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Piezoelectric activity in films of poly(1-bicyclobutanecarbonitrile)*

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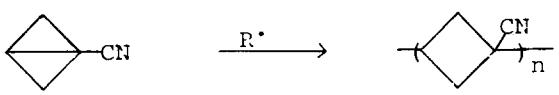
Abstract

We observed significant piezoelectric activity in cast films of poly(1-bicyclobutanecarbonitrile).

Introduction

Piezoelectric polymers are of current interest. The best-known polymer is crystalline polyvinylidene fluoride. Other crystalline polymers such as the odd-nylons and polyhydroxybutyrate also exhibit piezoelectricity. However glassy polymers with high concentration of dipoles can also exhibit it. The copolymer of vinylidene cyanide and vinyl acetate represents such a case.(1)

Polyacrylonitrile and polymethacrylonitrile have high concentrations of nitrile dipoles. However the helical structure of the polymer chains cause the radiating dipoles to cancel each other.(2) This cannot be the case for poly(1-bicyclobutanecarbonitrile),(3) as the rigid structure prevents helix formation.(4) Accordingly we prepared films of this polymer, and determined that they showed piezoelectric activity.



Experimental

α,α'-Azobisisobutyronitrile (AIBN) was recrystallized from methanol. Water used in an emulsion polymerization was distilled and degassed with argon. All other chemicals were used without purification.

Viscosity measurements of poly(1-bicyclobutanecarbonitrile) were carried out at 30°C with Ostwald-type viscometer. 1-Bicyclobutane-carbonitrile was prepared according to the method of Hall and coworkers.(5)

Free radical polymerizations were carried out in two ways.

Solution Polymerization

A mixture of 49.8 mg (0.37 mmol) of AIBN, 0.3 ml of isobutyraldehyde as chain transfer agent, 3.9 g of 1-bicyclobutanecarbonitrile, and 20 mL of γ-butyrolactone was kept at 80°C with stirring under argon atmosphere. The extent of the polymerization was checked by adding aliquots of the reaction mixture to methanol. After 1.5 hr it gave white fibrous polymer, so the whole reaction mixture was added into 400 mL of methanol via pipet. The polymer was filtered, washed with methanol, and dried to give 3.4 g (86%) of white fibrous polymer, η_{inh} 0.51 dl.g.$^{-1}$ (concentration 4.95 x 10^{-3} g/cm^3, N-methyl-pyrrolidone (NMP)). (I)

* Contribution from the C.S. Marvel Laboratories

Emulsion Polymerization

To a stirred mixture of 7.93 g of 1-bicyclobutanecarbonitrile in 50 mL of degassed distilled water under argon atmosphere were added a solution of 50.6 mg of potassium persulfate in 1.5 mL of water and a solution of 18.0 mg of sodium bisulfite in 0.5 mL of water. After 7 hr the white slurry was filtered and washed with water. It was blended with 200 ml of water, filtered, and washed. This operation was repeated with water and then with methanol three times. Drying in vac. at room temperature gave 3.14 g (39.6%) of white powdery polymer, ηinh 9.12 (concentration 1.00 x 10^{-3} g/cm^3, NMP)(II).

Both polymers were used to make films. Polymer I, 200 mg., was dissolved in 1 ml of NMP. This polymer solution was spread over a glass plate using a glass rod of which both ends were wound with tapes. Then it was dried overnight in a desiccator with a rotary vacuum pump at room temperature. The dried film on the glass plate was soaked in methanol twice, then the film peeled from the plate. Drying it in vac. at room temperature gave a clear, colorless flexible film. Polymer II film was made from a solution of 100 mg of polymer II in 5 ml of NMP by the same method.

The polymer in film form was poled by applying an electric field across the film thickness at an elevated temperature to orient the -CN groups in the film along an axis normal to the plane of the film. Samples of film (25 microns thick) were electroded with a conductive Ag paste composition and poled at 205°C with an applied field strength of 50 kilovolts/mm of film thickness.

Key piezoelectric coefficients of the poled film were measured to demonstrate its piezoelectric activity. The transverse piezoelectric coefficient (d31) was .3 pC/N and the hydrostatic piezoelectric coefficient (d_h) was 1.4 pC/N (pC/N = picoCoulombs/Newton). The dielectric constant of the film was 4.34 at 3 Hz. The dynamic mechanical modulus (c11) was 2.2 E10 dynes/cm2, also at 3 Hz.

Results and Discussion

The results of our piezoelectric measurements show significant activity. This shows that even modest concentrations of dipoles in a glassy polymer can be effective if they are unable to cancel each other within a polymer molecule. Further, the superior physical properties of poly(1-bicyclobutanecarbonitrile)(3) offer advantages over those of copoly(vinylidene cyanide - vinyl acetate).

The polymer's high Tg assures that the poled orientation will be locked over a wide range of lower temperatures. It has the highest Tg of any polymer that exhibits piezoelectric activity. This will permit its use as a transducer material to higher temperatures than heretofore possible.

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