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High-pressure elasticity of poly(methyl methacrylate) up to 31.5 GPa studied by Brillouin spectroscopy

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ABSTRACT

High-pressure acoustic properties of poly(methyl methacrylate) (PMMA) was investigated up to 31.5 GPa by using a Fabry-Perot interferometer and a diamond anvil cell. Both backscattering and forward, symmetric scattering geometries were used to derive the pressure dependences of the longitudinal sound velocity, the refractive index, and the density over the investigated pressure range. These physical properties showed rapid increases upon compression up to ~5 GPa, above which they exhibited sluggish increases upon further increase. The crossover behavior at ~5 GPa was attributed to the change in the densification of PMMA caused by complete collapse of free volume in this polymeric material.

1. Introduction

Pressure is one of the main thermodynamic variables by which the phase or state of condensed matters can be changed [1]. New phenomena may emerge under high pressure, which can be used to synthesize new materials or develop new devices. In general, pressure changes thermodynamic properties of condensed matters more significantly than temperature does, because interatomic forces in the matter can be modified substantially by pressure. Recently, polymer behaviors under high pressure have attracted great attention, since exact knowledge of high-pressure properties is directly related to polymer applications and may give us more insights into the glass transition phenomena of polymeric materials [2]. For example, there has been a surge of interest in polymer-based explosives, where density of each component comprising energetic materials changes significantly under high pressure during detonation [3]. Determination of equations of state (EOS), such as density-pressure relationship, is prerequisite to the development of insensitive explosives [4–6].

High-pressure Brillouin spectroscopy is one of the experimental methods for determination of equations of state of polymeric materials, in particular, of amorphous materials. Because of the amorphous or semicrystalline state of polymers, Brillouin scattering is more appropriate over other conventional methods to determine EOS, such as x-ray diffraction [7]. The probed acoustic properties are intimately related to mechanical properties, by which we can estimate elastic moduli, sound velocity, refractive index and density as a function of pressure [1].

Poly(methyl methacrylate) (abbreviated as PMMA henceforth) is one of famous polymeric materials which have wide applications in various fields. It is a transparent thermoplastic having a melting point of ~160 °C. Glass transition phenomena of PMMA have been investigated by various experimental methods, such as Brillouin scattering [8–11], ultrasonic spectroscopy [12,13], low-frequency mechanical [14] dielectric spectroscopy [15,16], etc. Glass transition process is commonly accompanied by a structural α process and other secondary processes [2]. PMMA is also characterized by α and β relaxation processes as revealed by dielectric spectroscopy [15]. The α process was attributed to the translational movement of molecular chains, while the β relaxation process to the flipping movement of the whole ester side group. Additional slow relaxation process denoted as α' was recently found by mechanical spectroscopic study, which was ascribed to the slow motion of longer chain segments or chains [14].

In spite of these previous studies, there are only few reports on high-pressure investigations of PMMA [17–20]. Pressure

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dependence of two elastic constants were reported in a rather low-pressure range from ambient pressure to 300 MPa by Weishaupt et al. [17]. Anomalous changes in acoustic properties were found at ~100 MPa. Interestingly, pressure-induced glass-to-glass structural transformation was suggested to occur in PMMA at ~116 MPa based on inelastic x-ray scattering investigations [20]. In contrast to these studies where the investigated pressure range was rather narrow and below 0.5 GPa, recent Brillouin scattering study was conducted in a wide pressure range from ambient pressure up to 11 GPa [21]. However, only the pressure dependence of the longitudinal sound velocity and the damping factor were investigated and reported. The present study is aimed at reporting acoustic properties of PMMA in a widest pressure range up to 31.5 GPa investigated by Brillouin scattering. This wide pressure range is exceptional in the study of polymeric materials except for Kel F-800, which was studied up to 85 GPa [4]. Pressure dependences of the sound velocity, the refractive index, and the density will be reported and discussed in relation to the glass transition phenomena of PMMA.

2. Experimental setup

The PMMA was purchased from Goodfellow company (Product number: ME303010/20) and used without any purification or treatment. The density and the refractive index supplied by the manufacturer were 1.19 g/cm^3 and 1.49, respectively. A small piece of PMMA was cut from the bulk and put into a hole of a steel gasket without any pressure medium. A diamond anvil cell (DAC) having a wide, symmetric aperture of an angle of 98° was used to apply pressure up to 31.5 GPa. A few ruby chips were included in the hole as a pressure marker. The fluorescent R lines of these ruby chips, excited by green laser at 532 nm, were measured by using a grating-based spectrometer (HR4000, Ocean Optics) to get the exact pressure values at each step. At least three ruby chips were measured to check the pressure gradient in the sample. The uncertainty in the measured pressure was about 0.2 GPa. Brillouin spectra were measured by using a conventional tandem six-pass Fabry-Perot interferometer (TFPI, JRS Co.). A forward, symmetric scattering geometry with a scattering angle of 63° was adopted for the measurement of the sound velocity. A micro-Brillouin spectrometer was used for the backscattering experiment, where a modified microscope (BX-41, Olympus) was adopted. A diode-pumped solid state laser (Excelsior 532-300, SpectraPhysics) at a wavelength of 532 nm was used as an excitation source. A conventional photon-counting system combined with a multichannel analyzer (channel number = 1024) was used to detect and average the signal. The details of the experimental setup can be found elsewhere [22,23].

