moisture absorption. In particular, the polymer based on compound **9** shows an increase in weight of only ~0.5% upon boiling in water for five days. Its analog based on monomer **13** shows an increase weight of ~0.7%.

Monomers and polymers based on monomers obtained according to Scheme 4 and containing similar vinylsiloxane

Scheme 3



Scheme 4



fragments with different lengths of siloxane bridges (**17** and **19**) were synthesized.⁵¹ Another difference of these compounds from compounds **9** and **13** was the substitution of the methyl group by the phenyl group. Obtained polymers showed moderately high glass transition temperatures (T_g (**17**) = 257 °C and T_g (**19**) = 383 °C), high decomposition onset temperature ($T_{d5\%}$ = 472 °C) for both polymers either in air or in the nitrogen atmosphere, as well as low values of the dielectric constant (k = 2.69 and 2.66, respectively) and water sorption (0.2 and 0.17%, respectively).

Several similar compounds containing siloxane connecting fragment have been reported in recent years. Thus, a method for the preparation of monomer compounds (Scheme 5) containing several siloxane fragments that bind benzocyclobutene groups was developed.⁵²

The attraction of this approach lies in the availability of the original organosilicon compounds, no need to use inorganic catalysts, including those based on precious metals, ease of synthesis, and high reaction yields. The starting 4-(chloromethylvinyl)silyl)benzocyclobutene is obtained in 76.9% yield by heating preliminary prepared mixture of dichloromethylvinylsilane and magnesium powder in THF for 3 h. Products **21**, **22**, and **24** were isolated at subsequent steps by mixing the components (**14** and the corresponding silanol derivatives **15**, **20**, and **23**) in the presence of triethylamine in THF in 86, 82, and 75% yields, respectively. Thermal polymerization in this case was carried out as for most similar polymers under

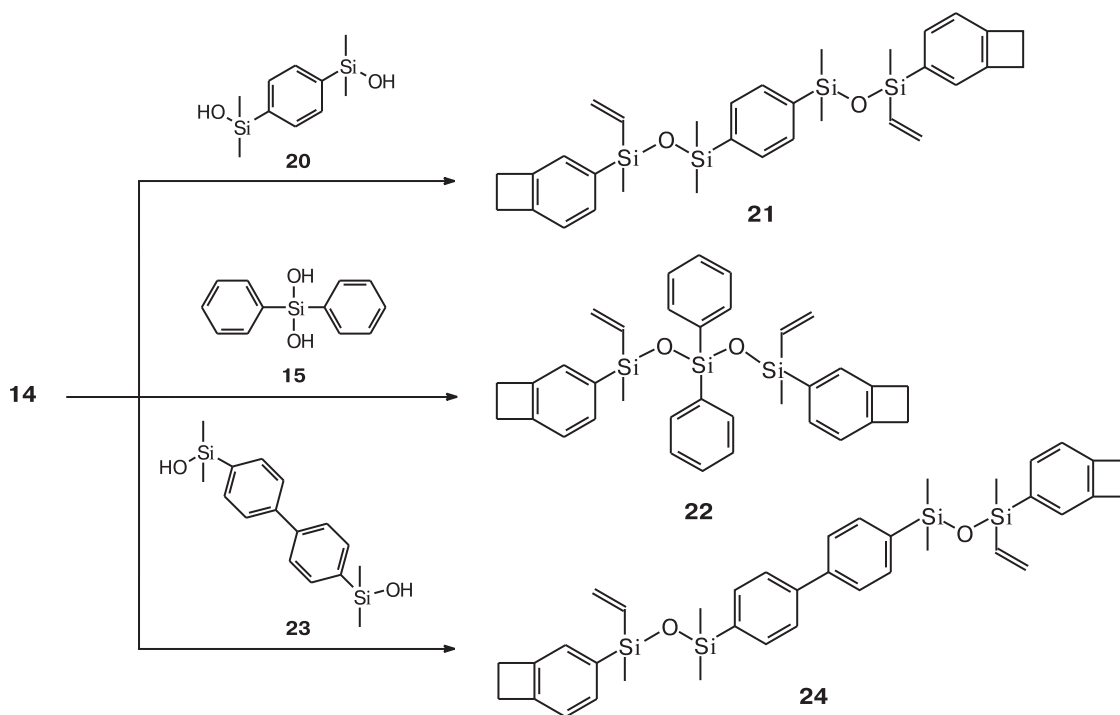
heating with a gradual increase in temperature (130 °C (0.5 h), 180 °C (1 h), 210 °C (1 h), 230 °C (1 h), 250 °C (1 h), 270 °C (1 h), 290 °C (0.5 h)). The values of the dielectric constants (k) of obtained polymers lie in the range of 2.69–2.87 and slightly exceed the values for commercial monomer **9**.

Two compounds containing Si—O—Si and Si—O—C bonds (Scheme 6) were proposed.⁵³

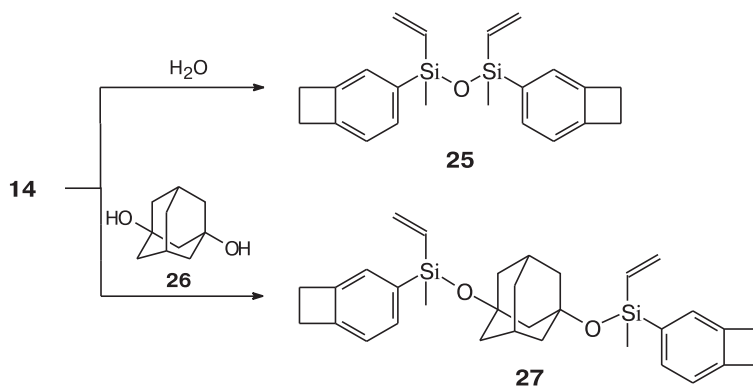
The authors set the task to obtain more affordable and cheaper compounds compared to the monomer **9**. 3-Bromobenzocyclobutene was used as a starting reagent. Synthesis of monomer was carried out in two steps. The intermediate 3-(chloromethylvinyl)silyl)benzocyclobutene was obtained in 76.9% yield by adding 3-bromobenzocyclobutene to a previously prepared mixture of dichloromethylvinylsilane and magnesium powder in THF at 45 °C. The cross-linking of two molecules of 4-(chloromethylvinyl)silyl)benzocyclobutene to give compound **25** was carried out by hydrolysis in a toluene—THF mixture containing pyridine and 0.85 equiv. of water. Stirring of the reaction mixture at 80 °C for 2 h, followed by processing, afforded the target compound in 86% yield. Compound **27** was obtained in 90% yield by reacting 4-(chloromethylvinyl)silyl)benzocyclobutene (**14**) with adamantane-1,3-diol (**26**) in the presence of imidazole and 4-dimethylaminopyridine (DMAP) in THF.

It should be noted that, compared with compound **9**, its analog **25** has somewhat improved thermal stability, significantly higher glass transition temperature (380 °C),

Scheme 5



Scheme 6



and significantly superior elastic modulus values at elevated temperatures (>300 °C). This is due to differences in the degree of cross-linking of polymers based on compounds **9** and **25**, **27**. Scheme 7 shows the key differences in the structure of polymers.

For the polymer based on monomer **9**, the cross-linking is carried out by means of siloxane bridges, each silicon atom being linked to two polymer units, whereas in the case of compounds **25** or **27** each silicon atom is linked to three polymer units. This ensures denser interaction of polymer fragments.

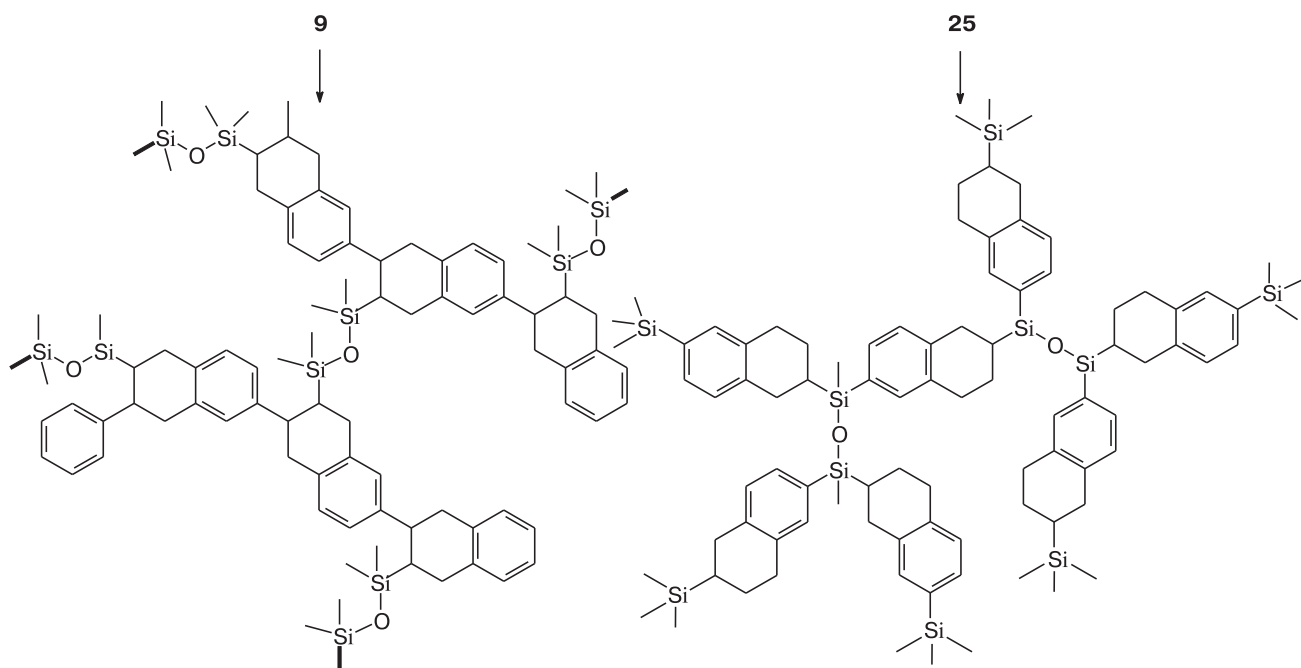
The dielectric properties of the obtained polymers remain almost unchanged in the frequency range from

100 kHz to 1.2 MHz, the values of k are 2.72 and 2.78 for polymers based on **25** and **27**, respectively.

Two samples of bis(dimethylamino)silane containing benzocyclobutene fragments were synthesized by Chinese group in an effort to obtain an analog of monomer **9**.⁵⁴ The polycondensation reaction of 1,4-bis(dimethylhydroxysilyl)benzene with bis(dimethylamino)methylsilanes gave copolymers that underwent cross-linking at elevated temperatures by opening of the cyclobutene ring (Scheme 8).

Fabricated materials have high values of glass transition temperature (218 and 256 °C), decomposition onset temperature ($T_{d5\%} = 553$ and 526 °C in nitrogen atmosphere, 530 and 508 °C in air), and dielectric constant (2.66 and

Scheme 7



2.64) for polymers **33** and **34**, respectively. Thus, cross-linked polysiloxanes **33** and **34** exhibit higher thermal stability, lower glass transition temperature, and comparable dielectric constant compared to monomer **9**. Other noteworthy properties of the materials studied in this work⁵⁴ are low moisture absorption ($\leq 0.28\%$) and high transmission in the visible light range, namely, 86% and 90% transmission at 450 nm for compounds **33** and **34**, respectively, at a threshold wavelength of 321 (**33**) and 314 nm (**34**).

