Study of anisotropy of acoustic wave propagation in stretched poly(vinylidene difluoride) film using the picosecond transient grating technique

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(Received 2 September 1988; accepted 1 October 1988)

The picosecond transient grating technique has been used to obtain acoustic speed as a function of film orientation in a uniaxially stretch-oriented film of poly(vinylidene difluoride) at liquid nitrogen temperature. By the analyses of acoustic speed anisotropy using the general Christoffel equation, we have obtained both the longitudinal and shear components of the elastic moduli of the film. Our results are in qualitative agreement with those of a published Brillouin scattering study.

(Keywords: picosecond transient grating technique; poly(vinylidene difluoride); acoustic speed anisotropy)

INTRODUCTION

Laser-induced ultrasonic phonons generated by the picosecond transient grating technique have been shown by Fayer and co-workers to yield valuable information on the acoustic properties of condensed media[1–4]. The method has also been used to study conformational dynamics in membranes[5]. Recently we have shown that the picosecond transient grating technique can successfully be used to obtain information on both the longitudinal and shear elastic moduli of an anisotropic polymeric film[6]. The only other technique which provides information on various elastic constants is Brillouin scattering[7]. However, the picosecond transient grating method is simpler and can be used to study a wide variety of samples thinner than one micron with great sensitivity. Ultrasonic phonons in the frequency range 10 MHz–10 GHz can be generated in the same experimental arrangement. The method can conveniently be used to investigate temperature dependence of elastic moduli and, therefore, study structural relaxations.

In this paper we investigate the elastic moduli of a stretch-oriented poly(vinylidene difluoride) film, abbreviated from here on as PVF_2, using the picosecond transient grating technique. Since the discovery of piezoelectric and ferroelectric effects in crystalline PVF_2 there has been a tremendous growth of interest in this polymer. In particular, studies were focused on potential applications of PVF_2 in piezoelectric and ferroelectric devices. Furthermore, PVF_2 has also been investigated for optical frequency doubling[8].

Crystallites of piezoelectric β phase have been reported to form upon stretching the isotropic film of the α-phase at high temperatures. The growth of β crystallites and chain orientation induced by film elongation also lead to a change in its mechanical properties. A recent Brillouin-scattering study reported anisotropy of acoustic velocities in uniaxially stretched PVF_2 films of the α-form[7]. This study also revealed that the sound velocity along the elongation axis decreases substantially when the film is heated from the glass transition temperature to about 400 K. Below T_g, the elastic compliances $s11$ and $s22$ were found to exhibit a two- to three-fold decrease upon cooling within a 50 K range[9].

In the present study, we have applied the transient grating technique to study the acoustic anisotropy of the PVF_2 polymer film leading to the determination of its elastic constants by using the general Christoffel equation. The study was conducted with the film at liquid nitrogen temperature.

EXPERIMENTAL

Polyvinylidene fluoride was purchased from Aldrich Chemical Company. To induce an optical absorption at the wavelength ~580 nm of our experiment and hence create a thermally induced density grating, the powder of PVF_2 was first dispersed in a very dilute solution of the Merocyanine 540 (Kodak) dye in methanol to form a uniform mixture. After the solvent was completely evaporated, the powder was compressed to form a film of about 200 μm thickness by applying a pressure at about 200°C. An optically clear 20 mm long and 10 mm wide strip was cut and subsequently stretched to about 6 times its original length. The thickness of the film was approximately ~50 μm. The film was mounted on an angular vernier scale to monitor the acoustic velocities along different directions of the film. The schematic layout of the experimental arrangement is shown in *Figure 1*. It consists of a CW mode-locked and Q-switched Nd:YAG laser which synchronously pumps a cavity-dumped dye laser. The output pulse duration at the wavelength used in this study was about 50 ps with a pulse energy of 15 μJ. To avoid sample damage, laser output was attenuated to about 1 μJ by means of neutral density filters. A backward

