

## Laser induced ultrasonic wave grating in polyacrylonitrile (PAN)

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### Summary

The picosecond laser-induced transient grating was used as a probe of the mechanical properties of polyacrylonitrile (PAN) ladder polymer in the glassy state. The application of laser-induced transient grating method yielded fit various elastic moduli isotropic films of pyrolysed doped and undoped PAN. Stiffness constants of these materials have been compared with values of Young's moduli for linear polymers in the glassy state.

### Introduction

The laser - induced transient gratings have been used to study a variety of dynamic processes in a wide variety of materials such as polymers<sup>1</sup>, plasmas<sup>2</sup>, dye solutions<sup>3</sup>, and semiconductors<sup>4,5</sup>. These experiments have been performed to measure nonlinear optical response<sup>1</sup>, molecular excited state energy relaxation rate<sup>6</sup>, carrier transport rate<sup>7</sup>, and diffusion and recombination coefficient<sup>8</sup>.

Laser - induced transient grating has also been used as a technique to optical generation of ultrasonic waves<sup>9-12</sup>. This technique, pioneered by Feyer<sup>9</sup> has been used to study important mechanical properties - elastic moduli (Young's modulus) of materials and anisotropy of these mechanical properties of polymer films<sup>13-16</sup>. The advantage of this optical method is to achieve a determination of stiffness constants for thin polymer films where the classical viscoelastic methods cannot be used.

### Materials and Methods

In this paper, we present an investigation of isotropic elastic modulus (stiffness constants) of a polymer with pseudo - one - dimensional ladder structure which can be obtained by pyrolysis of polyacrylonitrile (PAN). This polymer has been a subject of our interest as for its third order nonlinear optical susceptibility, doping mechanism, and in carbonized state large electrical conductivity. The pyrolysis leads to ring closure by the nitrile side groups, resulting in a ladder structure. The reaction is induced by heating the polymer. When the reaction is carried out under anaerobic conditions, the stabilized structure consists of a chain of C-C bonds and of a parallel chain of conjugated C=N double bonds. When stabilization takes place under aerobic (oxidative) conditions at temperature 200 - 300 °C, some skeletal carbon atoms may become unsaturated and take part in a fully delocalized condensed aromatic structure<sup>17</sup>. This second reaction used by us is demonstrated in Fig.1. The presence of the conjugated imine system is sufficient for the development of semiconducting properties in the pyrolysed PAN. However, as usual for  $\pi$  - conjugated pseudo-one-dimensional polymers, the electric conductivity of this

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systems can be drastically modified by introduction of suitable dopants or carbonization of ladder structure<sup>18</sup>.

