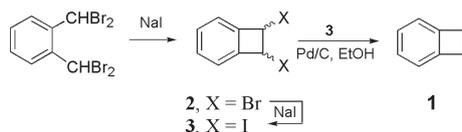


From Small Rings to Big Things: Benzocyclobutenes and High Performance Polymers

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The first report of a four-membered ring being fused across adjacent positions of benzene appeared in the 1909 doctoral thesis of Hans Finkelstein (*Über ein Derivat des Benzocyclobutans*) at the University of Strasbourg.¹ The subsequent paper that encompasses his dibromide **2** was published in 1910 in *Berichte der Deutschen Chemischen Gesellschaft*,² but Finkelstein's main concern lay in the replacement of bromides and chlorides by iodide in organic halides employing NaI in acetone (in which NaI is soluble but NaCl and NaBr are insoluble), a classical transformation known as the Finkelstein reaction. Benzocyclobutenes (BCBs) attracted no further attention until 1956 when Cava and Napier confirmed the original synthesis³ and transformed **2** into parent **1** via diiodide **3**, itself formed by Finkelstein reaction (Scheme 1).

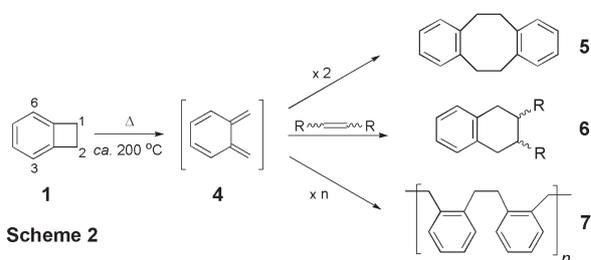


Scheme 1

Following this disclosure, BCBs became the subject of many reports (> 500 to 1986) that encompassed details of their synthesis, the chemistry of the strained ring system and the physicochemical properties recorded. Although some 40 patents were registered during this time (and a further 100 added during the next ten years), the fifth decade following Cava and Napier's epic communication³ (1996-2005) had more than 400 patents registered. The total now represents close to 30 % of the benzocyclobutene literature available on Scifinder®.

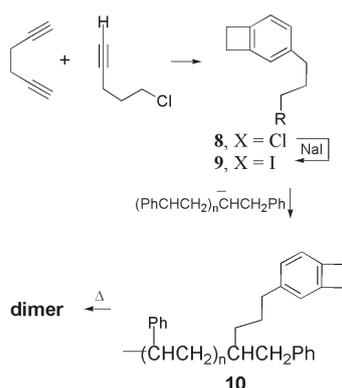
The volume of literature is clear in implying that **1** is an important entity and one must ask what is so significant about the humble C₈H₈ bicyclic hydrocarbon **1** to make it so attractive. The answer is simple and lies in its thermal chemistry. At ca. 200 °C, **1** undergoes electrocyclic ring-opening to the reactive quinodimethane **4**. This either dimerizes to dibenzocyclooctadiene **5** or yields poly-*o*-xylene **7** (Scheme 2), each with regeneration of the benzene ring. Although the dimerization is thermodynamically favoured, the presence of a separate and independent π bond – a dienophile – induces Diels-Alder cycloaddition at a temperature some 100 °C lower and a tetrahydronaphthalene, e.g. **6**, is formed under kinetic control. Thus, by comparison, the formation of **5** (or **7**) is inhibited⁴ compared with the diversion of **4** to a cyclohexane and this makes BCBs of major significance in the polymer industry.

Appropriately functionalized BCBs have use in the termination of polymerizations and give a polymer that is *end-capped* with an intact BCB moiety.⁴ This occurs with,