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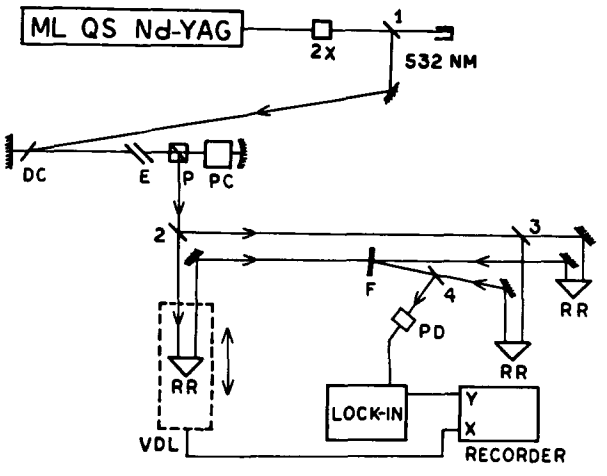

Figure 1 Schematic layout of the experimental instrumentation used in this work. DC = dye cell; E = etalon; PC = Pockels cell; P = prism polarizer; RR = retroreflector; F = sample; VDL = variable delay line; PD = photo diode; 1, 2, 3, 4 = beam splitters; $2X$ = doubling crystal

beam degenerate four wave mixing (DFWM) geometry was used for this work. This geometry has been described in detail in our earlier publications[6,10].

All our measurements were conducted far below the T_g of PVF_2 by placing the sample inside an evacuable optical dewar which was maintained at the liquid nitrogen temperature. The room temperature studies were not attempted because the sample revealed laser damage on prolonged exposure at this temperature.

RESULTS AND DISCUSSION

The details of the beam geometry in the experimental arrangement have been described elsewhere[6]. The parent laser beam is split by means of a beam splitter into three beams: I_1 and I_2 of the same intensity, and I_3 of much weaker intensity. The I_1 and I_2 beams, having the same frequency and polarization are crossed at an angle θ (11°) in the sample and made to arrive at the same time to create an optical grating (interference pattern). The third beam I_3, much weaker compared to pump beams which can be delayed with respect to I_1 and I_2, is used to probe this grating in the DFWM configuration. Because of the induced optical absorption followed by radiationless relaxation, the interference pattern results in the form of a periodic temperature distribution. The impulsive thermal expansion and compression, occurring at the intensity peaks and nulls, respectively, generate counterpropagating acoustic waves along the grating direction. This results in the acoustic wave oscillating at the speed of

$$v = \frac{\Lambda}{d} \tag{1}$$

The wavelength, Λ, of an acoustic wave is the same as the interference fringe spacing given by

$$\Lambda = \lambda/(2 \sin \theta/2) \tag{2}$$

Here λ is the wavelength of the pump beams I_1 and I_2; θ is the angle between them, and d is the acoustic period which is calculated from the periodicity of the diffracted signal.

Using cross polarizations for I_1 and I_2 (no signal observed after the zero time), we have concluded that the observed signal is due to thermally induced acoustic waves and not due to either electrostriction or Kerr grating. A detailed discussion of diffraction from these gratings has been presented by Nelson and Fayer[1-5]. Typical results of the transient grating experiment on the stretched PVF_2 film are shown in *Figure 2*, where the intensity of the diffracted DFWM signal is plotted *versus* the probe delay time. Inspecting *Figure 2*, it is evident that acoustic modulation of the diffracted intensity is superimposed on an excited state grating created by strong absorption of the dye molecules. In general, the observed signal can be derived from two types of gratings: a phase grating and an amplitude grating, which reflect changes in the real and imaginary part of the refractive index, respectively[2]. In the absence of any Kerr type or electrostriction grating, as in our case, one can express the efficiency of mixed thermal–acoustic and excited state gratings as follows[2,4,5]:

$$\eta \simeq [A \exp(-t/\tau_e)]^2 + \{B[1 - \cos(\Omega t)\exp(-\gamma t)] + c \exp[-t/\tau_e]\}^2 \tag{3}$$