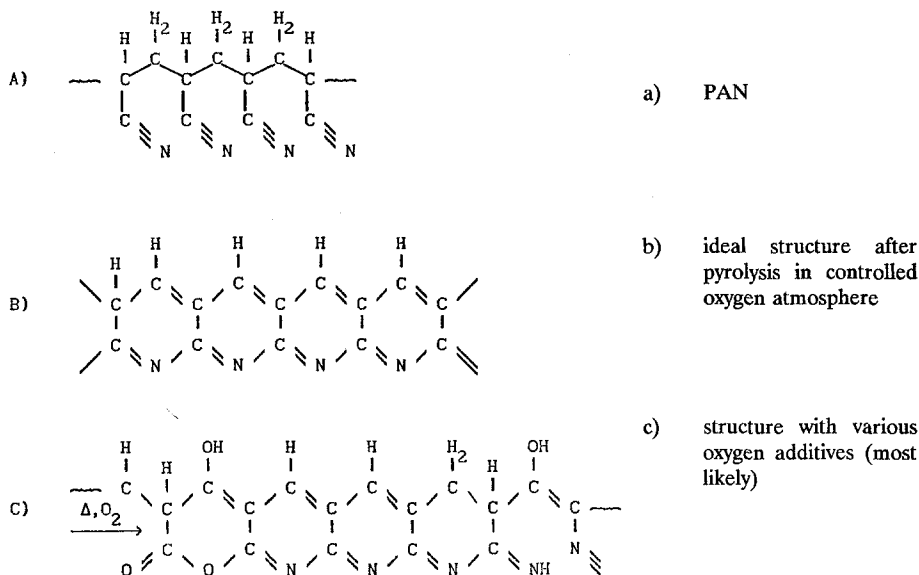


Fig. 1 Schematic description of aerobic stabilization reaction of PAN

### Sample preparation

PAN films were cast from dimethylformamide (DMF) solution, with a concentration of 10g/100ml. Films were prepared by spin coating the viscous solution of PAN, or PAN and dopants on glass/or quartz substrate or pressed as KBr pellets for IR measurements. The pyrolysis was carried out at 225°C in air and different degree of cyclization of six-member rings was obtained by different time-exposition of samples at a fixed pyrolysis temperature. Doping was carried out in solution, PAN was dissolved in DMF with electron acceptors ( $\text{NaAsF}_6$  and  $\text{FeCl}_3$ ). The change of optical absorption spectra due to cyclization and formation of charged species by doping was investigated UV-visible absorbance spectroscopy (Fig.2). IR spectrum, as seen in Fig.3, which shows the loss of the typical peak at  $2240\text{ cm}^{-1}$  assigned to the nitrile group  $\text{C}\equiv\text{N}$  while that of the imine bonds at  $1650\text{ cm}^{-1}$  increases as the reaction proceeds. New peaks appearing at  $1650\text{ cm}^{-1}$  and  $1360\text{ cm}^{-1}$  indicate the onset of polymer chain conjugation through the formation of  $\text{C}=\text{N}$  and  $\text{C}=\text{C}$  bonds<sup>19-20</sup>. Thickness of pyrolysed doped and undoped PAN samples (usually 1-4  $\mu\text{m}$ ) were measured with profilometer (Sheffield Instr.). The density of these films was determined by flotation techniques.

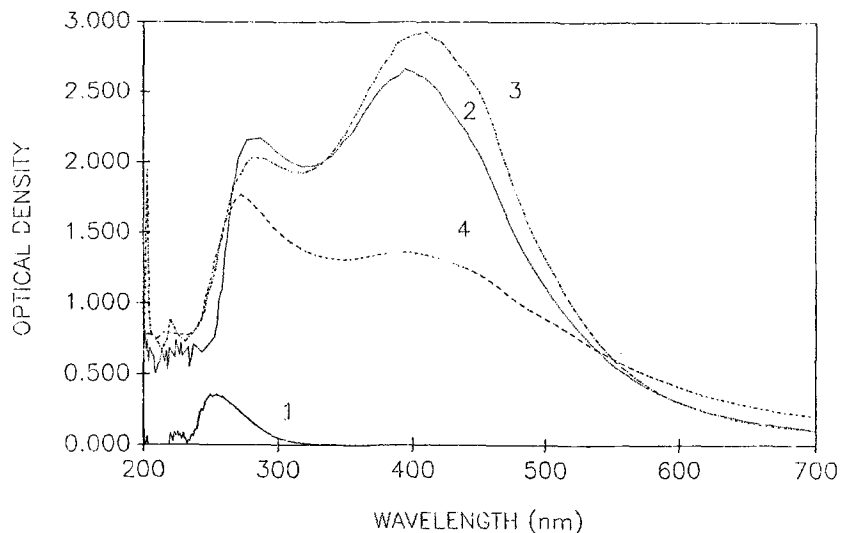


Fig.2. The UV - VIS absorption spectrum

PAN before pyrolysis - curve 1; pyrolyzed PAN - curve 2; pyrolyzed PAN doped  $\text{NaAsF}_6$  - curve 3; pyrolyzed PAN doped  $\text{FeCl}_3$  - curve 4