Scheme 2

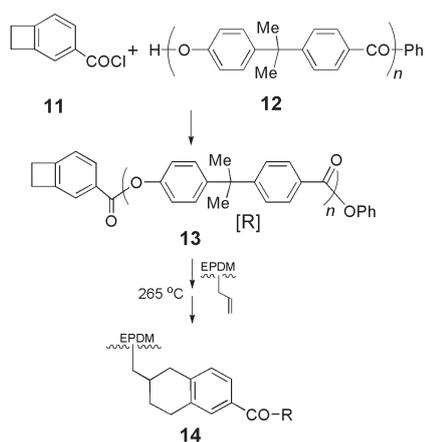
e.g. 4-(3-iodopropyl)- **9** and 4-benzocyclobutenoyl chloride **11**. Iodide **9** is easily prepared by metal catalysed cyclotrimerization to **8** that employs hexa-1,5-diyne and 5-chloropent-1-yne (Scheme 3), which then undergoes iodide-for-chloride replacement under Finkelstein conditions.⁴ When **9** is used to terminate the anionic polymerization of styrene, an end-capped polystyrene **10** is formed as shown in Scheme 3.⁵ Refluxing in triisopropylbenzene (236 °C) causes the BCB ring of this to open and dimerize to the dibenzocyclooctadiene analogue of **5**; the molar mass is doubled from a little fewer than 25,000 to close to 50,000 g/mol, a process is known as *chain extension*. Should the polymer be capped at both ends by BCB, then further polymerization can result in a new polymer of indefinite length. It is important to note is that these polymer extensions occur thermally without the evolution of by-products.



Scheme 3

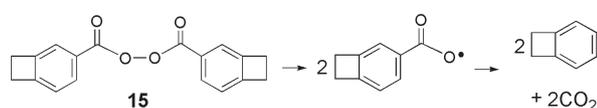
In a similar way, acid chloride **11** efficiently end-caps the phenolic benzoate polymer **12** to give polyacrylate chains **13**, almost all of which carry a BCB head group (Scheme 4).⁶ At 265 °C the BCB ring of **13** opens and, in the presence of an alkene π bond, the quinodimethane cycloadds, e.g. with an EPDM (ethylene propylene diene monomer) rubber⁷ to give, after compression moulding, a grafted polymer as shown stylized by **14** in Scheme 4. A variety of such polyacrylate thermoplastic elastomers have been prepared.⁶

Just as benzoyl peroxide (PhCO-O-O-COPh) initiates radical polymerization, so does benzocyclobutenyl per-



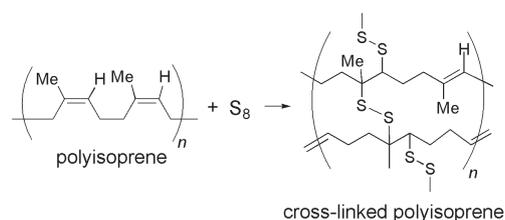
Scheme 4

oxide **15** (Scheme 5) and when used as radical initiator for styrene it can provide polymers with BCB moieties randomly attached to the chain and at the ends.⁸ Heating above 240 °C effects BCB ring opening and results in both chain extension and *chain branching*.



Scheme 5

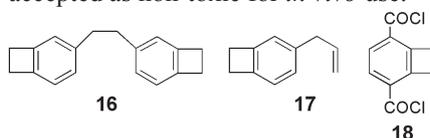
The ability to cross-link polymers and enhance their strength has been known since the mid-1800s and the times of Charles Goodyear. Thus, *while boiling gum with sulfur on his wife's cooking stove, Goodyear let fall a lump of the material on the hot stove, and it immediately vulcanized. He deduced through reasoning and further experiments that the more sulfur added to the mixture, the stiffer the material. Goodyear finally discovered that by using pressurized steam for four to six hours at 270 °F, he could produce the most uniform results.*⁹ Sulfur bonds to alkene sites in polyisoprene (natural rubber), brittle at low temperatures and sticky when heated, to give a cross-linked product with enhanced strength, rigidity and value (Scheme 6).¹⁰ A patent for vulcanization of rubber with sulfur was granted not simply to Goodyear in the USA (1844) but in the previous year to Hancock in England.⁹ The beneficial effects of organic accelerators in the cross linking process were not discovered until after the 1906 work of Oenslager.¹¹ In seeking ways to vulcanize cheaper (wild) rubbers as rapidly as those of high grade, he found that aniline and *p*-nitrosodimethylaniline accelerated the process. These became the first accelerants used in vulcanization but they were soon replaced by the less harmful thiocarbanilide [(PhNH)₂CS], which also gave the advantage of requiring less sulfur.