The hydrosilylation can be one example of the preparation of polymeric materials with Si—O bonds in a polymer chain containing benzocyclobutene fragments can be the hydrosilylation reaction (Scheme 9).⁵⁵ The authors used two schemes of the process, which differ in the source of the vinyl fragments. According to the first scheme poly(methylvinylsiloxane) (**37**) was modified by 4-[(1-hydroxy-1,1-dimethyl)silyl]benzocyclobutene (**38**) in the presence of platinum on carbon. According to the second scheme poly(hydromethylsiloxane-co-dimethylsiloxane) (**40**) was modified by 4-((1,1-dimethyl-1-vinyl)silyl)benzocyclobutene (**41**) in the presence of the same catalyst.

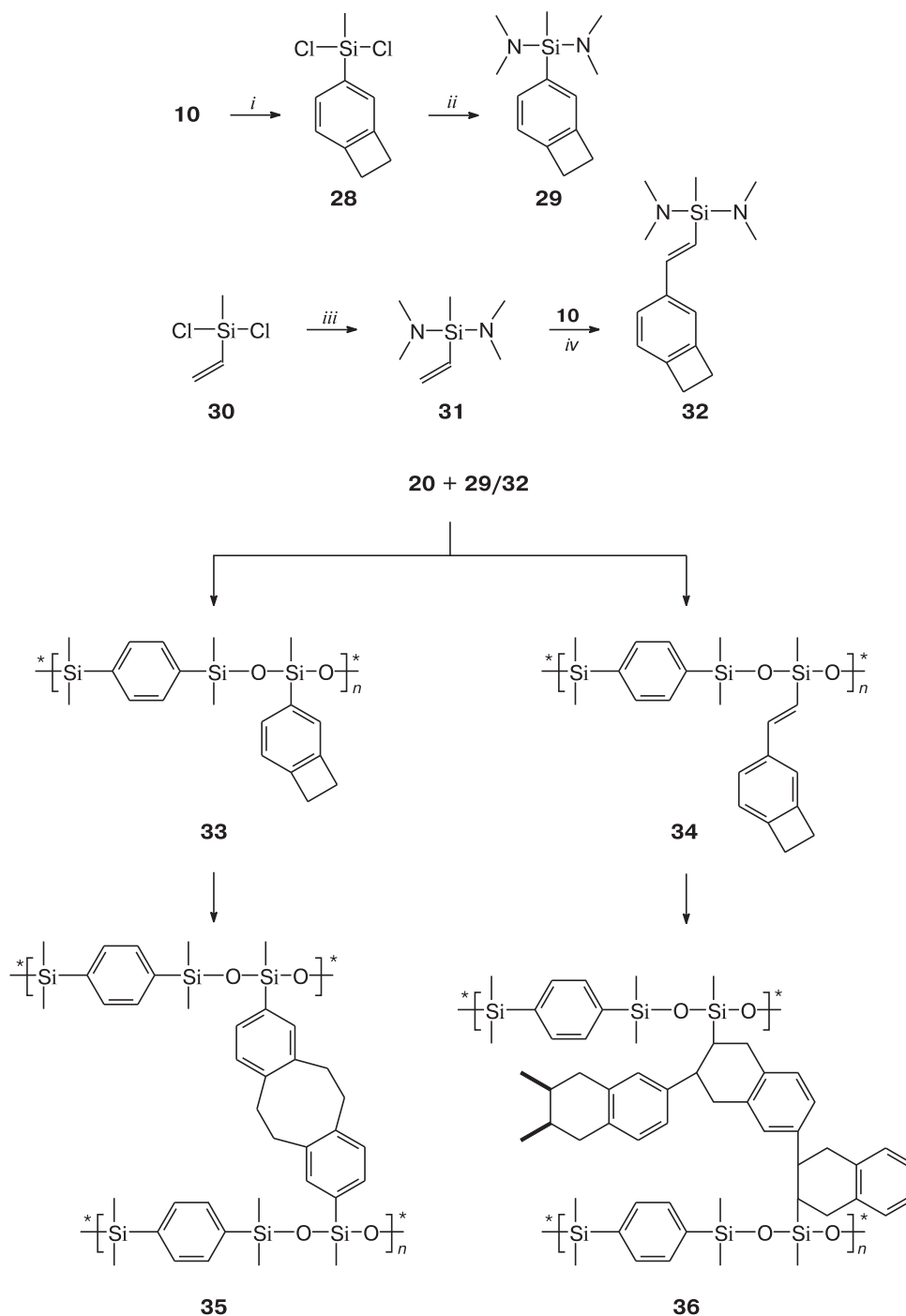
In the first case, polymers **39** containing 25.1, 30.4, and 48.8% of benzocyclobutene fragments in the structure were obtained. Decomposition onset temperatures after cross-linking substantially exceeded the corresponding values for the starting polysiloxane polymers and consisted of 466.1, 496.6, 518.4 °C, respectively.

The preparation of siloxane monomers **43** and **44** was described in Ref. 56. The synthesis was carried out according to Piers—Rubinsztajn reaction by action of methyl-dimethoxyvinylsilane and triethoxyvinylsilane, respectively, on (benzocyclobuten-4-yl)dimethylsilane in the presence of catalytic amounts of tris(pentafluorophenyl)borane). When compounds **43** and **44** are heated in steps from 180 to 300 °C for a long time, the resulting *o*-quinodimethane intermediates interact with each other to form conjugated cyclooctane rings, and also react with vinyl substituents at the silicon atom to form cyclohexane rings.

The values of the dielectric constant k of cross-linked polymers based on **43** and **44** for the frequency range from 0.15 to 30 MHz were 2.62 and 2.52, respectively. The authors note that functionalized siloxanes described in the literature, obtained by hydrolysis and alcoholysis, have high dielectric constants (>2.7) due to the influence of silanol groups in the polymer. Compounds **43** and **44**, obtained by the Piers—Rubinsztajn reaction, do not contain silanol groups in their composition, which had a positive effect on their dielectric properties.

The $T_{d5\%}$ values were 461 and 482 °C for polymers based on compounds **43** and **44**, respectively. This correlates with a higher cross-link density in the second polymer containing a greater number of benzocyclobutene fragments. The glass transition temperatures were also quite high, with a clear superiority of polymer based on

Scheme 8

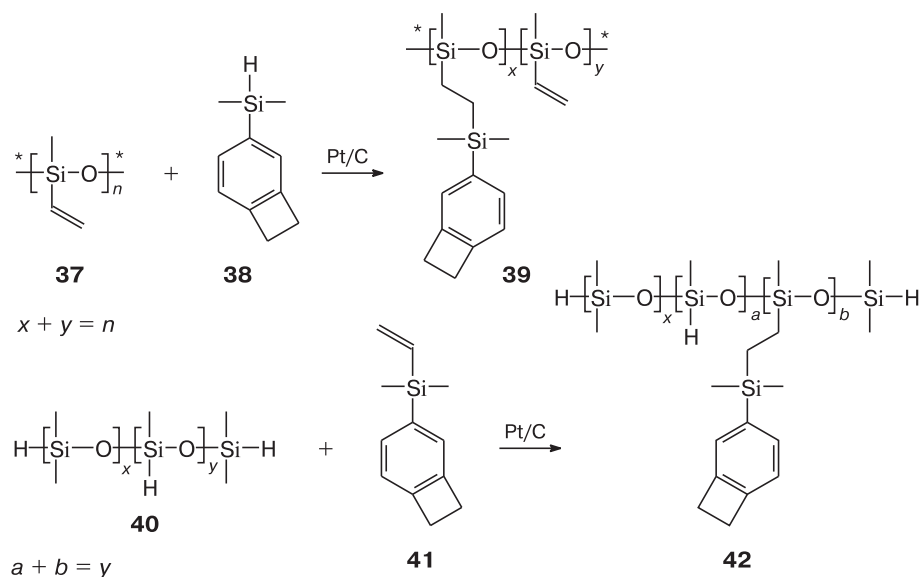


Reagents and conditions: *i.* 1) Mg, 2) MeSiCl_3 ; Et_2O , N_2 ; *ii.* $\text{HN}(\text{Me})_2$, Et_2O , N_2 ; *iii.* Me_2NH , Et_2O , N_2 ; *iv.* Et_3N , MeCN , $\text{Pd}(\text{OAc})_2$, $\text{P}(o\text{-Tol})_3$.

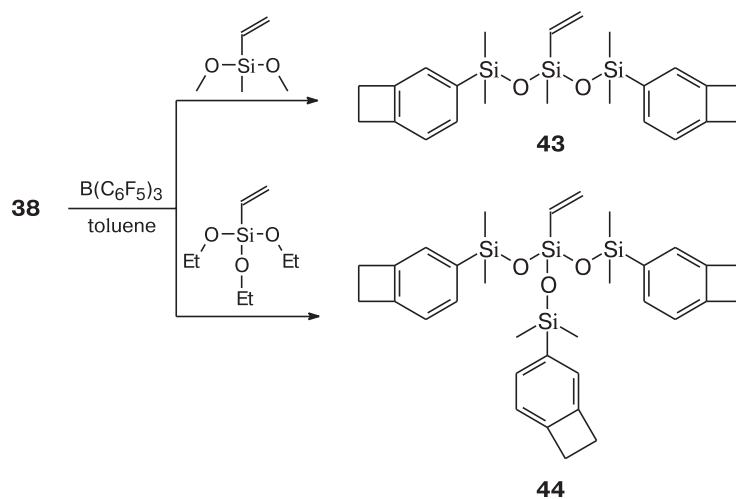
44 (208 °C for **43** and 350 °C for **44**). Water absorption during boiling of polymers in water for 72 h was <0.2%. These data correlate with data on the value of the water

contact angle (96° for **43** and 100° for **44**) of the surface of cross-linked materials, showing a high degree of hydrophobicity.

Scheme 9



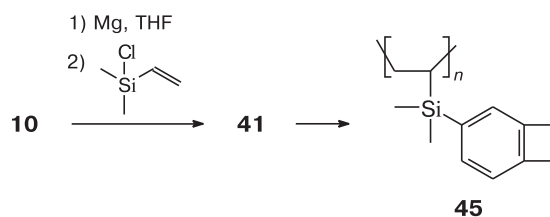
Scheme 10



Silyl compounds

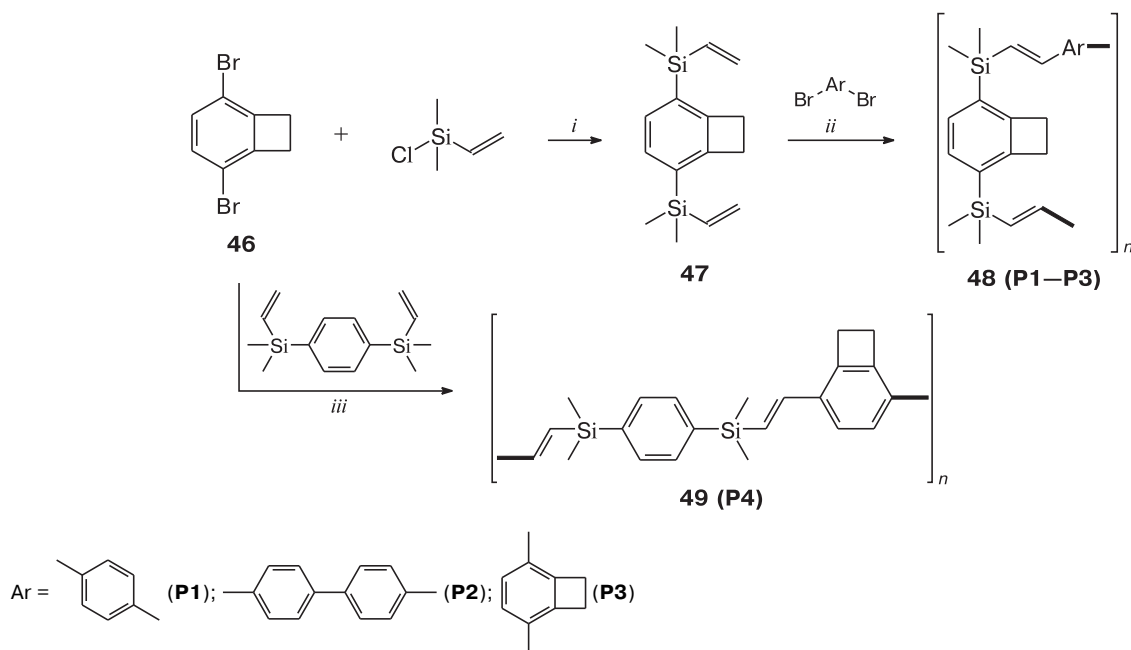
The simplest representative of this group of compounds is 4-(1',1'-dimethyl-1'-vinyl)silyl)benzocyclobutene (**41**). The synthesis of both the monomer itself (Scheme 11) and its homopolymers and co-polymers with styrene and 4-bromostyrene is described in Ref. 57. Reaction of homopolymerization under conditions of radical initiation is not typical for trialkylvinylsilanes and phenylvinylsilanes. The authors explain this fact by the low stability of the resulting radicals due to the electron-donor effect of the silane fragment. The homopolymerization reaction was successfully carried out in about 90% yield using *n*-butyllithium as the initiator. Poly{4-[(1',1'-dimethyl-1'-

