

PHOTO AND THERMAL DUAL-CURABLE POLYMERS

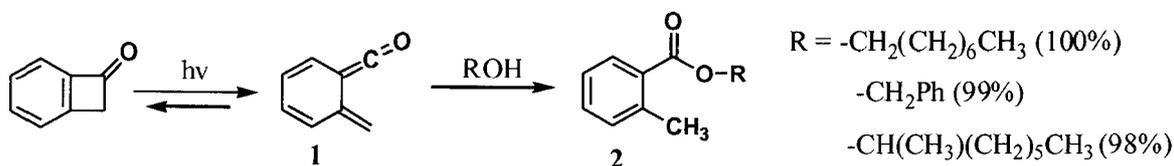
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Introduction

In the late 1970s, Dow Chemical Company explored the chemistry of benzocyclobutene (BCB), which led to the first patent describing the use of benzocyclobutenes in polymer synthesis in 1985¹. Since then, the study and applications of BCB polymers have rapidly expanded^{2,3,4,5}. However, the area of benzocyclobutene applications has been largely limited to interpolymer coupling reactions (just dimerization and Diels-Alder cycloaddition). Dienes are frequently used as co-monomers to produce linear thermoplastics. Other commercial materials such as diols and diamines could not be used, because many unpredictable side reactions were observed to occur with the *o*-quinodimethane intermediate. In addition, the applications of the BCB chemistry to vinyl polymers and polyols are scarce, as only a few reports on the modification of polystyrene have appeared. Thus, an effort was made to expand the range of available reactions by utilizing the chemistry of more versatile benzocyclobutenone (BCBO)^{6,7}.

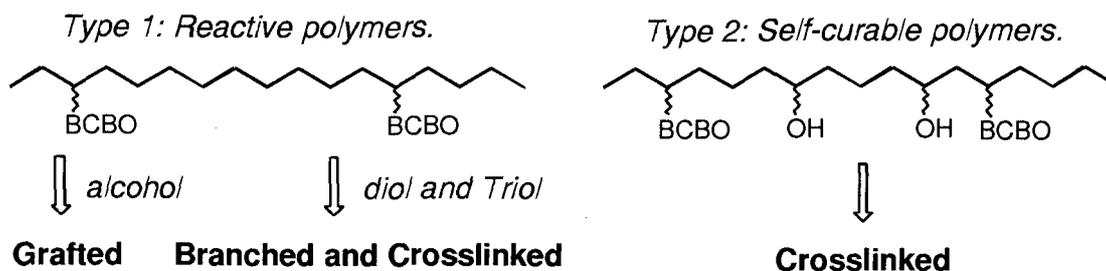
Benzocyclobutenone can be prepared in several ways^{8,9,10}. It is known to undergo cycloaddition reactions with dienophiles such as maleic anhydride, dimethyl fumarate, benzoquinones and [60]fullerene upon heating or flash photolysis¹¹. Recently, it was shown that BCBO and its derivatives undergo a thermal ring-opening reaction to form reactive α -oxo-*o*-quinodimethane (or vinyl ketene **1** in Scheme 1) that subsequently reacts with alcohols to yield esters quantitatively¹². Furthermore, the same coupling reaction can proceed photochemically at ambient temperatures to form the corresponding esters **2** (Scheme 1)^{13,14}. One of the attractive features of BCBO chemistry is that this coupling reaction produces no volatile organic compounds and proceeds without any catalysts or initiators.



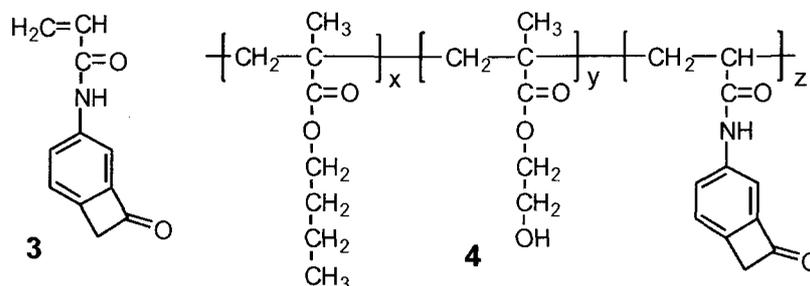
Scheme 1. Photochemical reaction of BCBO with alcohols.

Thermal and Photo-Curable BCBO Polyacrylates

Based on the BCBO chemistry, several new types of thermally and photo-curable polymers can be envisioned. The polymers of type 1 shown below contain a latent ketene group (BCBO) and are reactive toward alcohols. These polymers can be either thermally or photochemically grafted, branched and crosslinked depending the hydroxy compounds (e.g., PEG) used. The type-2 polymers contain both BCBO and hydroxy groups and are therefore self-curable by heat and light without using any catalysts.



