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The elastic properties and piezochromism of polyimide films under high pressure

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ABSTRACT

The elastic properties of a fully aromatic polyimide were measured for the first time by Brillouin scattering in a high-pressure diamond anvil cell. Its isothermal compressibility and pressure dependence of mechanical moduli (K_S, E, and G) were studied and determined up to 6.4 GPa. Further, piezochromic behavior of the polyimide film was observed and studied in detail by spectroscopic analysis. Pressure-induced red shift of the absorption edge and a hysteretic phenomenon were found, due to an enhancement of the van der Waals interaction upon decreasing the interchain distances and partially collapsing the free volume under extreme pressure. A comprehensive study of elastic properties and piezochromism behavior of polyimide film under high pressure will provide useful information for developing pressure sensitive coatings, pressure sensors, pressure resistance parts and components.

1. Introduction

Polyimides impact a wide range of advanced applications such as wire coatings, gas separation, adhesives and sealants [1–10]. Due to their high thermal stability and excellent mechanical strength, polyimides are usually used as special engineering plastics in aviation, aerospace, explosives, oil drilling, mining, and submarine. These materials are typically applied in high pressure and/or high temperature environment [11,12]. To fully harness the high performance of polyimides under extreme conditions, the mechanical properties of these polymers need to be thoroughly understood. Marsh and co-workers studied the dynamical behavior of polyimide using flyer driven by chemical explosion [13]. The plots of pressure vs. volume behind shock waves were measured in the pressure range of 0–56 GPa. Takamatsu and coworkers measured the equation-of-state (EOS) of polyimide at pressures up to 5.8 TPa using low-density foam with laser-driven shock waves [14]. Polyimide Hugoniot data were obtained up to 0.6 TPa with good accuracy. Recently, Chen et al. reported the measurement of the Mie-Grüneisen EOS for polyimide used on spacecraft and an inertial fusion energy shell [15]. The key parameters of the Mie-Grüneisen EOS based on the shock adiabat were determined with two-stage light-gas gun experiments. However, previous approaches to measure the mechanical properties of polyimides normally suffer from complicated procedures, rigorous experimental conditions, and sophisticated equipment. It is therefore of interest to develop convenient analysis methods to investigate the mechanical properties and physical/chemical characteristics of polyimides under extreme conditions.

The diamond anvil cell (DAC) is among the most versatile devices used to create extreme pressures, and is usually applied in conjunction with Raman scattering or X-ray diffraction [16–19]. Brillouin scattering spectroscopy is an effective and nondestructive method to provide insight into the elastic and bulk mechanical properties of optically transparent materials by measuring their acoustic velocities [20–22]. Recently, some universal polymer samples, such as polyolefins and polysiloxanes, have been studied by a high pressure Brillouin scattering spectroscopy technique [23–31]. Accurate acoustic and elastic properties under high pressure were measured and reported, indicating the feasibility of in-situ high pressure Brillouin scattering for determining the

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mechanical properties of polymeric materials. To our knowledge, there are no reports measuring the acoustic and elastic properties of polyimide under high pressure.

Pressure is not only able to influence the elastic and mechanical properties of materials, but also has a significant impact on their optical, electrical, and thermal properties. Piezochromism, the property of substances to change color under external pressure, is perhaps the quintessential example. Due to their potential application in pressure sensitive paints, pressure sensors and optoelectronic devices, piezochromic materials continue to attract great research attention. Recently, a number of piezochromic behavior resulting from energy level disturbances, aggregation transformation, along with molecular tautomerization and geometric isomerism, have been investigated and disclosed [32–40]. To better understand the detailed mechanism and expand practical applicability, more piezochromic polymers need to be explored, with emphasis of materials with good film-forming properties and processability.

Although the aggregation and optical properties of aromatic polyimide films have been characterized by wide-angle X-ray diffraction and UV–vis absorption spectroscopy at high pressure [41–43], its acoustic, mechanical properties and piezochromic properties still require comprehensive and detailed investigation for use as theoretical reference in designing practical materials. Herein, the isothermal compressibility and pressure dependence of mechanical moduli were determined for the aromatic polyimide through high-pressure Brillouin scattering to 6.4 GPa. Additionally, a quasi-reversible piezochromic behavior was studied in detail using UV–vis absorption and photoluminescence spectra at elevated pressures up to 20.2 GPa.