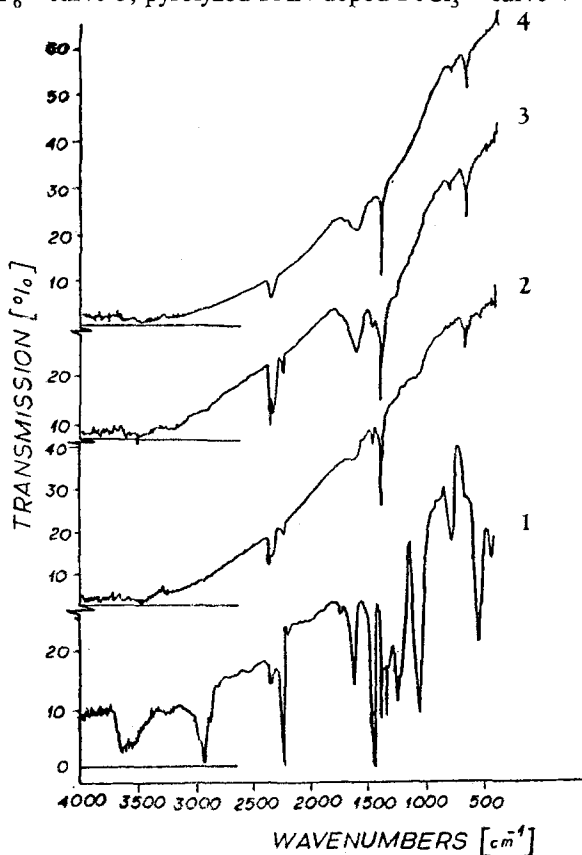


Fig.3

Infrared absorption spectra PAN before heating (curve 1) PAN heated in air, heating rate  $5^\circ \text{C}/\text{min}$   
 - immediately after achieving  $225^\circ \text{C}$  (curve 2)  
 - heated at  $225^\circ \text{C}$  for 60 min (curve 3)  
 - heated at  $225^\circ \text{C}$  for 180 min (curve 4)

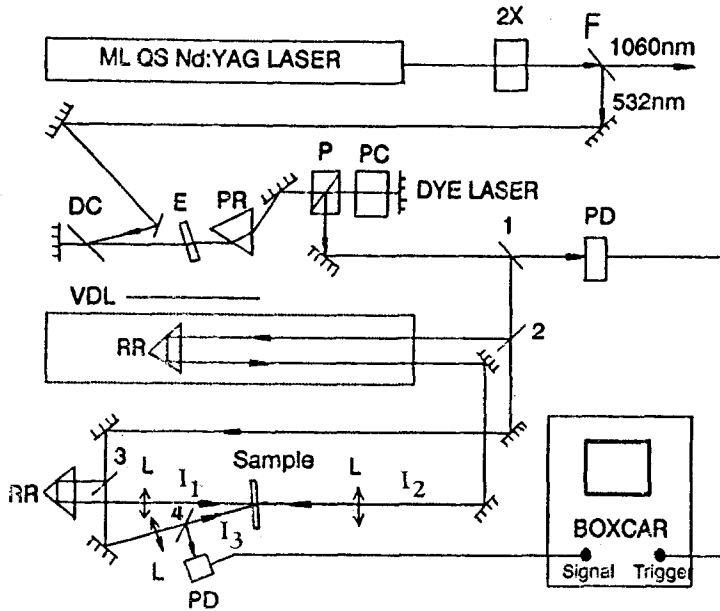


Fig.4. Experimental setup for the transient grating measurement

PC = Pockel's cell, P = polarizer, E = etalon, DC = flowing dye cell, 1,2,3,4 = beam splitters, PR = prism, PD = photodiode, VDL = variable - delay line, RR = retroreflector, L = lenses

### Experimental

The experimental arrangement used for the present study is shown in Fig.4. The laser system used for this experiment is a cavity-dumped dye laser which is synchronously pumped by the frequency doubled output from a acousto-optically mode-locked and Q-switched cw Nd:YAG laser. The laser system operates at 500 Hz (DQ switch frequency of the YAG laser). The pulse-width of the dye laser pulses around 50 ps with about 14  $\mu$ J energy per pulse at the wavelength of 575 nm. The laser beam intensity can be attenuated by using neutral density filters.