Scheme 11



vinyl)silyl]benzocyclobutene} was pre-crosslinked by partially opening the cyclobutene rings at 160–170 °C in an inert atmosphere for 10 h. This increased the viscosity of the solution required for application of the composition

Scheme 12



Reagents and conditions: *i.* Mg, THF, 25–40 °C; *ii.* P(*o*-Tol)₃, Buⁿ₃N; Pd(AcO)₂; *iii.* P(*o*-Tol)₃, Buⁿ₃N; Pd(AcO)₂.

to the substrate by spin-coating. The next step to obtain a highly cross-linked polymer proceeded at 200 °C for 8 h. The material that passed through all the cross-linking steps had excellent dielectric ($k = 2.45$) and thermal ($T_{d5\%} = 380$ °C) properties.

There are other examples of the synthesis of silicone monomeric and polymeric compounds based on benzocyclobutene. Thus, the synthesis of dimethylvinylsilanes **47** and their polymerization (Scheme 12) were considered in Ref. 34.

Described polymers **P1–P4** possess acceptable properties for use as insulating materials. The polymers have a high decomposition temperature in nitrogen ($T_{d5\%}$ (**P1**) = 443 °C, $T_{d5\%}$ (**P2**) = 467 °C, $T_{d5\%}$ (**P3**) = 492 °C, $T_{d5\%}$ (**P4**) = 424 °C). At the same time, polymers **P1–P3** have low stability in air at temperatures above 300 °C, while for **P4**, weight loss of 5% occurs at a temperature of ~450 °C. The dielectric constant of polymer **P3** is 2.5 (1–10 MHz).

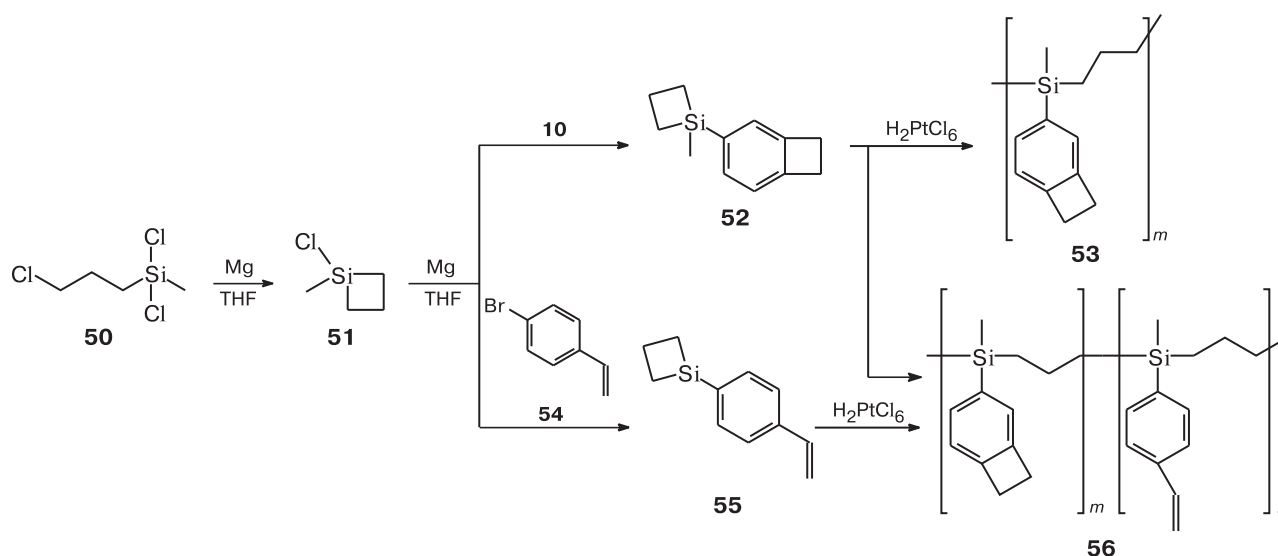
The authors pursued the goal of obtaining a material with photopolymerization and thermal polymerization properties, low dielectric constant (<2.5), glass transition temperature above 400 °C, and decomposition onset temperature above 450 °C in accordance with the requirements of technological processes for fabrication of integrated circuits.³⁵ In particular, the polymer coating used for this purpose should not be deformed and undergo changes in volume during the process of high-temperature metallization, which takes several hours. The monomers based on silacyclobutene have been proposed to solve the problem (Scheme 13).

The synthesis of silacyclobutane-containing components was carried out by the Grignard reaction of the corresponding bromo derivatives of arenes with 1-chloro-1-methylsilacyclobutane generated from 1,1-dichloro-3-chloropropyl-1-methylsilane in a *one-pot* reaction, in total 61–64% yields for cyclobutene- and vinylbenzene-containing monomers, respectively. Polymerization with the opening of the silacyclobutane ring was carried out using hexachloroplatinic acid as a catalysis at 60 °C for 12 h. The obtained polymer was dissolved in toluene, and then applied by spin-coating (2500 rpm) on a silicon substrate. Cross-linking was carried out in two steps, namely, UV irradiation at ~20 °C for 2 h, and heating at 280 °C for 0.5 h. It is noted that UV irradiation has a small effect on the benzocyclobutene fragment, as evidenced by the change in the IR characteristic signal at 1456 cm⁻¹.

The authors³⁵ note that polymers **53** and **56** obtained in this way possess high values of the decomposition onset temperature. Thus, $T_{d5\%} = 477$ °C for polymer **53**, and $T_{d5\%} = 473$ °C for polymer **56**. The dielectric constants of polymers lie in the range of 2.32–2.4 (1 kHz–1 MHz). It is noted that the value of k depends on the completeness of the polymerization processes, namely, before heat treatment, the typical value for polymers was $k = 2.6$.

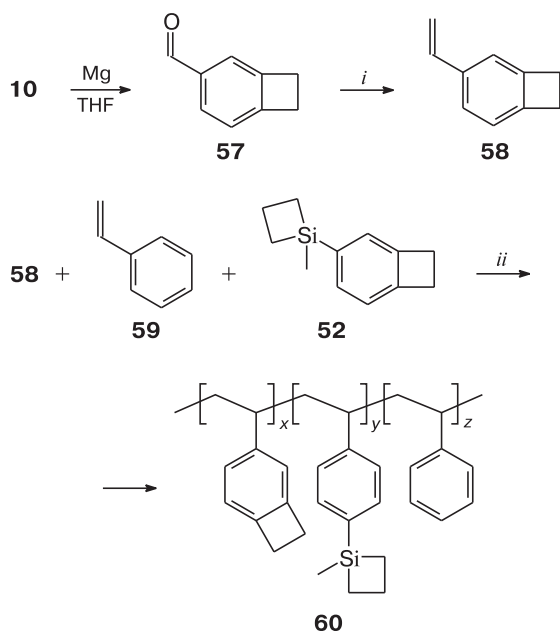
A similar process of copolymerization of 4-vinylbenzocyclobutene, styrene, and 1-methyl-1-(4-vinylphenyl)-silacyclobutene with a different ratio of components (Scheme 14) was considered.⁵⁸ The process proceeded during heating (90 °C) of a mixture of monomer components in toluene in the presence of catalysts based on

Scheme 13



copper halides and *N,N,N',N',N'*-pentamethyldiethylamine (PMDETA) for 24 h. Cross-linking was carried out in two steps photopolymerization under irradiation with UV light (365 nm) and subsequent heating for 6 h at temperatures of 170 °C (2 h), 220 °C (2 h), and 260 °C (2 h). Cross-linked polymer **60** is characterized by high thermal stability ($T_{5\%} = 386$ °C) and low $k = 2.3$ (10 MHz).

Scheme 14



Reagents and conditions: *i.* $\text{PPh}_3 \cdot \text{CH}_3\text{I}$, Bu^nLi , -78 °C, RT; *ii.* CuCl , CuBr_2 , 90 °C, PMDETA, BzBr.

Among other things, the ability of 4-methylsilacyclobutane fragment to open and polymerize not only under

the action of catalysts based on $\text{Pt}(\text{acac})_2$ or hexachloroplatinic acid, as in the previous example, but also under the action of UV irradiation, was revealed.⁵⁸ Moreover, the authors noted the ability of silacyclobutane and benzocyclobutene fragments to react with each other at a temperature of ~ 230 °C. This is reflected in the DSC curves of the samples treated with $\text{Pt}(\text{acac})_2$ catalyst (Fig. 2, *a*), the starting material (see Fig. 2, *b*), and polymers **60** irradiated with UV light (see Fig. 2, *c*, Scheme 15). For this series of polymers, a maximum at 143 °C corresponding to the opening of the silacyclobutane ring is observed on the DSC curves upon heating in the presence of a platinum catalyst. A maximum at 258 °C responsible for the opening of the benzocyclobutene ring (see Fig. 2) is also detected. Thermally unprocessed polymer **60** is characterized by the appearance of a shoulder at 230 °C that is absent in Fig. 2. This can be explained by the interaction of the silacyclobutane and benzocyclobutene fragments. Finally, the signal at 258 °C is also characteristic of the pre-irradiated polymer, and there is no signal (shoulder) responsible for the activity of the silacyclobutane ring.

This finding opens up new possibilities in the field of polymer design and polymerization technology.

Poly(silamethylene)s **69** were synthesized by copolymerization with ring opening of disilacyclobutene, functionalized with fragments of benzocyclobutene and phenyldisilacyclobutane.⁵⁹ The content of benzocyclobutene fragments was controlled by varying the ratio of monomers (Scheme 16).

