

## **Molecular Behavior of Amorphous Polystyrene Under Tensile Stress**

**S. Sikka**

University of Dayton, Research Institute, 300 College Park Avenue,  
Dayton, Ohio 45469, USA

### SUMMARY

Molecular level changes occurring due to external stress application have been studied by the dynamic infrared spectroscopic technique using Fourier Transform Infrared Spectrometer. The "subtraction" spectrum (stressed - 88% unstressed) of polystyrene has shown even minute changes in 540, 903, 1154, 1310, 1376, and 1602  $\text{cm}^{-1}$  infrared bands assigned to various vibrational modes of phenyl side groups. Both infrared and x-ray results have indicated certain conformational rearrangements (under stress) of these bulky phenyl side groups present in the PS chains.

### INTRODUCTION

The infrared vibrational frequency of a molecule is known to depend on the force constants (which are determined by the strength of atomic bonding) and bond angles. It is well known that the deformation of atomic bonds and their angles by an external stress can cause a shift of skeletal vibration. The amount of shift can provide a measure of the magnitude of the mechanical stress acting on the polymer chain. ZHURKOV et al. (1969) made use of these principles to learn about the overstressed bonds, true stresses and stress distributions in oriented films of polypropylene, poly(ethylene terephthalate) and nylon 6. These authors compared the infrared spectra of unstressed and stressed polymer film to determine the shift of vibrational frequencies of C-C backbone bonds in the polymer chain. These studies led the authors to postulate that the distortions of the IR band shape on the low frequency side are caused by non-uniform stress distribution on the atomic bonds while a peak shift is due to equal stressing of a large number of backbone bonds. This technique of dynamic infrared spectroscopy was then successfully applied by WOOL (1975) to investigate the molecular mechanics of highly

oriented polypropylene during stress relaxation and creep and has been described in detail by WOOL et al. (1978). MOCHERLA (1975), and SIKKA (1979a) applied it to understand the stress-strain behavior of PETP on the molecular basis. SIKKA (1976, 1979b) has expanded this method further using Fourier Transform Infrared Spectroscopy (FTIR) to relate molecular response of amorphous polymers resulting from their macroscopic deformations to understand the physical phenomena of fatigue and crazing. Amorphous glassy polymers polystyrene and polycarbonate were studied under tensile stress, cyclic fatigue and crazing conditions. In the present publication, only the molecular behavior of PS under stress is presented.

## EXPERIMENTAL

### Infrared Spectra

The Fourier Transform IR spectra and "subtraction spectra" were obtained on a Digilab's Fourier transform spectrometer model 14-B. The spectra were recorded at a resolution of  $2\text{ cm}^{-1}$  after computer-averaging a total of 20 scans. The PS film was stressed in a mechanical stretcher and strains were measured by Calipers. The stress on the sample was determined from the stress-strain curve obtained from the Instron machine.

### X-ray Scattering Data

The x-ray scattering data from unstressed and stressed PS films were obtained on a flat film placed in Statton's box camera using Cu target (at 50 kV and 20 mA) and Ni filter. The scattering patterns were scanned by a Joyce-Loeble automatic recording densitometer (Model MD III CS).

## RESULTS AND DISCUSSION

The superimposed FTIR spectrum of stressed PS film over the unstressed PS film is shown in Figure 1. The IR bands at 540, 903, 1310, 1376, 1492, and  $1602\text{ cm}^{-1}$  are not exactly superimposed. On subtraction of 88% IR spectrum of unstressed PS (shown in solid line) from that of stressed PS (shown in broken lines), one would expect shoulders to appear at the low wavenumbers side of 903, 1154,  $1310\text{ cm}^{-1}$  and toward higher wavenumbers side of 1376, 1492, and  $1602\text{ cm}^{-1}$  IR bands. This is indeed observed in the FTIR "subtraction" spectrum (stressed -88% unstressed) shown in Figure 2. Besides the anticipated additional bands at 889, 1141, 1400, and  $1506\text{ cm}^{-1}$ , the IR bands