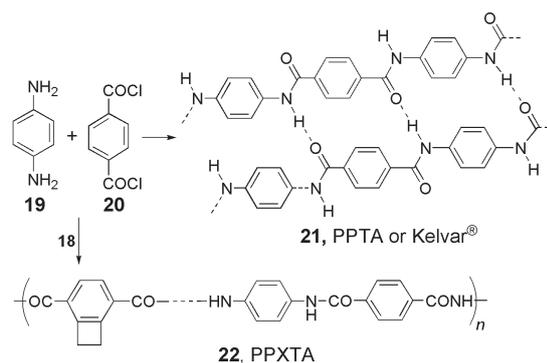
Scheme 6

Similar vulcanization of styrene-butadiene rubber (SBR) can be brought about by cross-linking with bis(benzocyclobutenyl)ethane **16**.

Upon heating, the quinodimethane entities formed add to residual π bonds of the polymer chain giving a product, which, depending upon the amount of BCB used, can have enhanced properties compared with a sulfur cross-linked equivalent.¹² A polymer developed by the Goodyear Tyre and Rubber Company is produced from hex-1-ene and 5-methylhexa-1,4-diene¹³ and known as *Hexsyn*. In its vulcanized form it found biomedical usage, *e.g.* in totally synthetic hearts, hip prostheses and artificial finger joints. A perceived disadvantage of the material was in the slight toxicity of the vulcanizing agents used in its production. However, the polymer can be cross-linked with BCB substrates of which 4-allylbenzocyclobutene **17** is most efficacious,¹⁴ and when used as a co-monomer in *Hexsyn*, even in the presence of carbon black, it gives rise to cross-linked material from Diels-Alder cycloadditions (*cf.* Scheme 2). The mechanical properties of the sulfur and BCB vulcanized materials are comparable and the BCB-containing materials were accepted as non-toxic for *in vivo* use.¹⁵

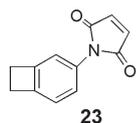


Fibres made from poly(*p*-phenyleneterephthalamide) **21** (PPTA or Kelvar[®]) developed by DuPont have high tensile but poor compressive strength because the polymer chains buckle. Thus, the polymer chains need to carry a reactive group that is dormant during the initial stages of fibre processing but which can be triggered into a reactive state later, *i.e.* cross-link chemistry that can be initiated during a post-spinning heat treatment. Incorporation of the BCB diacid dichloride **18** (known as XTA-Cl) in controlled amounts with the polymer monomers, terephthaloyl dichloride **19** and *p*-phenylenediamine **20** (Scheme 7), provides material **22** (PPXTA) that has the BCB randomly incorporated. It differs from PPTA only by the presence of some four-membered rings, and thus retains the favourable mechanical properties of PPTA. Cross-linking of PPXTA fibres occurs *above* 350 °C presumably by quinodimethane dimerization. While this is well below the cracking temperature of the polymer, it is some 100 °C above the temperature usually needed to open the four-membered ring. Despite this, the temperature needed for processing is much lower (*ca.* 80 °C lower)¹⁶ and it leads to fibres that take almost double the strain before they kink. The copolymer fibres exhibit increased resistance to creep and lateral deformation after heat treatment.¹⁷