Thus, varying degrees of cross-linking during the thermal opening of the cyclobutene ring allowed the authors to improve the dielectric properties of the material and its thermal stability. Thus, the $T_{d5\%}$ of cross-linked polymer **69** increased from 404 to 462 °C (Fig. 3) with an increase in the content of these fragments from 9.5 to 28.9%. At

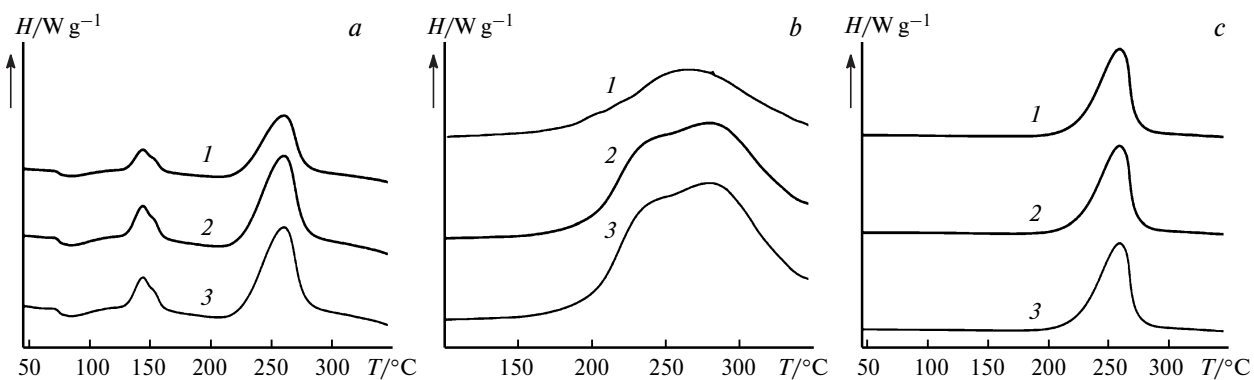
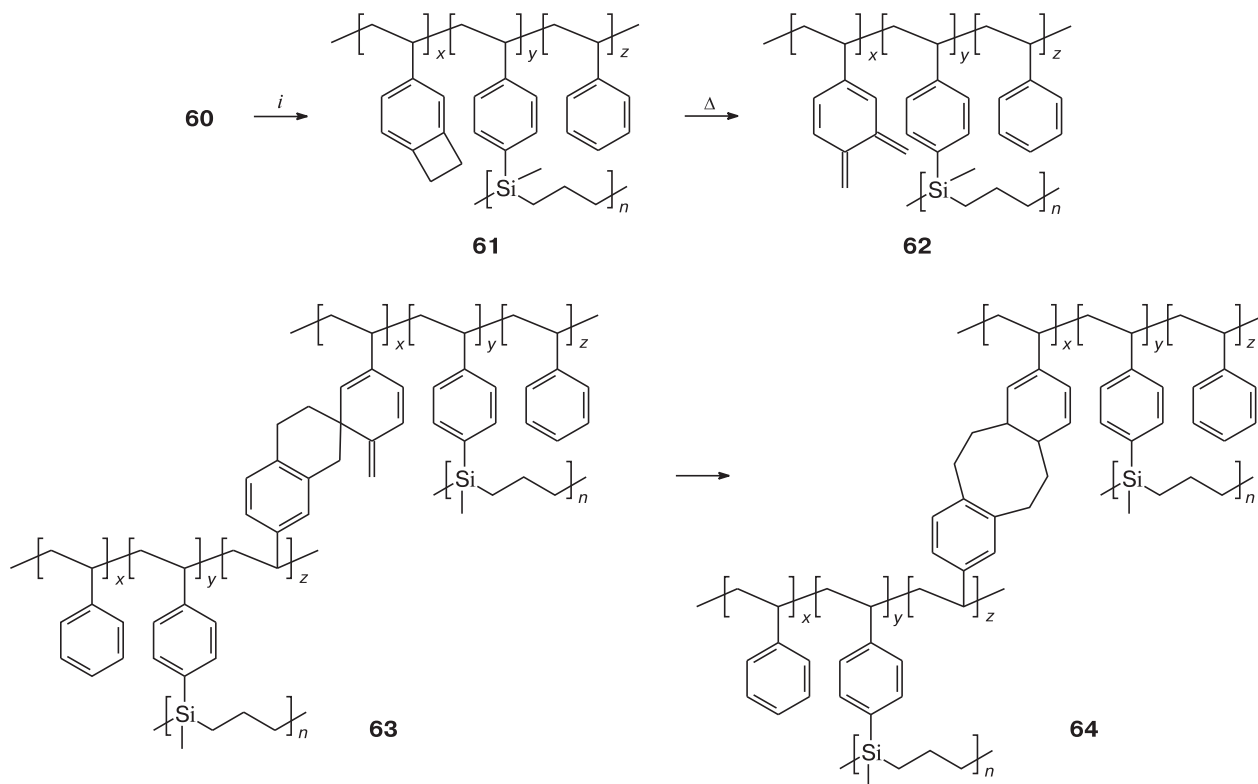


Fig. 2. DSC curves of polymer sample **61** obtained by catalysis using $\text{Pt}(\text{acac})_2$ (a), starting polymer **60** (b), and polymer **61** obtained by UV-irradiation (c).

Scheme 15



Reagents and conditions: *i.* $\text{Pt}(\text{acac})_2$, *hv*, 20 °C.

the same time, the dielectric constant decreased from 2.59 to 2.41 at 10 MHz.

Fluorine-containing aliphatic polymers

Fluorine-containing aliphatic derivatives are fewer common fragments in the chemistry of modern benzocyclobutene-based dielectric materials. Some examples of such structures are compounds **76** and **77** or their analogs⁶⁰ (Scheme 17).

Since fluorine-containing polymers have low dielectric constants,^{61–68} and their linear structure does not provide sufficient thermal stability, the authors used perfluorinated perfluoro-1,2-dihydroxycyclobutane as a basis. Despite the multistep synthesis (see Scheme 17), the total yields of benzocyclobutene-containing monomers are greater than 40%. The polymerization was carried out at sufficiently high temperatures and prolonged heating conditions, namely, 180 °C (4.5 h), 200 °C (4 h), 220 °C (5 h), 240 °C (3 h), and 250 °C (5 h). The obtained polymer has

Scheme 16

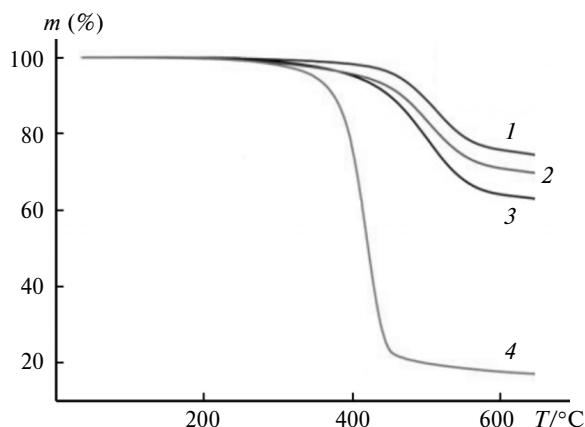
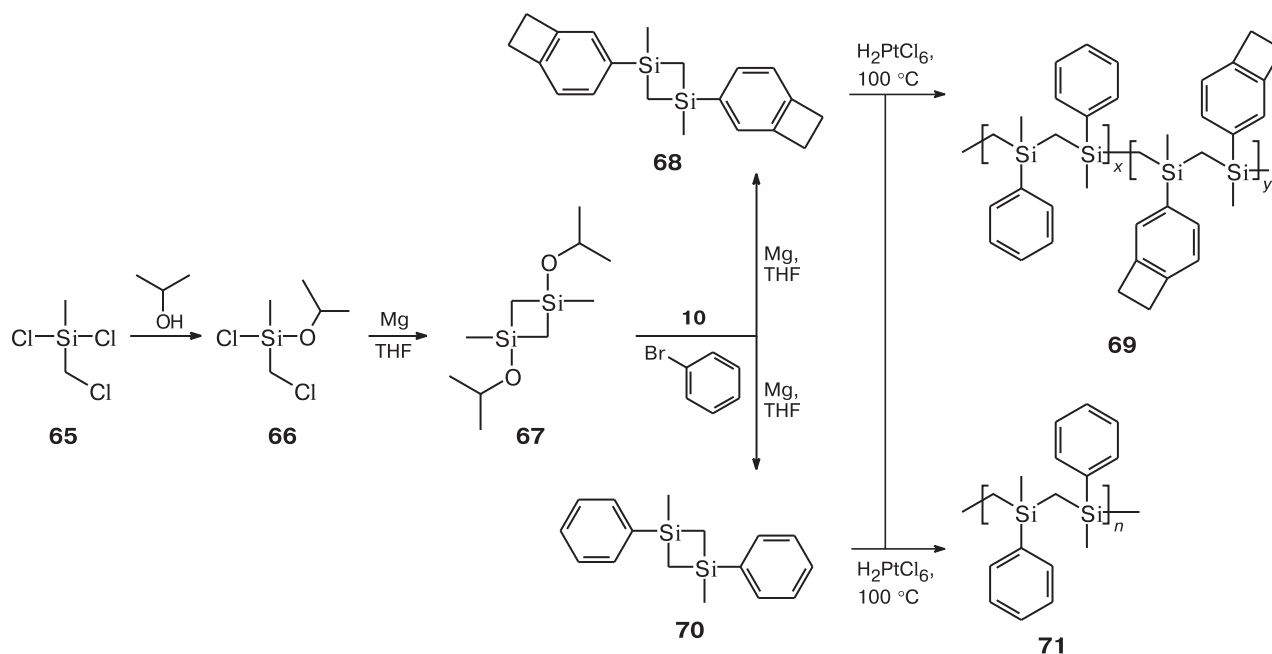


Fig. 3. TGA curves of poly(methylphenylsilylmethylene) (71) and poly(methylphenylsilylmethylene) (69) with incorporated benzocyclobutene fragments with their content from 9.5 (1) to 28.9 (4).

relatively low values of $k = 2.4$ (0.1–30 MHz) and low moisture absorption. The increase in polymer weight was only 0.11–0.31% upon boiling for 96 h. The comparison of the properties of polymers based on 76 and 77 with the properties of a polymer based on 79 (see Scheme 17) allowed the authors to evaluate the contribution of the perfluorocyclobutane fragment. Thus, a polymer based on 79 exhibited significantly higher values of the dielectric constant (2.71) and a much greater ability to sorb water (0.67%). Polymers based on 76 and 77 showed high values of thermal stability ($T_{d5\%} > 460\text{ }^\circ\text{C}$). It should be noted that these monomers do not contain active double bonds,

therefore the polymerization proceeds only in one direction and only upon thermal initiation (Scheme 18).