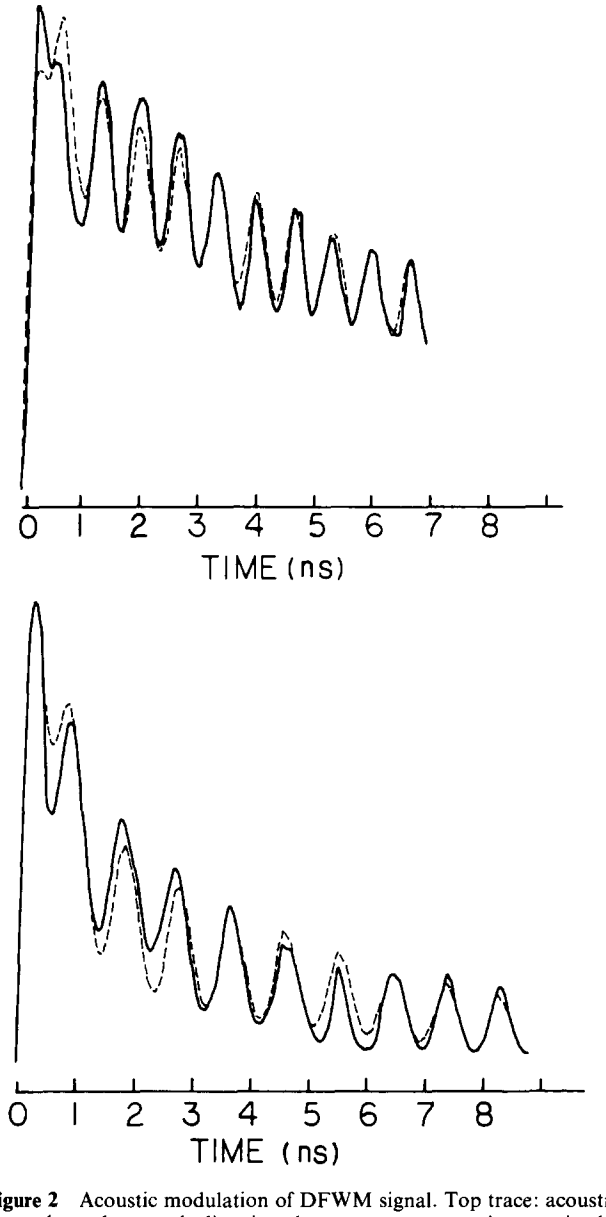

Figure 2 Acoustic modulation of DFWM signal. Top trace: acoustic wave along the stretch direction; bottom trace: acoustic wave in the direction perpendicular to the stretch direction. The calculated curves are represented by the dashed lines

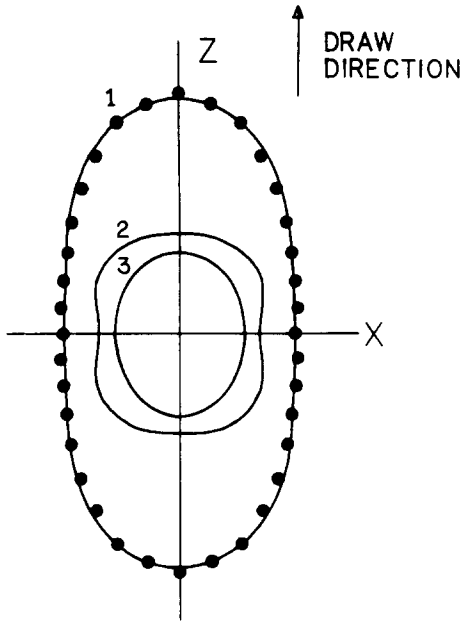

Figure 3 Polar plot of the sonic speed in the *ac* plane of the PVF_2 stretched film. Solid lines represent calculated curves. 1, Quasilongitudinal mode; 2 and 3, quasitransverse modes; ●, experimental data points

The first term of equation (3) describes the contribution of the excited state amplitude grating, with τ_e being the excited-state lifetime. The next term is the acoustic phase grating contribution where Ω stands for the acoustic frequency and γ is the damping factor for the acoustic oscillation. The third term denotes the contribution from the excited-state phase grating. To describe adequately our experimental results we must also include the pump–pulse convolution which overlaps with the first thermal peak. Therefore, equation (3) is modified as:

$$\eta \simeq [1-\exp(-t/\tau_p)]^2[A\exp(-t/\tau_e)]^2 + \{B[1-\cos(\Omega t)\exp(-\gamma t)]+c\exp[-t/\tau_e]\}^2 \quad (4)$$

where τ_p is the pump pulse duration.