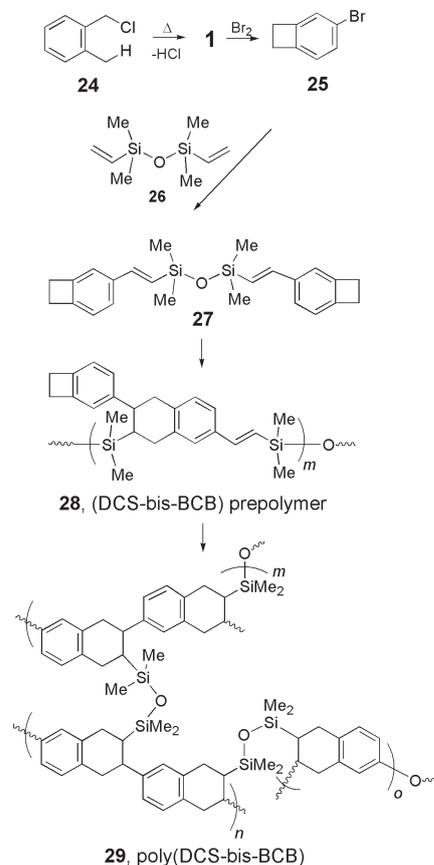
Scheme 7

The family of BCBs itself provides a series of thermally polymerizable monomers that can be classified into two groups.¹⁸ The first encompasses molecules that contain only benzocyclobutene moieties while the second has monomers that contain sites of unsaturation elsewhere in the molecule. The monomers can be *partially polymerized* in a process termed B-staging, where the molar mass of the monomer (or monomers) is advanced by heating to give a *prepolymer* that can be processed into a desired form before completing the polymerization with final curing. Such polymerizations provide processing advantages for various composite fabrication techniques. Those monomers that contain multiple benzocyclobutene moieties, optionally with separate sites of unsaturation, transform into multifunctional network junctions when the thermosets are fully cured – the four-membered ring opens to the *o*-quinodimethane and it adds to a site of unsaturation on the same or a different chain, *cf.* **1** → **6** (Scheme 2). As an example, 3-*N*-maleimidobenzocyclobutene **23** thermally polymerizes to a substantially linear polymer with a high glass transition temperature (T_g). Thus, BCB polymers encompass materials that have properties ranging from high T_g thermosets to those of substantially linear thermoplastics. Some polymers exhibit an excellent retention of their room temperature mechanical properties to at least 200–250 °C, qualifying them as high performance polymers for high-temperature coatings with applications in the aerospace industry. Other polymers have outstanding electrical properties, including very low dielectric constants and water pickup that make them useful in electronic applications.¹⁸ The performance enhancements seen from this technology come in part from the thin film polymeric dielectrics used in their fabrication. Polymer performance is based on the complex interrelationship between such properties as adhesion, stress, moisture absorption, and thermal and chemical stability and the inherent electrical and mechanical properties.



These last properties have triggered considerable attention to BCB-incorporated polymers. In the late 1980s, the Dow Chemical Company began to develop a series of BCB-based polymers with low dielectric constants for use in microelectronic packaging and interconnect applications.¹⁹ The early studies provided commercially successful products in, *e.g.* the fabrication of gallium arsenide (GaAs) integrated circuits, bumping and redistribution,²⁰ and for planarization and isolation in flat panel display materials.²¹ A commercial synthesis of **1** from pyrolysis of α -chloro-*o*-xylene **24**, subsequent bromination²² to **25**, and then coupling with divinyltetramethylsiloxane **26** gave **27**, known as DVS-bis-BCB (Scheme 7).²³ This monomer, which can be purified to the ppb level if needed,¹⁹ is of immense value and was the first BCB introduced for application in microelectronics.²⁰ On heating, **27** can be B-staged to prepolymer **28** without production of volatile side-products through Diels-Alder cycloaddition of the quinodimethane to a vinylic group of another molecule. Product **28** has excellent film-forming properties, shows

less than 5 % shrinkage on cure and has a relatively low molar mass as applied, and gives > 90 % planarization from a single application. It can be processed and then cured at a later stage to give a product, *e.g.* **29**, with very desirable electrical, thermal, and planarization properties.²⁰ These properties, coupled with the low absorption of water and low dielectric constant make it superior to *e.g.* polyimides.



Scheme 8

The widespread use of polymers as insulating layers in microelectronic structures is relatively recent. As electronic devices become smaller, there is a continuing desire to increase the circuit density in electronic components, *e.g.* integrated circuits, multichip modules and the like, without degrading electrical performance, and to increase the speed of signal propagation in these components. One method of accomplishing these goals is to reduce the dielectric constant of the polymer used as the interlayer insulating material in the components. BCB-based polymers find use for this and in stabilizing the surface and preventing oxidation.