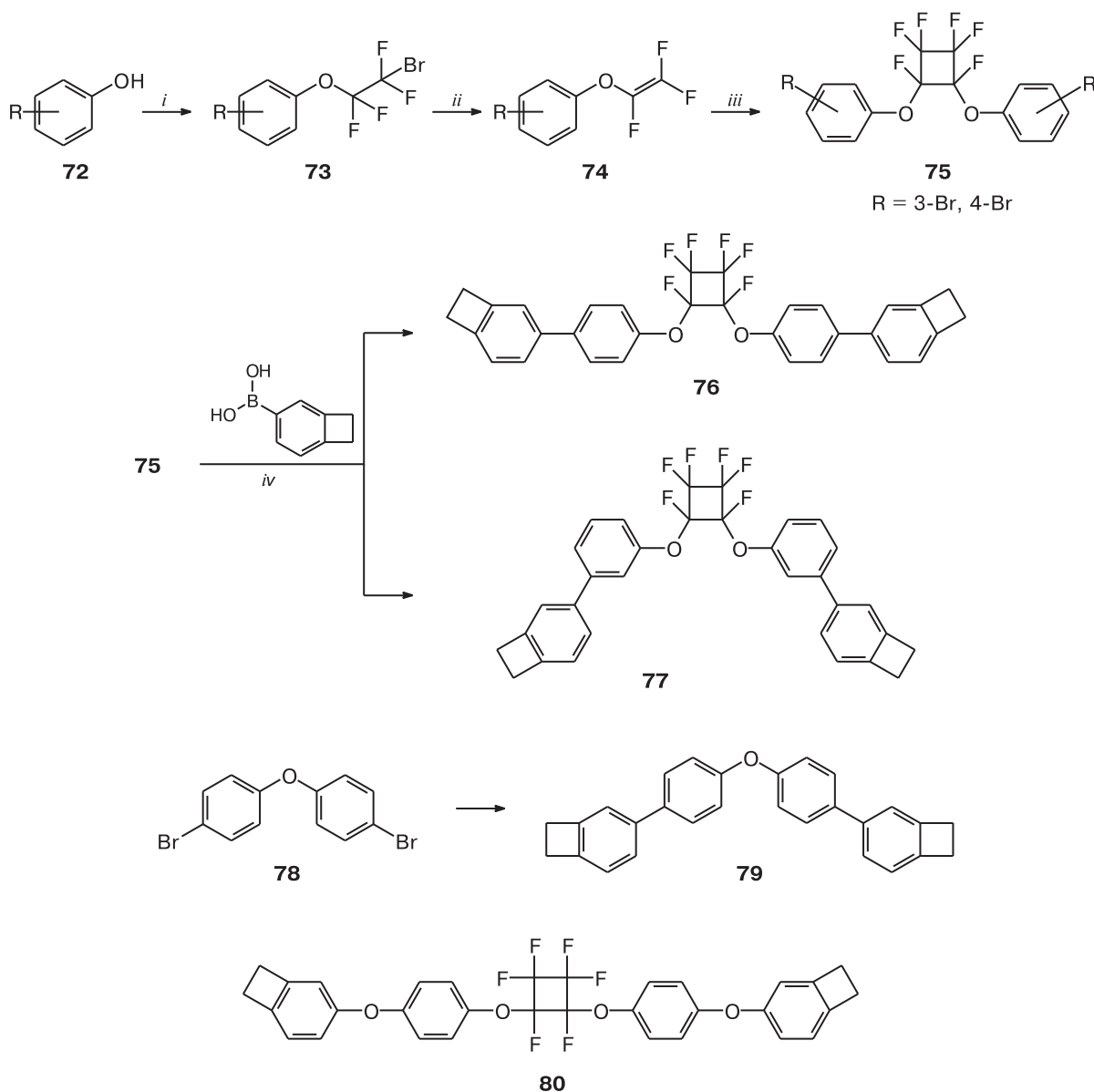
The derivatives containing perfluoro-1,2-dihydroxycyclobutane adamantyl fragment in the side chain (Scheme 19) were described in Ref. 69. The aim of the authors was to study how simultaneous presence of adamantyl, perfluorocyclobutyl, and benzocyclobutene fragments will affect the properties of the final polymer. The obtained material showed properties similar to those of polymers based on monomer 76, namely, the value of the dielectric constant was 2.38, and $T_{d5\%} = 447\text{ }^\circ\text{C}$. Thus, the properties do not change fundamentally in the transition from monomer 76 to monomer 90 containing adamantyl fragment.

Carboxylic acid derivatives containing benzocyclobutene fragment (acrylates)

Polymers with benzocyclobutene fragments obtained by radical polymerization of acrylic acid esters or by polycondensation of amines and carboxylic acid derivatives are quite often described in the literature. The presence of acrylic fragments in the structure of monomers is attractive for the fabrication of active photopolymerizable materials. Photolithographic processes are actively used in the creation of electronic boards and contribute to the miniaturization of electronic devices.

An example of one of such polymers is the product of acylation of 4-hydroxybenzocyclobutene with acrylic acid chloride followed by radical polymerization in the presence of AIBN^{70,71} (Scheme 20).

Scheme 17



Reagents and conditions: *i.* 1) KOH, DMSO; 2) $\text{CF}_2\text{BrCF}_2\text{Br}$, 50 °C; *ii.* Zn/MeCN; *iii.* 175 °C; *iv.* $\text{Pd}(\text{PPh}_3)_4$, 2 M aq. KOH, 80 °C.

The authors^{70,71} note the demand for polyacrylate-based polymers because of their low cost and good mechanical and electrical properties. However, the polyacrylates usually have low glass transition temperatures (<100 °C), which limits their scope of application. Modification of acrylates with a benzocyclobutene fragment allows to obtain highly cross-linked polymers with outstanding properties. The authors obtained both homopolymer and co-polymers with *n*-butyl acrylate and styrene as examples. All materials did not show any T_g in the region up to the decomposition temperature. For the homopolymer $T_{d5\%} = 405$ °C, the polymer is resistant to acids, alkalis, and solvents.

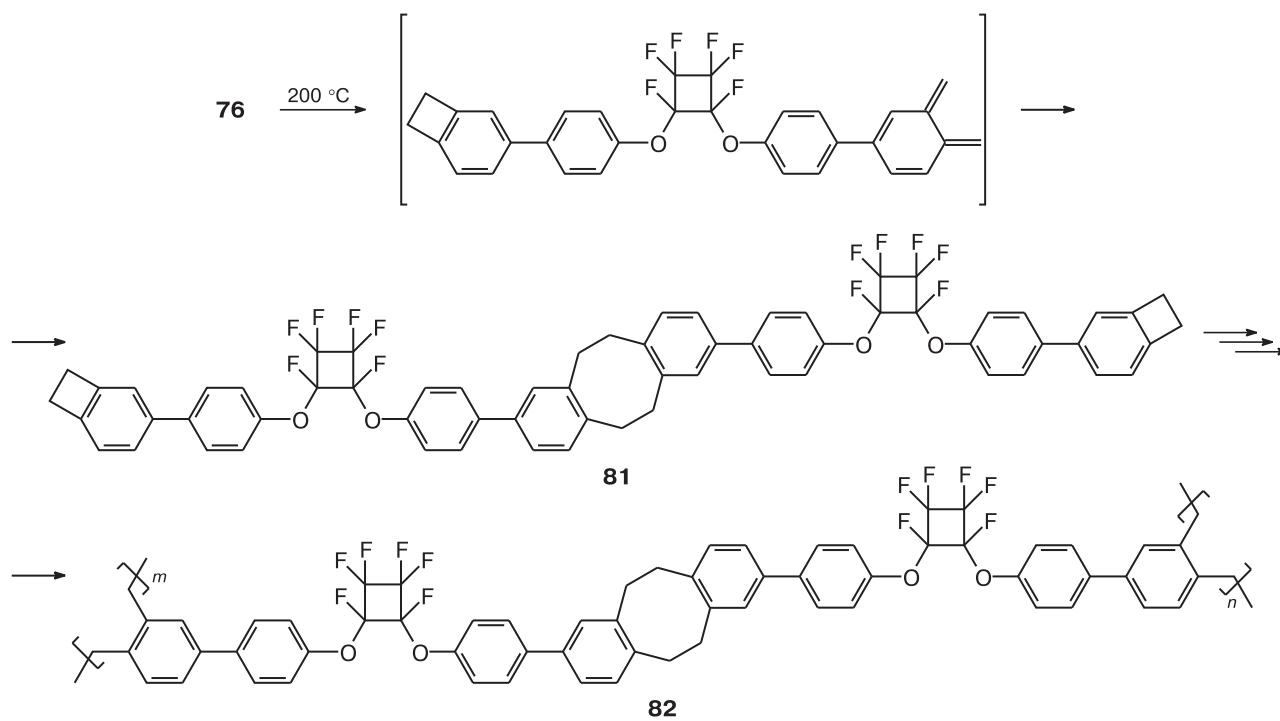
The analog containing acryloyloxy group in position 1 of benzocyclobutene is known⁷² (Scheme 21).

Another example is the derivative of benzocyclobutene and methacrylic acid described in the patent⁷³ (Scheme 22).

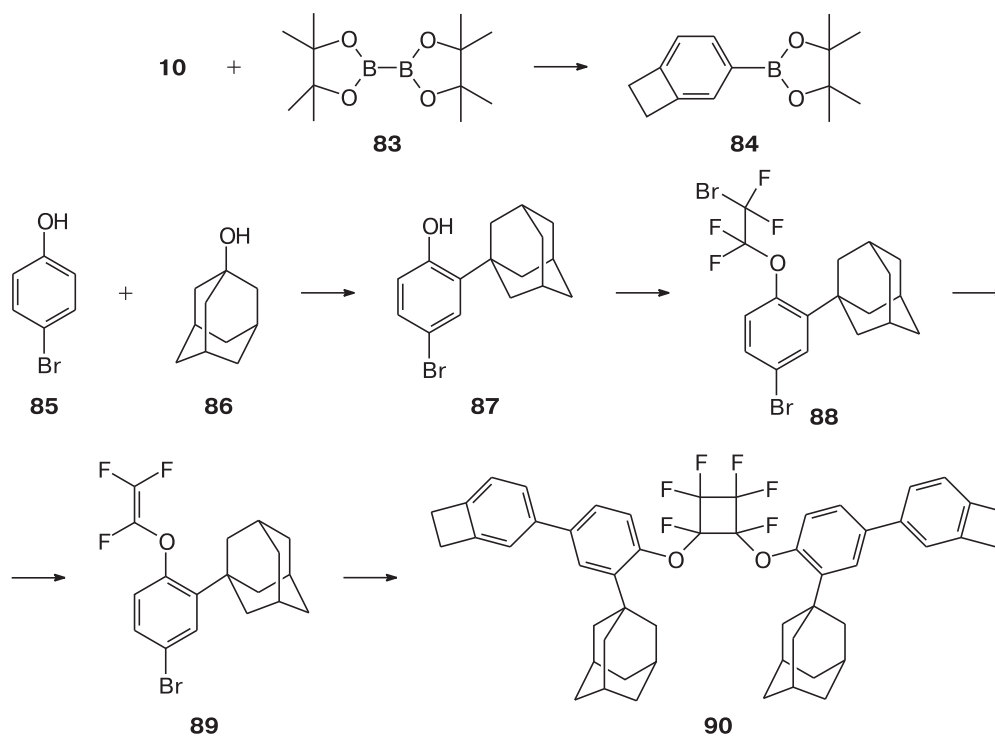
The authors of this patent obtained materials that are epitaxy. These materials were based on esters of methacrylic, 4-benzocyclobutenecarboxylic acids, and diols (see Scheme 22).

Benzocyclobutene derivatives are often used as an additive to the base polymer in the production of dielectric coatings to improve their thermal and mechanical properties. However, stresses often occur in such polymers. This leads to the product bending or tearing off the dielectric

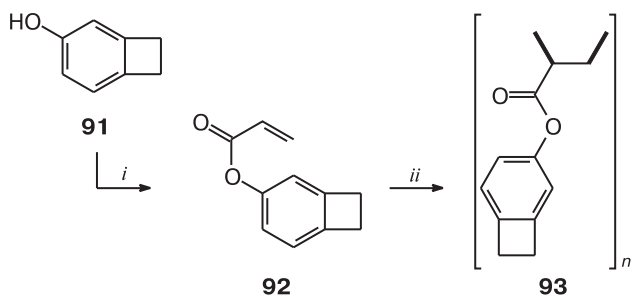
Scheme 18



Scheme 19

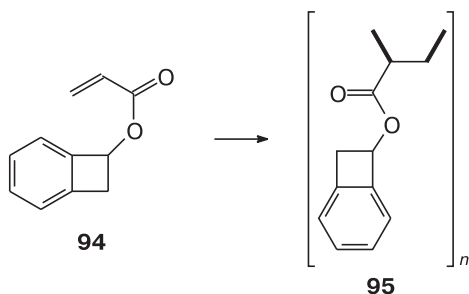


Scheme 20

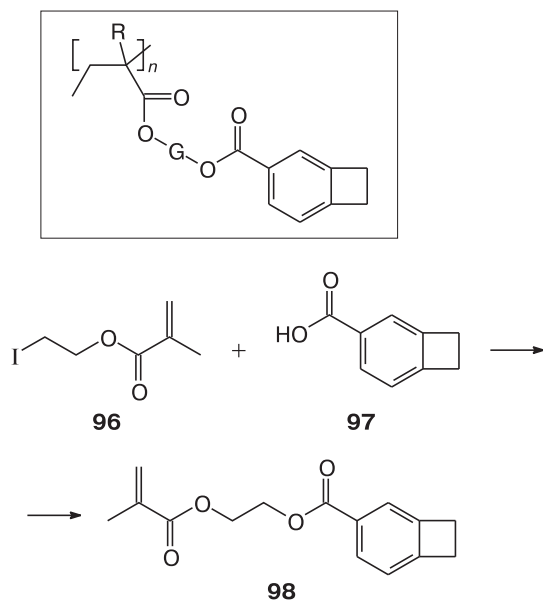


Reagents and conditions: *i.* $\text{Cl}-\text{CH}=\text{CH}_2$, Et_3N , CH_2Cl_2 , $0\text{ }^\circ\text{C}$;
ii. AIBN, $60\text{ }^\circ\text{C}$, 10 h.