The above expression was used to compute the diffracted signal intensity for the values of Ω and τ_p found in our experiment. This theoretical curve fits the experimental data satisfactorily and is also shown in *Figure 2* (thin dashed line). Since the main goal of our work is to find elastic moduli of the PVF_2 film, we will not discuss the excited-state grating parameters any further.

Now we focus on the analysis of the acoustic anisotropy and elastic properties of the stretched PVF_2 film. Experimental results of the in-plane acoustic speed in various directions of the PVF_2 film are shown in *Figure 3* (full circles). This polar plot of acoustic speed *versus* direction of wave propagation clearly shows that the stretched film exhibits an in-plane anisotropy of sound velocities, with the greatest speed along the stretch direction and the smallest in the direction perpendicular to it. The detailed analysis of the experimental data revealed that observed acoustic waves are quasilongitudinal.

A complete analysis of our results required a knowledge of the sample symmetry. For an oriented PVF_2 sample of the *I* form, an orthorhombic symmetry has been reported with space group *Cm2m* and lattice parameters $a=0.858$ nm; $b=0.491$ nm; $c=0.256$ nm; axis c being along the stretch direction[11]. For an orthorhombic system the elastic constant matrix C_{KL} has nine independent components. Therefore, with at least nine independent measurements of sound velocities along different directions, the general Christoffel equation

$$k^2(l_{iK}\mathbf{C}_{KL}l_{Lj})V_j = k^2\Gamma_{ij}V_j = \rho\omega^2 V_i \quad (5)$$

can be solved, yielding the complete set of elastic constants. In equation (5) $\Gamma_{ij}=l_{iK}\mathbf{C}_{KL}l_{Lj}$ is the Christoffel matrix; l_{iK}, l_{Lj} are the symmetry operations in the rectangular coordinates. V_i and V_j represent the particle displacements along i, j. $\mathbf{C}_{KL}$ is the stiffness matrix.

The experiment was performed in the plane of the film, which in our case can be assumed to be *ac* (*b* axis normal to the film plane[12]). This experimental geometry reduces the number of elastic constants involved in equation (5) to 6, which now can be simplified to the following form:

$$V^3 - V^2\rho^{-1}(\alpha+\beta+\gamma) + V\rho^{-2}(\alpha\beta+\beta\gamma+2\alpha-\varepsilon^2) - \rho^{-3}(\alpha\beta\gamma-\beta\varepsilon^2)=0 \quad (6)$$

In the above equation, $\sqrt{V}=\omega/k$ is the phase velocity of the acoustic wave and

$$\alpha=\mathbf{C}_{11}l_x^2+\mathbf{C}_{55}l_z^2$$
$$\beta=\mathbf{C}_{66}l_x^2+\mathbf{C}_{44}l_z^2$$
$$\gamma=\mathbf{C}_{55}l_x^2+\mathbf{C}_{33}l_z^2$$
$$\varepsilon=(\mathbf{C}_{13}+\mathbf{C}_{55})l_x l_z \quad (7)$$

Here l_x and l_z are the direction cosines of the propagation direction with respect to the crystallographic axes.

At first we solved equation (6) by assuming a hexagonal symmetry, the highest symmetry for a uniaxial system. This assumption reduces the number or stiffness constants to 5 ($\mathbf{C}_{55}=0$).