We have used the phase conjugate degenerate four-wave mixing (DFWM) geometry in this experiment. The backward probe beam (beam  $I_2$  in Fig.4) is delayed by a long optical delay line with a maximum delay of 10 ns. The angle  $\theta$  between beams

$I_1$  and  $I_3$ , which induce thermal grating in the films, is  $11.2^\circ$ . The angle between the normal of the film and the bisector of beams  $I_1$  and  $I_3$  is selected to be small in order to avoid the interference from the reflection of beam  $I_1$ . Therefore, the acoustic wave propagates in the film plane. The four-wave mixing signal is detected by a photodiode and processed by boxcar averager (EG&G Princeton Applied Research Model 4200). The wavelength of pump beam is within the absorption spectrum (see Fig.2). Under this resonance condition, the DFWM signal is detected.

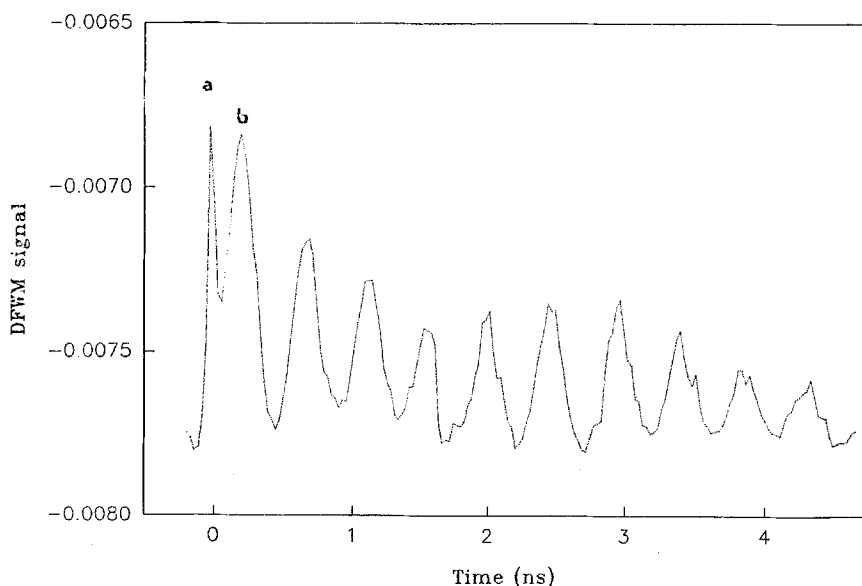


Fig.5. The observed DFWM signal (superposition of the excitation states and acoustic grating). The modulation of the DFWM signal is derived for the acoustic grating

### Results and Discussion

The experimentally measured degenerate four-wave mixing (DFWM) signals obtained as a function of the delay time of probe beam  $I_2$  are shown in Figs. 5,6,7 for undoped and doped pyrolysed PAN. Analysis of all important contributions to the DFWM was performed in<sup>13-16</sup>. We conclude that the observed DFWM signal is derived from the excited states and acoustic gratings.

In the thermal mechanism of acoustic grating generation, the time delay between two successive diffraction peaks gives the acoustic period. The acoustic velocity can be derived as

$$v = \Lambda / d$$

where  $\Lambda = \lambda / (2 \sin \Theta/2)$  defines the acoustic wavelength. Here,  $\lambda$  is wavelength of the pump beams,  $\Theta$  is the angle between the pump beams  $I_1$  and  $I_3$ ,  $d$  is acoustic period. In an isotropic material, the acoustic velocity is constant in all directions and has the value  $v = (c / \rho)$ , where  $c$  is stiffness constant and  $\rho$  is density of material. The Young's modulus  $E$  is a fundamental measure of the stiffness of the material. The higher its value the more resistant the material is to being stretched. A wide range polymer (linear amorphous polymers) having the value of Young's modulus below the glass transition temperature of the order  $10^9$  Pa. This value is close to values obtained from our experiments for undoped and doped PAN samples (see Table 1). In the case of doping species, change in mechanical properties of doped polymer films has been observed. The agents from oxidizing reaction of PAN polymer ( $AsF_3$  and  $FeCl_2$ ) can affect the mechanical properties of thin films doped polymers.  $AsF_3$  appears to be playing the role of plasticizing agent for the pyrolysed PAN film doped with sodium hexafluoroarsenate.