Scheme 21



Scheme 22

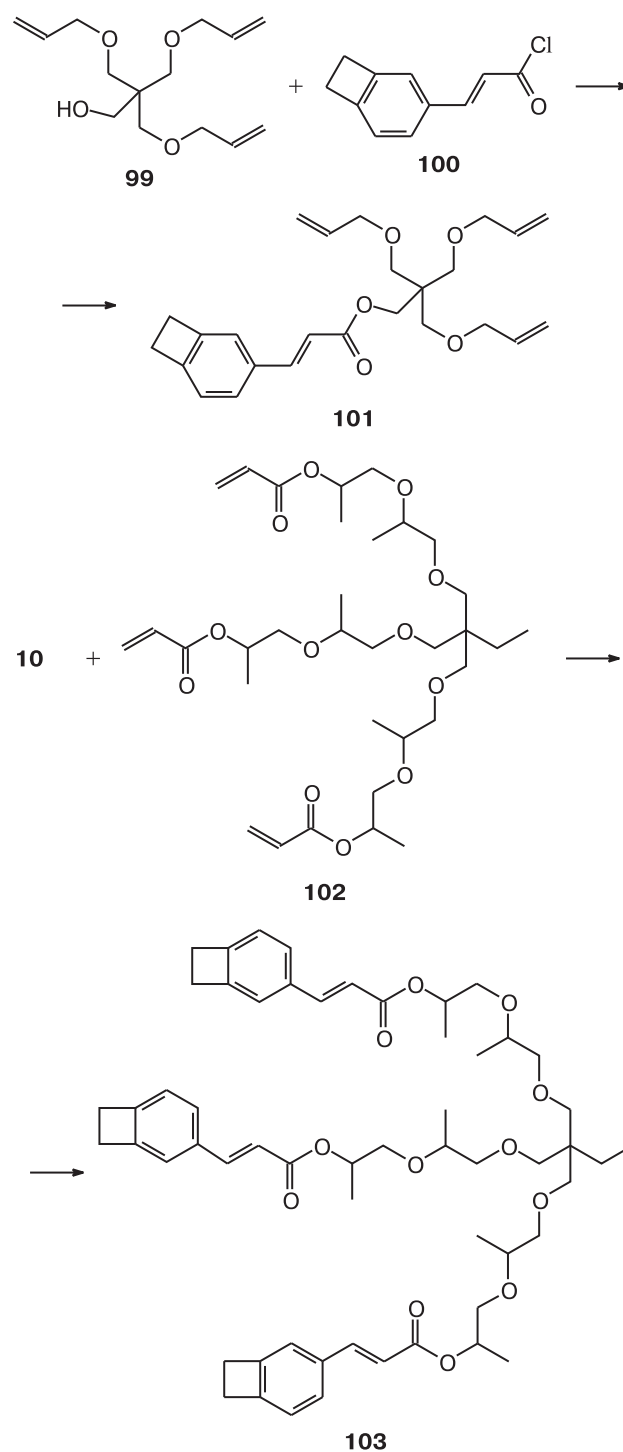


film, which imposes certain restrictions on the thickness of the dielectric layers used.

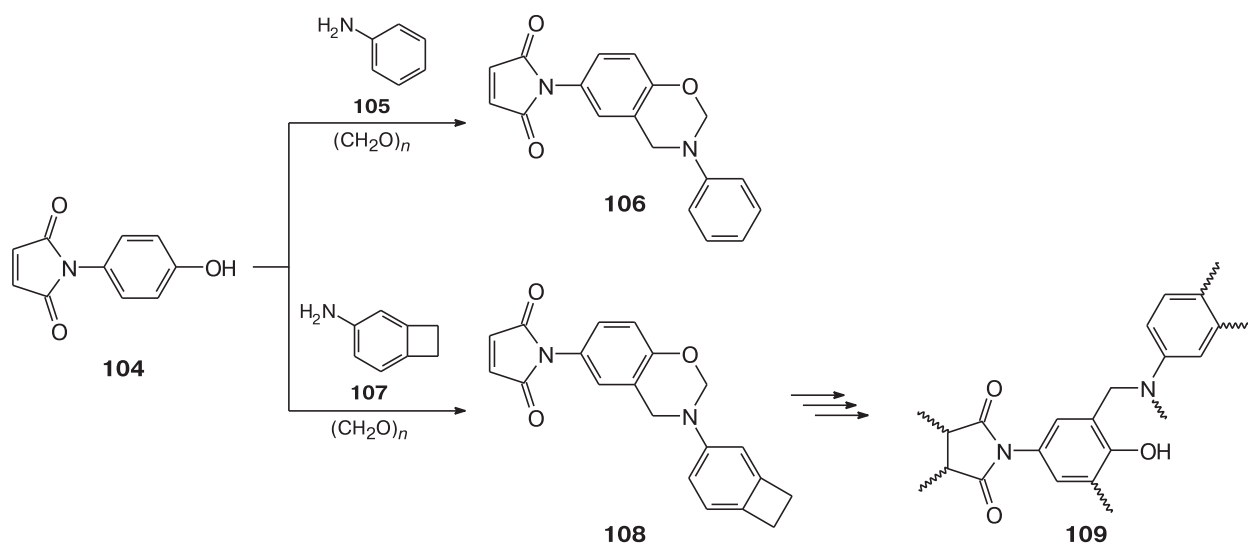
The authors of the patent⁷⁴ have developed the methods for producing polymers with low internal stress based on

pentaerythritol esters. This is achieved by introducing into the polymer of the fragments of cyclobutene derivative of cinnamic acid. Examples of oligomeric polyfunctional materials containing acrylic or allylic benzocyclobutene derivatives, cross-linked with polyester units (Scheme 23), are presented.

Scheme 23



Scheme 24



Amides, imides

Compounds based on amides or imides containing a benzocyclobutene fragment are no less attractive.

Starting reagent 4-aminobenzocyclobutene is convenient for the synthesis of compounds of this group. This imine can be successfully (in 88% yield) obtained by substituting bromine in 4-bromobenzocyclobutene in the presence of copper oxide and ammonium hydroxide.⁷⁵ In particular, the possibility of synthesis of maleimide-containing monomer **108** based on 4-aminobenzocyclobutene and further multistep polymerization was demonstrated (Scheme 24).⁷⁶

The introduction of the benzocyclobutene fragment into the monomer structure increases the glass transition temperature, improves the mechanical properties and thermal stability of the final polymer due to the thermal opening of the cyclobutene fragment and the additional cross-linking of the polymer fragments. The polymer based on compound **106**, which does not contain a benzocyclobutene fragment, has a glass transition temperature $T_g = 250$ °C. The decomposition occurs upon further

heating ($T_{d5\%} = 346$ °C). At the same time, its analog on the basis of **108**, containing a benzocyclobutene fragment, shows significantly increased parameters ($T_g = 350$ °C and $T_{d5\%} = 384$ °C).

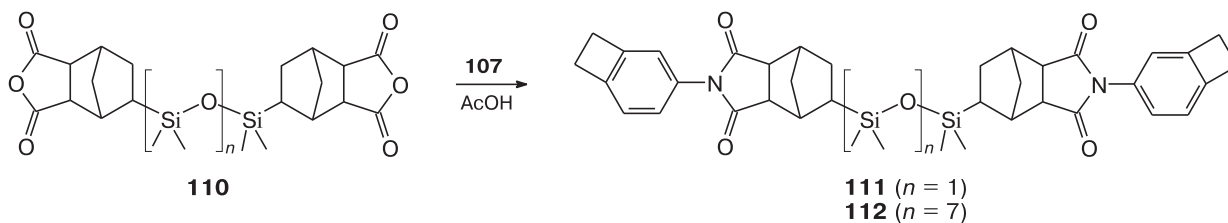
The polymers with low dielectric constant $k = 2.74$ (**111**), $k = 2.69$ (**112**) (1 MHz), good thermal stability ($T_{d5\%} = >485$ °C (**111**), >487 °C (**112**)), and low water sorption capacity were obtained on the basis of 4-aminobenzocyclobutene (**107**) and siloxane-containing dianhydrides with different bridge lengths (Scheme 25).

Often, 4-bromobenzocyclobutene (Scheme 26) is used in the preparation of polyimide polymers as a component of the Heck reaction. The polyimides obtained in this way are widely used as dielectrics, buffer or intermediate layers in microelectronics. In particular, monomers **114**–**116** readily soluble in organic solvents (see Scheme 26) were obtained.⁷⁸

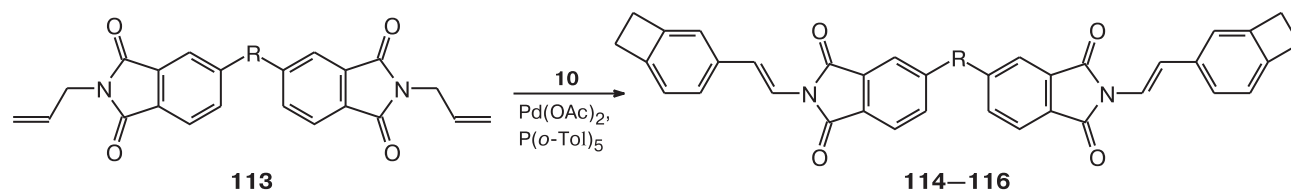
Polymers based on these compounds showed high thermal stability up to 435°C.

A series of copolymers with different ratios of the components ($x = 0, 5, 10, 20,$ and 40%) were obtained based on 4,4'-(2,2,2-trifluoro-1-phenylethane-1,1-diyl)-dianiline (**118**) and compound **119** (Scheme 27), which

Scheme 25



Scheme 26



R = -CO (**114**), C(CF₃)₂ (**115), O (**116**)**

is the product of the interaction of 4-trifluoroacetylbenzocyclobutene and aniline using cyclizing system pyridine-acetic anhydride at 140 °C.⁷⁹

Polymers with a high content of monomer **118** showed improved thermal and mechanical properties.

The study of the copolymers by the method of differential scanning calorimetry (DSC) (Fig. 4) showed that with the introduction into the copolymer from 0 to 40% of monomer **118**, the glass transition temperature increases from 329.2 to 400 °C.