Dow has formulated solutions of B-staged BCB prepolymer **28** and commercialized them as a series of resins marketed as Cyclotene[®]. The products are specifically engineered to meet industrial microelectronic needs for extendible, integratable dielectrics. Cyclotene resins exhibit < 5 % shrinkage on cure and have a relatively low molar mass as applied and result in > 90 % planarization from a single application.²⁰ Cyclotene resin is currently being used to planarize thin film transistor (TFT) flat panel display plates, which allows subsequent indium tin oxide (ITO) deposition on a completely planarized surface. This results in a larger viewing angle and low-

er power operation. The 3000 series of dry-etch resins finds use in applications where film thicknesses are controllable from 1.0 to 26.0 μm . Dow Cyclotene[®] 3022 is a low permittivity insulator developed in response to the need for faster integrated circuits with higher packing densities. The 4000 series are photosensitive resins (Photo-BCB)²⁴ ideal for wafer level applications where a thin dielectric layer is required, or where a protective layer is needed for passivation or chemical resistance. They contain photosensitive additives to render the formulation photoimageable, are active to broad band UV radiation, and are negative acting dielectrics (the unexposed material is removed during solvent development). Different formulations provide for differing film thicknesses (Cyclotene[®] 4024-40: 3.5-7.5 μm ; 4026-46: 7-14 μm) and processing is similar to that for other negative photoresists; the present Cyclotene[®] range of polymers finds extensive use.²⁵

Various approaches have been adopted to enhance the ductility of DVS-bis-BCB polymers,²⁶ one of the more recent being addition of a styrene-butadiene-styrene (SBS) triblock copolymer.²⁷ This consists of polystyrene sequences (or blocks) at each end of the chain and a polybutadiene sequence in the centre. The polystyrene end-blocks of adjacent chains collect together in small *domains*, so that clusters of polystyrene are distributed through a network of polybutadiene. Such a structure makes SBS a thermo-plastic elastomer with the elasticity and resilience of polybutadiene along with the permanence of the fixed ends. When the DVS-bis-BCB monomer **27** was B-staged with SBS added, the prepolymer had advantageous properties. Moreover, a high proportion of SBS could be used, thereby reducing the cost of the final product. Fracture toughness improved without any notable loss of the poly(DVS-bis-BCB) properties.²⁷

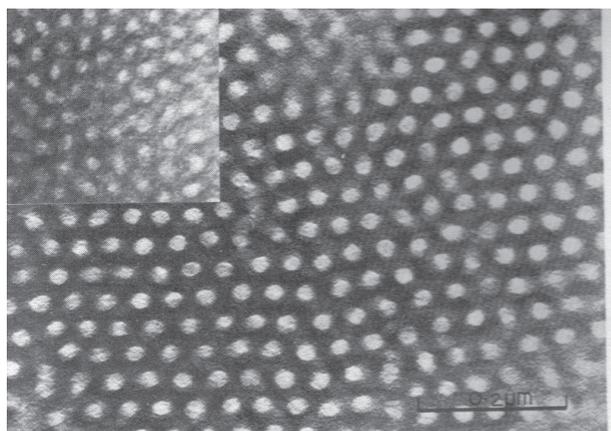


Fig. 1. An early transmission electron micrograph of an SBS triblock copolymer (from http://en.wikipedia.org/wiki/Image:Sbs_block_copolymer.jpg; accessed 12 May 2008).

Current research has focussed on the evaluation of BCB-bonded and thinned wafer stacks for three-dimensional integration.²⁸ A fully wafer-level packaged single-crystal silicon multiple ported microelectromechanical (MEM) switch using benzocyclobutene as a packaging adhesive layer has appeared.²⁹ Finally, a self-priming and photosensitive aqueous-base developable BCB dielectric material curable in air has been made from **27** and BCB-acrylic

acid. Whether cured in nitrogen or in air, the formulation produces a film with optical, electrical, thermal, and mechanical properties desired for many microelectronic applications, such as packaging applications and a planarization layer or insulation layer in display applications.³⁰

As pointed out in the earlier articles in this series,³¹ the recognition, use, and transformation of small ring organics into materials of industrial importance has come from initially non-targeted, curiosity-driven research.