A simple way to introduce the BCBO group into a polymer is by copolymerization of BCBO-containing vinyl monomer (e.g., **3**) with commercial vinyl monomers such as styrene and acrylates (e.g., MMA and BMA). As an example for type-2 self-curable polymers, a polyacrylate derived from n-butyl methacrylate (BMA), BCBO acrylate **3** and hydroxyethyl methacrylate (HEMA) was prepared.



Its IR spectrum (Figure 1) shows the characteristic peaks for the ester at 1732 cm^{-1} and for the BCBO's ketone group at 1765 cm^{-1} . The N-H stretches at 3440 cm^{-1} and N-H bending at 1674 cm^{-1} were observed, besides a broad OH stretching peak.

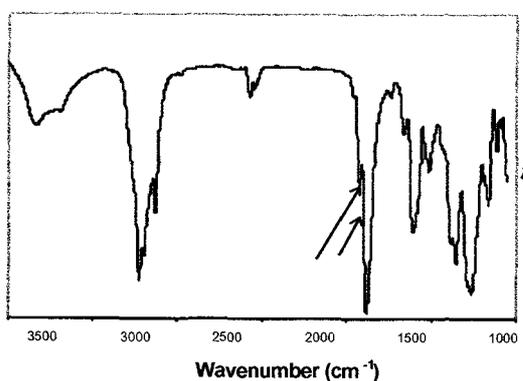


Figure 1. IR spectrum of polymer 4.

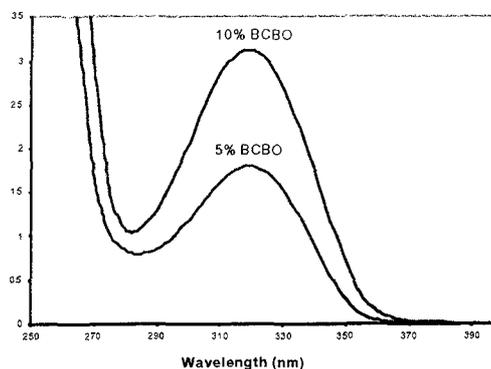


Figure 2. UV-Vis spectra of polymers 4.

The NMR spectrum of polymer 4 displays a singlet peak at 4.1 ppm, which is assigned to the methylene protons from BCBO. The UV spectra of polymers show a max absorption at 320 nm due to the BCBO moiety and its absorptivity is proportional to the amount of BCBO incorporated in polymers (Figure 2). Hence, the actual BCBO amount in the polymers can be determined by UV-vis calibration method. The molar percentage of BCBO incorporated in polymers 4 were determined to be 7.8% and 13% for the two batches with the feed ratios of 5% and 10%, respectively.

Thermal crosslinking of BCBO-containing polymers **4** is apparent and is evident by DSC study. The T_g values were 55 °C and 80 °C for polymers **4** with 7.8% BCBO and 13% BCBO, respectively. The BCBO ring-opening exothermic peak or crosslinking can be seen in the first DSC scan, with onset temperature typically around 200 °C. In the second DSC scan, the exothermic transition disappeared. FTIR was run on the polymer sample after the second DSC heating and showed no ketone at 1765 cm⁻¹ or BCBO group left in the polymer. Heating the polymer sample at 200-220 °C resulted in a significant change in solubility and the cured polymer was insoluble in common organic solvents.

The solutions (15 - 20 wt %) of the polymers in chloroform were UV irradiated at wavelength 320 nm with the light intensity of 500 mW/cm². The polymer was self crosslinked because of the coupling reaction of BCBO and hydroxyl groups in the polymer chain. The polymer solution was mobile before UV curing (Figure 3a), whereas gel formation occurred after one-minute irradiation (Figure 3b). Figure 3c shows the broken gels.