The elastic constants obtained for the hexagonal system were used in solving equation (6) for the orthorhombic symmetry by a nonlinear least-squares fitting procedure. The density of the PVF_2 film required for these calculations was taken from reference 7. *Figure 3* gives the theoretical fit obtained from our analyses (solid line V_1). The calculated curve matches satisfactorily with the velocity contour observed by the experiment.

There are three solutions to equation (6) which are also shown in *Figure 3*. The particle displacement polarizations calculated for each of the theoretical curves indicate that V_1 is of quasicompressional character while V_2 and V_3 are quasishear modes. Because only V_1 follows the anisotropy contour obtained from the experiment we conclude that we observed only quasilongitudinal acoustic waves. The elastic constants obtained by our calculation are listed below (all in GPa):

$$\mathbf{C}_{11}=11.44 \quad \mathbf{C}_{13}=2.21 \quad \mathbf{C}_{33}=29.5$$
$$\mathbf{C}_{44}=3.71 \quad \mathbf{C}_{55}=5.70 \quad \mathbf{C}_{66}=3.60$$

At liquid nitrogen temperature, the observed velocities range from 4.2×10^3 ms^{-1} along the stretch direction to 2.5×10^3 ms^{-1} perpendicular to it. Our results are in qualitative agreement with the Brillouin scattering results of Sessler[9]. Our values are greater than those reported by Sessler at the room temperature. This is in general agreement with observations that material stiffness increases as the temperature is lowered. However, the temperature dependence reported by Sessler does not seem to be consistent with our observation. Sessler[9] found $\mathbf{C}_{11}$ to almost triple its room temperature value when cooled to about 170 K. We have not observed such a

drastic change in the C_{11} value (C_{22} could not be determined in our experiment), after cooling down the sample from dry ice temperature to the liquid nitrogen temperature. Comparing our stiffness constants to that reported for room temperature[7] we observe about a 50% increase in the C_{11} and C_{44} values; a 38% increase in the C_{33} value and a 50% decrease in the C_{13} values.

CONCLUSIONS

In conclusion, the transient grating technique used in our experiment has proved to be useful in determining the mechanical properties of oriented films. Our study of orientational anisotropy of the supersonic velocity in a polymer film yielded both the longitudinal and shear components of the elastic constants tensor.

ACKNOWLEDGEMENTS

This research was supported by the Directorate of Chemical Sciences, Air Force Office of Scientific Research and Air Force Wright Aeronautic Laboratory Polymer Branch under contract number F4962087C0042 and by the Office of Innovative Science and Technology Defense Initiative Organization under contract number F4962087C0097.

REFERENCES

1 Fayer, M. D. *Ann. Rev. Phys. Chem.* 1982, **33**, 63
2 Fayer, M. D. *IEEE J. Quant. Electr.* 1986, **QE 22**, 1437
3 Nelson, K. A. and Fayer, M. D. *J. Chem. Phys.* 1980, **72**, 5202
4 Nelson, K. A., Casalegno, R., Miller, R. J. D. and Fayer, M. D. *J. Chem. Phys.* 1982, **77**, 1144
5 Eyring, G. and Fayer, M. D. *J. Chem. Phys.* 1984, **81**, 4314
6 Rao, D. N., Pang, Y., Burzynski, R. and Prasad, P. N. *Macromolecules* in press
7 Wang, C. H., Liu, Q.-L. and Li, B. Y. *J. Polym. Sci., Polym. Phys. Edn.* 1987, **25**, 485
8 Lovinger, A. J. in 'Developments in Crystalline Polymers – 1' (Ed. D. C. Bassett), Elsevier, London (1982)
9 Sessler, G. M. *J. Acoust. Soc. Am.* 1981, **70**, 1598
10 Rao, D. N., Burzynski, R., Mi, X. and Prasad, P. N. *Appl. Phys. Lett.* 1986, **48**, 387
11 Kobayashi, M., Tashiro, K. and Tadokoro, H. *Macromolecules* 1975, **8**, 158
12 Newman, B. A. and Scheinbeim, J. I. *Polym. Preprints* 1982, **23**, 164