Acknowledgements

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Dates of Note

Oct 10 is the 75th anniversary of issue of US Pat. 1,929,453 *Synthetic Rubber-like Composition and Method of Making Same to Waldo Semon*. It was for his method of making plasticized PVC, now known simply as vinyl. Initially, hard and difficult to form into useful articles, Semon found a way to make it in a rubber-like form that involved dissolving the polymerized vinyl halide in a non-volatile organic solvent at elevated temperature. On cooling a stiff rubbery gel appears. It is also the 75th anniversary of the marketing of the first detergent containing a surfactant (*Dreft*) by Procter & Gamble. Additionally, *Earle Dickson*, the inventor of the Band-Aid, was born on this day in 1892.

Oct 12 marks 300 years since the birth of *Vincenzo Dan-dolo*, the Italian pharmacist, natural scientist, writer and statesman. He studied chemistry at the University of Padua, and championed new scientific theories, especially those of Lavoisier. He was committed to the advancement of secondary education in general and to health care in particular.

Oct 15 is the 400th birthday of *Evangelista Torricelli* whose barometer experiment with quicksilver filling a tube then inverted into a dish of mercury created a vacuum. Oct 20 is the 25th anniversary of the redefinition of the metre. Originally based on one ten-millionth of the distance from the North Pole to the equator, it was re-established as the distance that light travels in a vacuum in 1/299,792,458 sec.

Oct 21 is the 175th anniversary of the birth of *Alfred Nobel*. On the same day in 1895 *Linde* reported the liquefaction of air. The 22nd of October represents the 165th anniversary of *Stephen Babcock*, the American agricultural chemist, regarded as the father of scientific dairying. In 1880 he developed his (Babcock) test of measuring the butterfat content of milk. It consists of liberating the fat globules by dissolving the casein in a strong acid and then separating the fat by means of a centrifuge. The test discouraged milk adulteration. It also provided for the first time an adequate standard by which fair payment for milk could be determined, stimulated improvement of dairy production, and aided in factory manufacture of cheese and butter. This day also marks 70 years since *Chester F. Carlson* demonstrated xerography for the first time.

Isidor Traube, the German physical chemist who founded capillary chemistry and whose research on liquids advanced knowledge of critical temperature, died 65 years ago (27 Oct 1943). On the same day in 1873, farmer *Joseph F. Glidden* applied for a patent on barbed wire. The barbs were cut from sheet metal and were inserted between two wires which were twisted considerably more than with today's common design.

Oct 29 is the 85th birthday of *Carl Djerassi*, noted for establishing physical methods for determining organic molecular structure and for contributions to synthetic organic chemistry. This day also marks the 50th anniversary of the first coronary angiogram, performed by Dr. *F. Mason Sones, Jr.*, a pediatric cardiologist at the Cleveland Clinic in Ohio, USA.

On Oct 30, 1888, the first US patent for a ballpoint pen (No. 392,046) was issued to *John J. Loud* of Weymouth, MA, whilst the 31st marks the 5th anniversary of the US Food and Drug administration releasing its summary findings that cloned farm animals and their offspring pose little scientific risk to the food supply. The 31st also marks 120 years since *Dunlop* patented pneumatic bicycle tyres.

Nov 4 marks 135 years since the first US patent for a gold tooth crown was issued to Dr *John B. Beers* of San Francisco while the 7th is the 120th anniversary of the birth of *Chandrasekhara Venkata Raman*, recipient of the 1930 Nobel Prize for Physics for his 1928 discovery of what is now known as Raman scattering. On Nov 7, 100 years ago, Prof *Ernest Rutherford* announced in London that he had isolated a single atom of matter.

Ernst Otto Fischer who, with Sir *Geoffrey Wilkinson*, solved the structure of ferrocene and received the 1973 Nobel Prize, was born on Nov. 10, 1918. The day also marks the 25th anniversary of then student *Fred Cohen* providing information of the first documented computer virus, created as an experiment in computer security.

Nov 13 marks 115 years since the birth of *Edward Adelbert Doisy*, the American biochemist who discovered and synthesized vitamin K; he shared the 1943 Nobel Prize for Physiology or Medicine with Henrik Dam. The 14th is also the anniversary of the death of French chemist *Nicolas-Louis Vauquelin* (1829) who discovered chromium