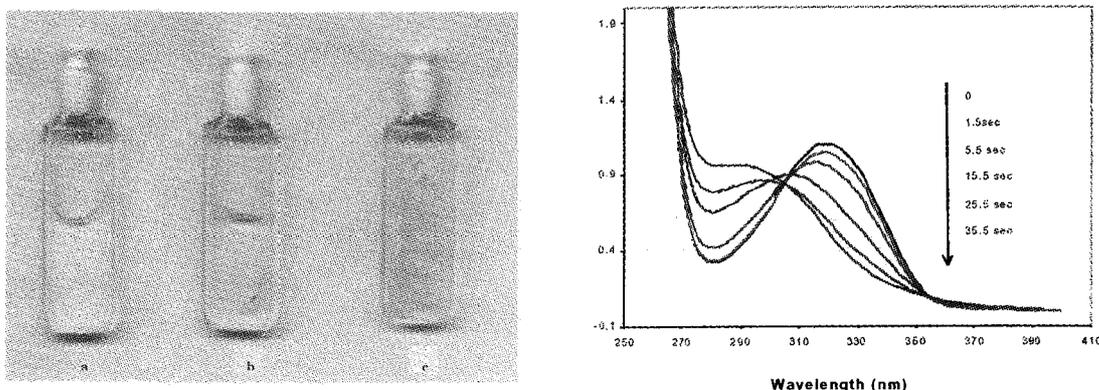


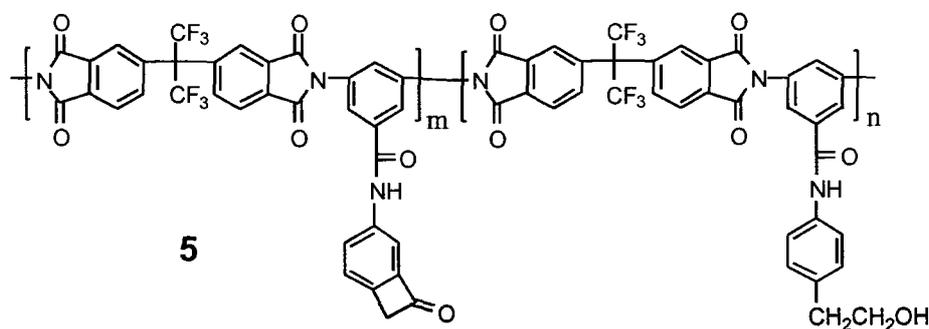
Figure 3 (left). Pictures of polymer **4**: (a) in chloroform solution, (b) the gel formed immediately after UV curing, (c) gels broken with a needle. **Figure 4** (right). UV-vis spectra of polymer **4** being photo-cured at different time.

UV-vis spectra of a thin film of polymer **4** (13% BCBO) at different times during irradiation are shown in Figure 4. The maximum absorbance at 320 nm decreased with an increase in the irradiation time, indicating that the photochemical reaction of BCBO groups via the ketene intermediate with hydroxyl groups proceeded in a time-dependent manner to form

ester groups. Moreover, as the curing extent or degree of cross-linking increased, the peak became smaller, the shape changed and eventually blue shifted to approximate to 295 nm when the UV curing was near the completion. The photo-curing reaction of BCBO with hydroxyl groups in the solid polymers occurs fast and completes in less than one minute.

Photosensitive BCBO Polyimides

The preparation of photosensitive polyimides (e.g., **5**) containing BCBO group as a latent photoreactive site was accomplished through a coupling reaction of carboxylic acid group from the parent polyimides with the amino group from 5-aminobenzocyclobutenone. The coupling reaction was done at room temperature in N,N-methylformamide using EDC as a coupling reagent.



The film of polyimide **5** spin coated on a NaCl plate was UV cured at ambient temperatures and followed by FT-IR spectroscopy. The peak at 1767 cm^{-1} due to imide and BCBO decreased, while the peak at 1736 cm^{-1} increased due to the resulting ester group. However, not all the BCBO in the solid film reacted at room temperature. However, this result still indicates a possibility of the formation of photopatterns on a substrate using the photosensitive polyimide **5**. Thus, the polyimide film was spin coated on a silicon wafer from 1 wt% tetrachloroethane solution. After irradiation through a photomask for 2 minutes (UV intensity 500 mW/cm^2), the irradiated areas were crosslinked and thus became insoluble and the shadow areas were washed off using chloroform. The patterns were visible without further baking and were photographed by scanning electron microscopy (SEM). The SEM photographs (Figure 5) showed

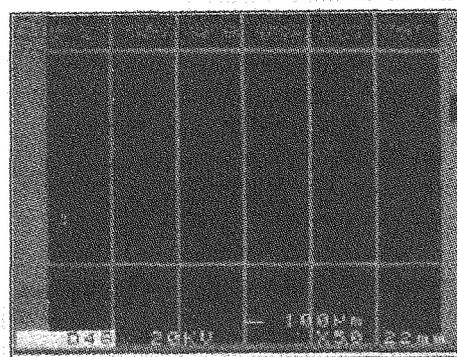


Figure 5. Photopatterns of polyimide **5**.

the polyimide region in dark and the silicon wafer in white with the resolution down to 3 μm . Using a surface profiler, it was found that the vertical distance was approximately 700 nm and the width was in agreement with the line width of the mask used.

In summary, the BCBO chemistry allows for the development of new reactive polymers for applications as adhesives, sealants and coatings. The BCBO-based polymeric materials are storable at ambient temperatures over a long period and are yet curable without using any catalysts by heat, light or both.

This work was financially supported by the Natural Sciences and Engineering Research Council of Canada.

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