2. Experimental section

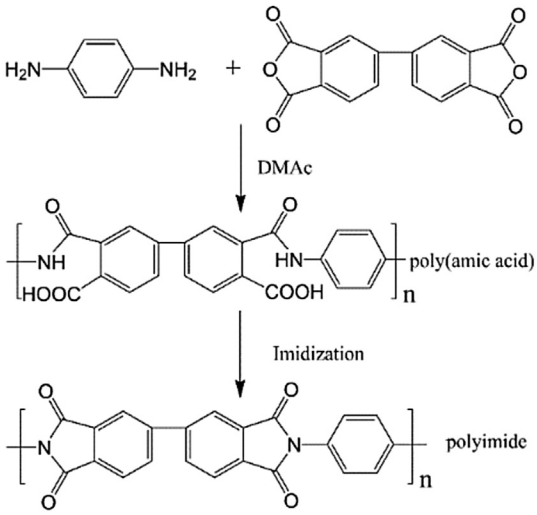
2.1. Materials

3,4,3′,4′-Biphenyltetracarboxylic dianhydride (*s*-BPDA) and *p*-phenylene diamine (*p*-PDA) were purchased from Sigma–Aldrich. *N,N′*-Dimethylacetamide (DMAc) was obtained from commercial sources and used as received without further purification. Silicon oil, used as the pressure transmission medium, was purchased from Sigma–Aldrich.

2.2. Preparation and characterization of polyimide films

The synthetic route and molecular structure of the fully aromatic polyimide are shown in the Scheme 1. Firstly, the fully aromatic poly(amic acid), as the precursor of the polyimide, was synthesized by mixing equimolar amounts of *s*-BPDA and *p*-PDA in DMAc with stirring under dry argon. After stirring at room temperature for 48 h, the precursor solution was diluted and then bladed coating on the silica substrates. Then the sample was heated and imidized by temperature programing as follow: soft-baking at 90 °C for 12 h, 180 °C for 1 h, 350 °C for 1 h. The heating rate between set point values are 10 °C/min. The imidization procedure was conducted under a nitrogen atmosphere. FTIR (KBr, cm^{-1}): 1713 ($\upsilon_{C=O}$), 1720 ($\upsilon_{C=O}$), 1515 ($\upsilon_{C=C}$ of benzenoid rings), 1360 (υ_{C-N}), 737 ($\delta_{C=O}$). GPC results: Mn: 64750, Mw: 144400, PDI: 2.23.

The thickness of the polyimide film was about 25 μm measured by spiral micrometer and microscope. Fourier transform infrared (FTIR) spectra were recorded on a BRUKER VECTOR x80 V FT-IR Spectrometer. The information of molecular weight was measured on Shimadzu gel permeation chromatography (GPC) unit equipped with a Shimadzu GPC-802D gel column and SPD-M10AVP detector. *N,N′*-Dimethylformamide was used as the eluent at a flow rate of 1 mL/min. The aggregation structure of polyimide film was confirmed by X-ray diffraction (XRD) measurement using the Empyrean X-ray diffractometer from PANalytical B.V.



Scheme 1. The synthetic route and molecular structure of the fully aromatic polyimide used in this study.

2.3. High pressure experiments

High-pressure experiments were conducted in a symmetric DAC with a large conical opening aperture. The culet size of diamond anvils is 400 μm in diameter. A polyimide film with dimentions of 120 μm × 120 μm × 25 μm was enclosed into 200 μm diameter hole of T301 stainless steel compressible gasket. Silicon oil was utilized as the pressure transmission medium. A small annealed ruby chip was loaded into the chamber together with silicone oil for in situ pressure calibration.

Brillouin scattering experiments were performed in symmetric platelet (60°) scattering geometry. A single-frequency 532 nm laser was used as Brillouin excitation source. The Brillouin spectra were collected by 3 + 3 pass tandem Fabry Perot interferometer, which was designed by Sandercock. Ruby fluorescence was recorded through Raman spectroscopy system using Acton SpectraPro 500i spectrometer with a liquid nitrogen-cooled CCD detector (Princeton Instruments). All the measurements were carried out at room temperature.

UV–vis absorption spectra were measured using an Ocean Optics QE65000 spectrophotometer.

Photoluminescence measurements under high pressure were performed using Acton SpectraPro 500i spectrometer with a liquid nitrogen-cooled CCD detector (Princeton Instruments) and the excitation source was 532 nm laser.

3. Results and discussion

3.1. Structure of polyimide

The polyimide was synthesized by nucleophilic polycondensation, and subsequential cured as depicted in Scheme 1. FTIR, GPC and XRD were applied to confirm the structure of polyimide. To confirm the imidization degree, the FTIR spectroscopy of poly(amic acid) and polyimide were performed and presented in the Fig. 1. Before curing, the poly(amic acid) displays the characteristic absorption around 1653 cm^{-1} corresponding to the C=O (CONH) stretching vibration, and around 1550 cm^{-1} due to the