Many polyimides are characterized by low solubility and high melting points, which complicates the process of their molding. Such properties are due to the rigidity of the backbone framework, as well as strong intra and intermolecular interactions. Monomers based on 1-amino-methylbenzocyclobutene (**124**) (Scheme 28) were synthesized by Chinese group in order to improve these characteristics.⁸⁰ Compound **124** was synthesized in two steps. In the first step, 1-cyanobenzocyclobutene was obtained

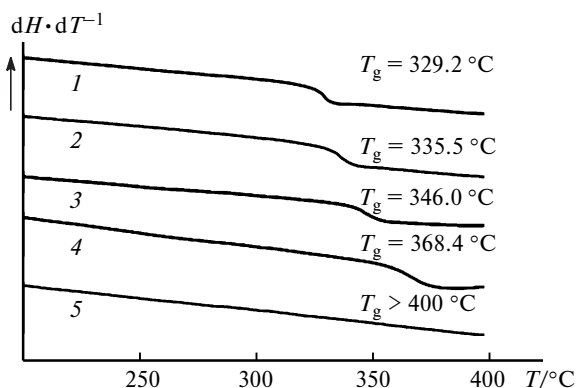
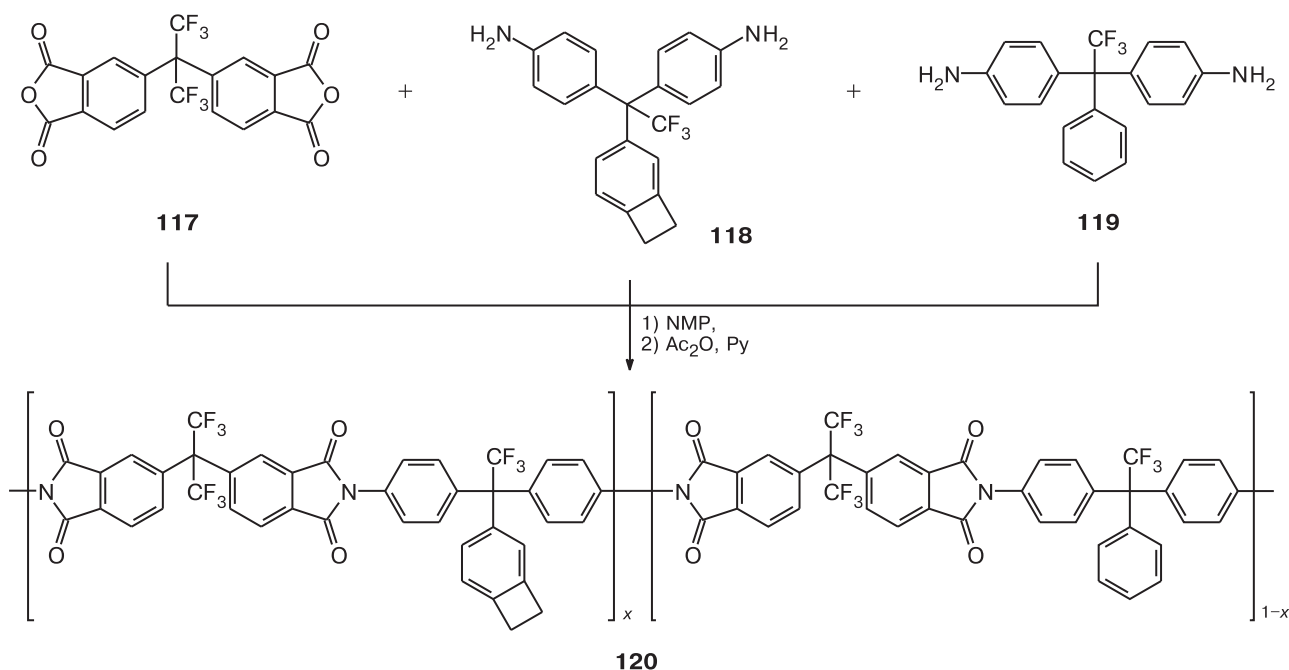


Fig. 4. DSC curves of copolymers **120** with different content of compound **118** (mol.%): 0 (**1**), 5 (**2**), 10 (**3**), 20 (**4**), 40 (**5**).

by cycloaddition of acrylonitrile to dehydrobenzene generated from anthranilic acid by the standard method using isoamyl nitrite as a diazotizing agent and trichloroacetic

Scheme 27



acid as a catalyst. The reaction product was reduced with sodium borohydride in the presence of Raney nickel. The resulting amine was reacted with a number of commercially available dianhydrides. Thus, the imide fragment is linked to the cyclobutene ring in the structure of the obtained monomers to limit the conjugation chain and reduce the possibility of a charge transfer complex formation. The presence of a mobile methylene group also increases the processing ability of materials.

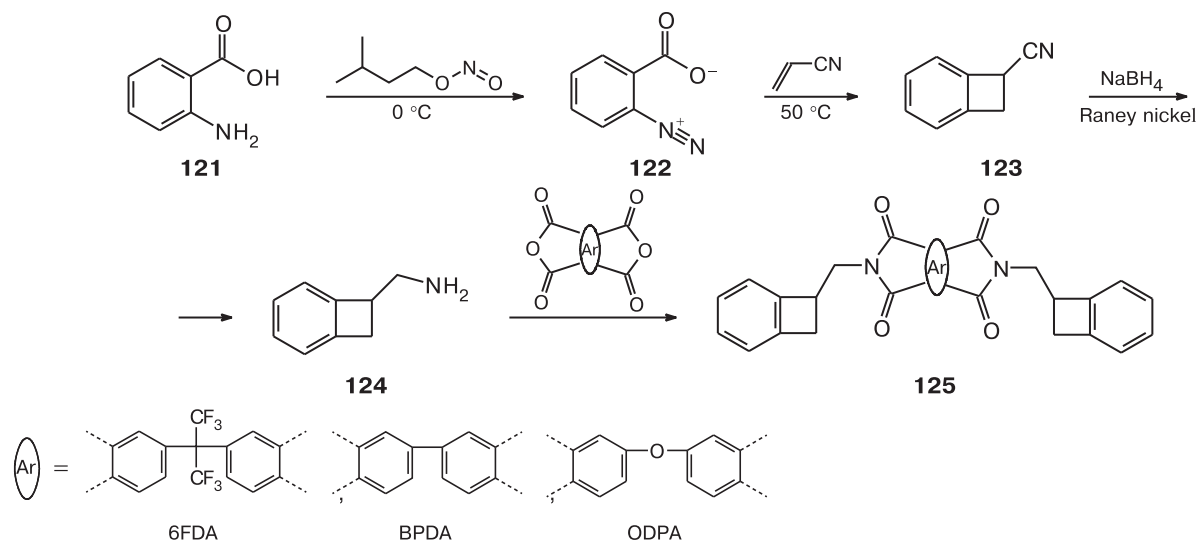
The polymers were synthesized by thermal opening of the cyclobutene fragments of the obtained compounds by heating from 150 to 300 °C for several hours. Due to the high crosslink density and stability of the imide group, the obtained materials are characterized by high decomposition onset temperatures, namely, $T_{d5\%} = 443, 450,$ and 452 °C for compound **125** with fragments of **6FDA**, **BPDA**, and **ODPA**, respectively. The values of the dielectric constant were 2.81, 2.92, and 3.07 for compound **125** with fragments **6FDA**, **BPDA**, and **ODPA**,

respectively. Water absorption was 0.68, 0.77 and 0.81 %, respectively.

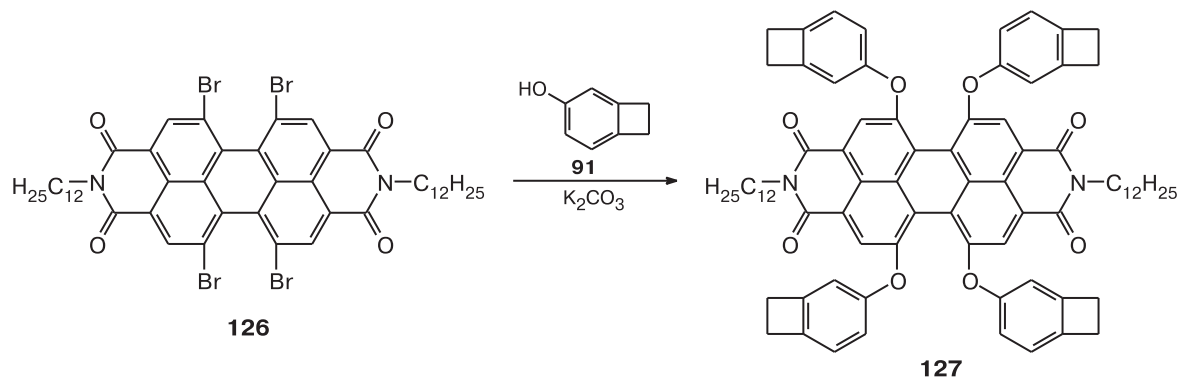
There are examples of the synthesis of polymers containing a fluorescent functional fragment or fragments providing $n-p$ transitions in photovoltaics, OLED, and other devices. An example is a polymer based on fluorescent perylene bisimide (Scheme 29).⁸¹ A polymer based on functionalized perylene bisimide **127** capable of thermal polymerization at a temperature from 228 to 250 °C for 6 h (see scheme 2, direction *A*), and a copolymer with methylvinylsilicone (see Scheme 2, direction *B*) capable for polymerization at 220 °C (72 h) were obtained.⁸¹

An example of the production of polyamides, incorporating benzocyclobutene fragment, is described in Ref. 82. The authors applied a two-steps synthesis of diamine by acylation of benzocyclobutene in the presence of iron oxide and 3,5-dinitrobenzoyl chloride followed by the reduction of the obtained compound with NaBH_4 , $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ (Scheme 30). This compound was used to

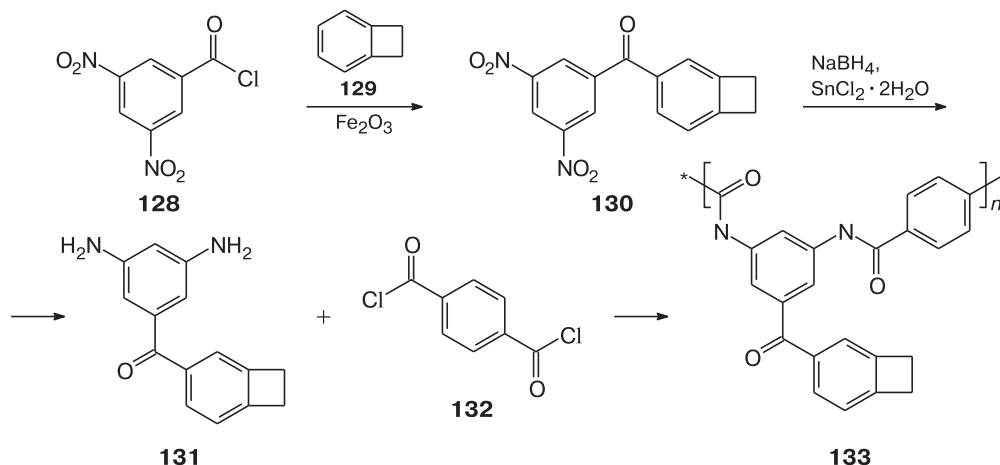
Scheme 28



Scheme 29



Scheme 30



obtain target polyamide by further functionalization with derivatives of terephthalic acid or other dicarboxylic acids resulting in the production of targeted polyamides.

Synthesis of polymers based on benzocyclobutene incorporated into polyolefin or polyarene chain

The simplest representative of this group is 4-vinylbenzocyclobutene (**58**). The compound is obtained in several ways (Scheme 31), one of which is based on the Wittig reaction, the other proceeds according to the Heck

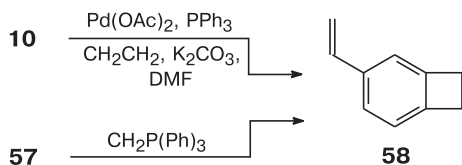
reaction. The target product is isolated, respectively, in 78 and 75.8% yields.⁸³

Compound **58** has been described for a long time and is often used in modern studies as a monomer in copolymerization reactions.^{58,84} Thus, the authors⁸⁴ studied the conditions of copolymerization and the properties of the resulting nanoscale structures of copolymers based on 4-vinylbenzocyclobutene, styrene, and *n*-butyl acrylate.