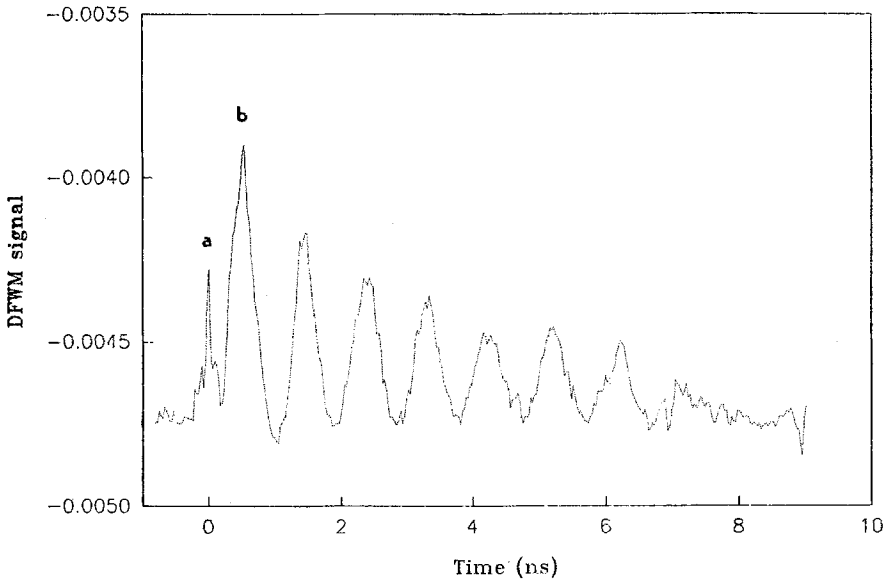


Fig.6. Pyrolyzed PAN lightly doped with  $FeCl_3$  (5% wt) Contribution to DFWM signal - excited states (a), - acoustic grating (b)

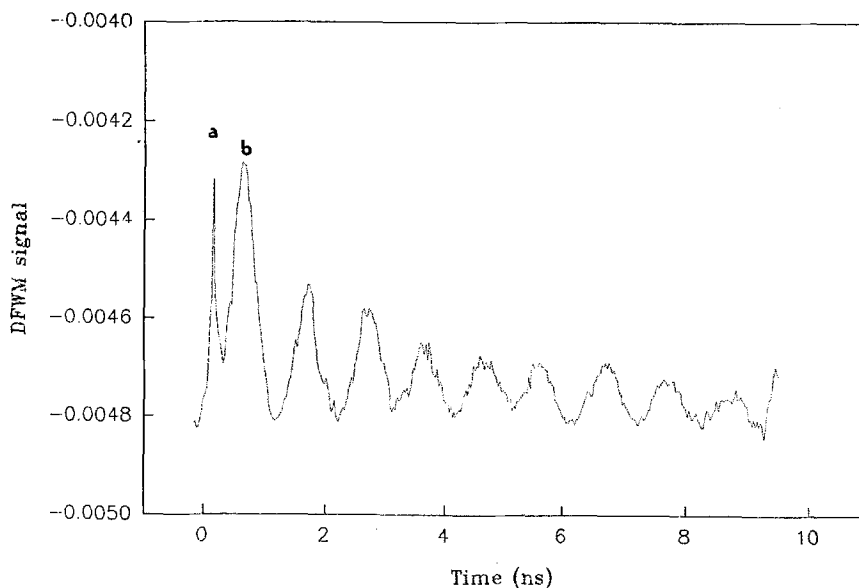


Fig. 7. Pyrolysed PAN heavily doped with  $\text{NaAsF}_6$  (50% wt) Contributions to DFWM signal - excited states (a), acoustic grating (b)

Table 1

material	acoustic velocity $v$ [ $\text{cm sec}^{-1}$ ] $\times 10^5$	density [ $\text{gcm}^{-3}$ ]	Young's modulus $E$ [MPa]
PAN pyrolysed	( 3.42 0.05 )	1.70	19.6
PAN pyrolysed lightly doped with $\text{FeCl}_3$ (5% wt)	( 3.38 0.04 )	1.75	19.9
PAN pyrolysed heavily doped with $\text{NaAsF}_6$ (50% wt)	( 2.96 0.02 )	1.90	16.6

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