3. Results and discussion

Fig. 1 shows pressure dependence of the Brillouin spectra of PMMA at the backscattering geometry. The spectrum consists of one Brillouin doublet corresponding to the longitudinal acoustic (LA) mode, which is related to the elastic constant C_{11}. The peak position of the Brillouin doublet increases from ~25 GHz at 1.30 GPa to ~68 GHz at 31.5 GPa. Brillouin spectra measured at the forward, symmetric scattering geometry exhibit similar frequency increase upon compression, but the peak positions are systematically lower than those obtained at the backscattering geometry due to the difference in the scattering wavevector. In this scattering geometry, the LA mode appears only at the polarized scattering geometry, which is consistent with the Brillouin selection rule. Transverse acoustic (TA) mode corresponding to C_{44} (=$(C_{11}-C_{12})/2$) is allowed only at the forward, symmetric scattering geometry. However, TA mode was not observed in this study. This may probably be due to

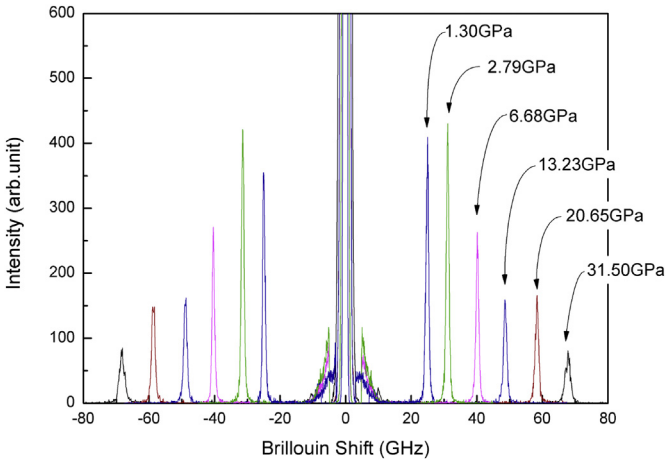

Fig. 1. Pressure dependence of the Brillouin spectra of PMMA measured at the backscattering geometry.

weak scattering intensity (i.e., weak Pockel coefficient) or proximity of the TA mode to the Rayleigh line. The Brillouin frequency shift ν_B is related to the scattering wavevector q as $2\pi\nu_B = qV$, and the sound velocity V can be expressed according to the following equations for each scattering geometry.

$$V = \frac{\lambda\nu_B}{2n_s} \quad \text{(backscattering)} \tag{1}$$

$$V = \frac{\lambda\nu_B}{2\sin(\theta_s/2)} \quad \text{(forward, symmetric scattering)} \tag{2}$$

In these equations, λ is the wavelength of the probe beam, n_s is the refractive index of the sample, and θ_s is the scattering angle, 63° in the present case. These equations explain why there are large differences in ν_B between the two scattering geometries.

Brillouin spectra were fitted by using a Lorentzian function convoluted with the Gaussian instrumental function. Pressure dependence of ν_B was obtained over the whole pressure range up to 31.5 GPa, which was shown in Fig. 2. The ν_B increases rapidly at low pressures below 5 GPa and then the increasing rate ($d\nu_B/dP$) becomes lower upon further compression. Eq. (2) can be used to

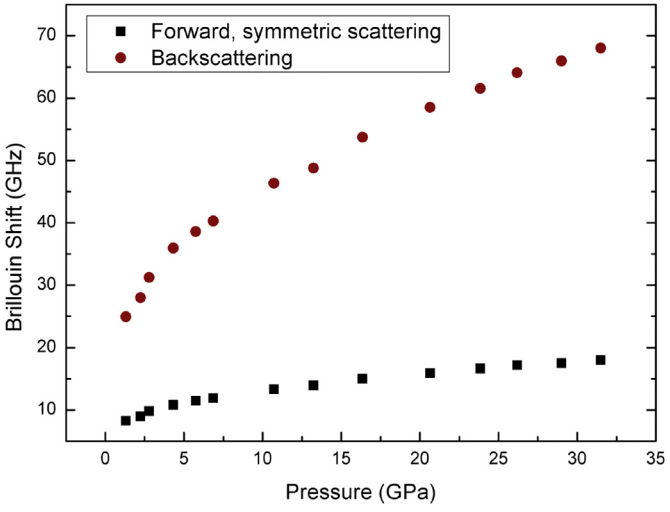

Fig. 2. Pressure dependence of the Brillouin frequency shift of the LA mode of PMMA measured at both the forward, symmetric scattering and backscattering geometries.