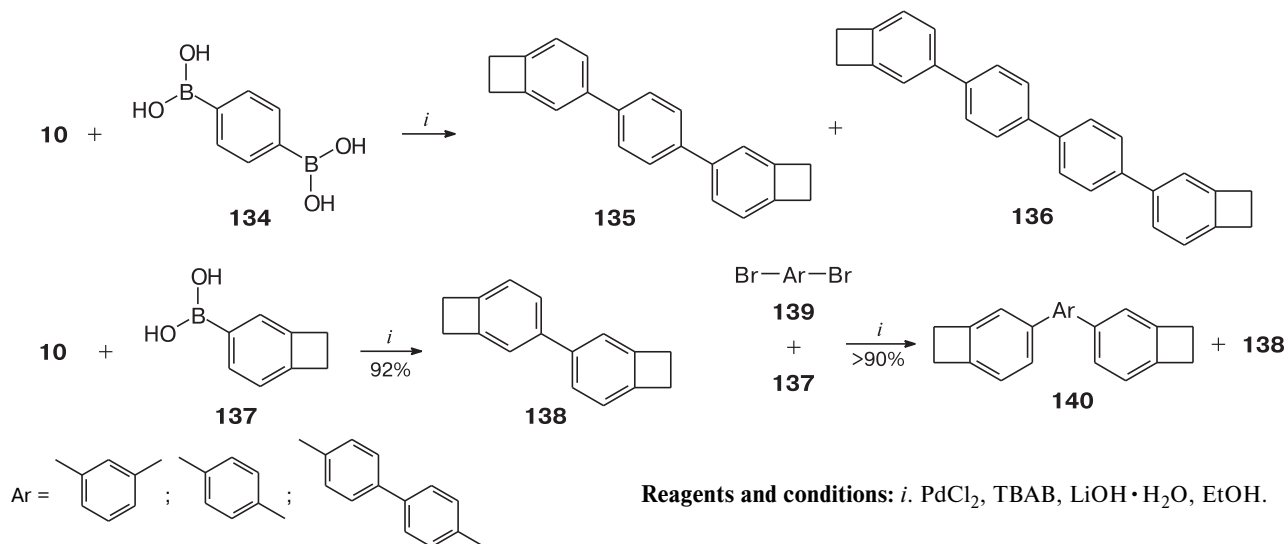
4-Bromobenzocyclobutene is widely used in the synthesis of monomers, based on the reaction of cross-coupling (Scheme 32).⁸⁵

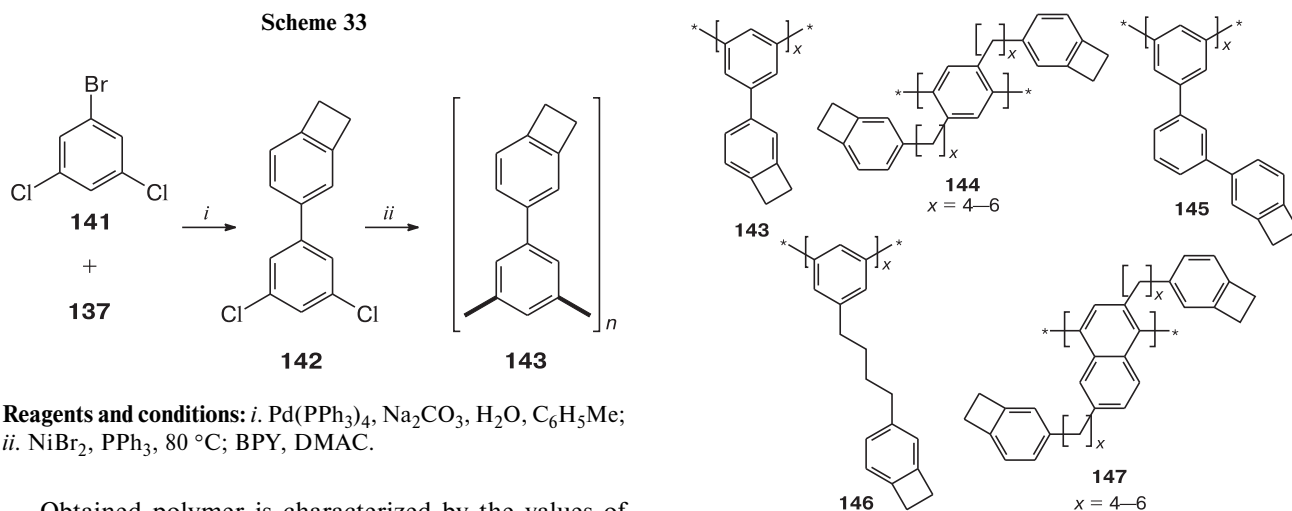
The synthesis of a polymer by cross-coupling of 4-benzocyclobutylene-4-boronic acid (Scheme 33) and 3,5-bromodichlorobenzene in the presence of a palladium catalyst followed by polymerization with the formation of polymer **143** is described in Ref. 86. This polymer has good solubility in most organic solvents, but when heated above 200 °C the cross-linking proceeds with the formation of insoluble product.

Scheme 31



Scheme 32

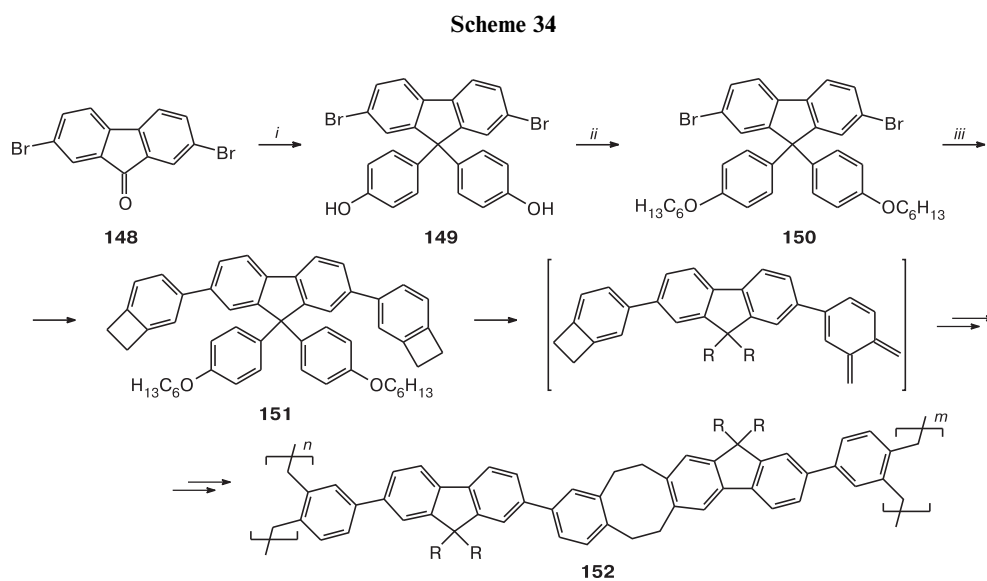




Obtained polymer is characterized by the values of $k = 2.62\text{--}2.69$ in a wide frequency range (0.1 MHz–30 MHz) and a high decomposition onset temperature (a weight loss of 5% is achieved when heated to 416 °C), which makes the resulting material a candidate for formation of dielectric coatings.

The use of benzocyclobutene in combination with aromatic and polyaromatic derivatives (fluorene,^{87–89} carbazole,⁹⁰ triphenylamine^{91–98}) as hole-conducting polymers, fluorescent polymers, dielectric and electrically conductive materials for microelectronic devices has become increasingly common in the literature in recent years. Thus, a number of structures **143–147** containing a benzocyclobutene fragment in a polyaromatic chain for electroluminescent devices with increased efficiency were considered in recent patent.⁹⁹

The synthesis of a monomer based on fluorene, obtained from 2,7-dibromofluorenone in three steps (Scheme 34), was described in Refs 100 and 101. Starting 2,7-dibromofluorenone reacts in the first step with phenol in the presence of trifluoromethanesulfonic acid to give bisphenol, which is then alkylated with hexylbromide. The fragments of benzocyclobutene were introduced into the structure at the last step by the reaction of cross-coupling with benzocyclobutene-4-boronic acid. The polymer was synthesized in argon with gradual heating of the melt of 2,7-dibromofluorene-9-one derivative from 150 to 280 °C for many hours. Thus obtained material showed high values of $k = 2.7$ in the frequency range from 0.15 to 30 MHz, which is comparable with the characteristics of



Reagents and conditions: *i.* -OH, MeSO₃H; *ii.* Br, K₂CO₃, DMSO, 75 °C; *iii.* **137**, Pd(PPh₃)₄, K₂CO₃, toluene.

commercially available dielectric coatings based on polyimides, SILK polymers, and most of the benzocyclobutene-containing polymers. Polymer **152** showed high thermal stability with $T_{d5\%}$ values of 437 and 372 °C in nitrogen and air, respectively.

Conclusions

Thus, we can confidently assert that the field of materials containing benzocyclobutene is a promising and actively developing research area. Analysis of the structural features and properties of the polymers examined in the review shows that their thermal stability ($T_{d5\%}$) is in the range from 300 to 550 °C. The highest values (508–526 °C (in nitrogen) and 526–553 °C (in air)) were achieved for a group of siloxane polymers, which exhibit from moderately high (208 °C) to high (> 400 °C) glass transition temperatures. The dielectric properties are characterized by the value of constants lying in the range of $k = 2.52$ – 2.87 . The largest constants are characteristic of polymers containing diphenyl fragment (**24**) (2.87), the same pattern is observed for compounds of the polyimides group. When going from polymers with **6FDA** without conjugated fragments to **BPDA** containing diphenyl fragment, the dielectric constant increases from $k = 2.81$ to $k = 2.92$. The largest contribution to the growth of the dielectric constant is made by the fragment of diphenyl ether **ODPA** (3.07). The lowest values of k were obtained for polyfluorinated polymers ($k = 2.38$, in the range from 0.1 to 30 MHz) and compounds of the silane group ($k = 2.3$ – 2.59 , 1 kHz–10 MHz). However, the latter compounds, compared with the siloxane group, have lower thermal stability (<300 °C) in air and comparable stability in an inert atmosphere. In most cases, copolymers are characterized by an increase in thermal stability and glass transition temperature with an increase in the amount of benzocyclobutene monomer. These characteristics are especially sensitive when the copolymer is saturated with a benzocyclobutene-based monomer units in the range of 10 to 40%. At the same time, thermal stability increases up to 400 °C and higher. Further saturation of the copolymer with benzocyclobutene monomer leads to significantly smaller changes in both thermal stability and mechanical properties.

Such a set of characteristics makes these materials attractive in the production of compact electronic devices, including those capable of functioning in extreme conditions. The potential of benzocyclobutene application is virtually unlimited. New photo- and thermo-curable materials based on benzocyclobutene derivatives in electronics and microelectronics can play an extremely important role in the creation of insulating structures in silicon, gallium arsenide, and ceramic devices. This includes the microwave range, insulation of mesostructures (instead of silicon oxide) with low-temperature (no more than 300–400 °C) deposition, isolation of laser structures in quantum cascade lasers, insulating layers in multifunc-

tional high-density electronic modules, created by the technology of 3D microsystems, polymer insulators for optocouplers (including those with the possibility of photocuring) that provide high breakdown voltages (not less than 3 kV with a thickness of 0.5 mm), insulators in micro-motors and microgenerators devices, multilayer waveguide structures that provide coupling with the optoelectronic interface for optical input-output of the optical system-on-chip, coatings of high frequency printed circuit boards for telecommunications, photoresists for plasma-chemical and ion etching when obtaining precision elements of the topology of microcircuits and switching boards.

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