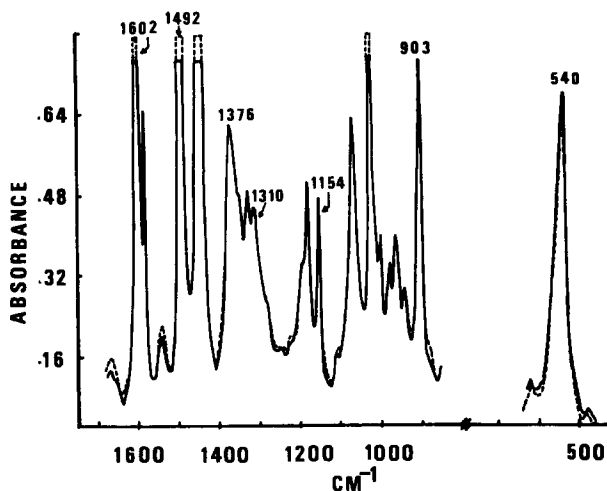


Figure 1. Superimposed Fourier Transform IR Spectrum of Stressed (----) and Unstressed (—) Atactic Polystyrene.

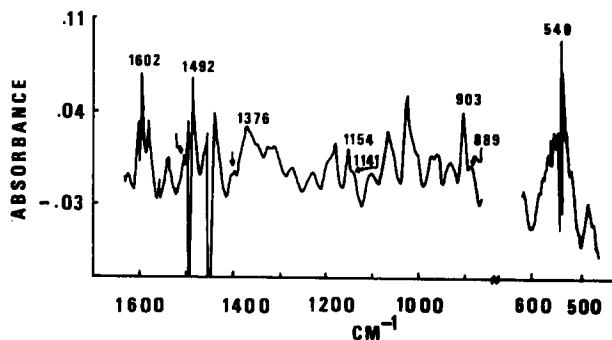


Figure 2. Fourier Transform IR Spectrum of (Stressed-88% Unstressed) Atactic Polystyrene Film.

at 540, 1448, 1492, and 1602  $\text{cm}^{-1}$  exhibit splittings. These splittings can be due to changes in the band distribution or resolving of the band into several peaks and/or shift in wavenumbers, etc. All these changes of the IR bands are related to the various vibrational modes of the phenyl side group LIANG et al. (1958). Therefore, it is suggested that phenyl groups on the adjacent chains interact extensively, under stress, changing the electron distribution on the phenyl

rings. Such changes are responsible for shifting the absorption frequencies of various vibrational modes. If such shifts are large, they show up as separate bands or shoulders to the existing bands. When the shifts are small, they show up as band splittings.

In the present results, the  $1154\text{ cm}^{-1}$  band exhibits the most distortions. It is assigned to  $\nu_{15}B_1$  mode, i.e., the bending mode of C-H atom located on the para position of the phenyl groups (with respect to the main chain substitution position), LIANG, et al. (1958). This implies that highly entangled PS chains rearrange themselves under stress. This has also been indicated by the increase in inter- and intra-chain distances studied by x-ray scattering. However, such chain motions are highly restricted due to steric hindrances of the phenyl side groups located on the adjacent chains. Some of these steric effects are reduced under stress when conformational rearrangements of phenyl groups and breakage of weaker Van der Waal's bonds take place. Such rearrangements allow localized chain slippage or motion.

Since all the affected vibrational modes (in the present data) are associated with the phenyl groups such as hydrogen stretching modes at the para position of the ring, ring vibrations, out of plane vibrations, etc., it is evident that the presence of phenyl side groups strongly interfere under stress. Thus molecular behavior of amorphous PS is highly dictated by the phenyl side groups and influences its mechanical properties.

#### ACKNOWLEDGMENT

The author gratefully acknowledges the financial support from the U.S. Air Force, Office of Scientific Research under Grant No. 75-2827. This work was performed at the Department of Materials Science, University of Utah, Salt Lake City, Utah 84112.

#### REFERENCES

1. LIANG, C.Y. and KRIMM, S., J. Polym. Sci., 27, 24 (1958)
2. MOCHERLA, K.K.R. and STATTON, W.O., Symp. High Polym. Phys. and Chem., Seoul, Korea, 1, (1975)
3. SIKKA, S., "Molecular Behavior of Amorphous Glassy Polymers Under Tensile Stress, Cyclic Fatigue and Crazing Conditions," Ph.D. Dissertation, University of Utah, Salt Lake City, Utah, (1976)

4. SIKKA, S.S. and KAUSCH, H.H., Colloid and Polym. Sci., 257, 1060, (1979)
5. SIKKA, S., Matl. Sci. and Eng., 41, No. 2, 265, (1979)
6. WOOL, R.P., J. Polym. Sci., 13, 1795, (1975)
7. WOOL, R.P. and STATTON, W.O., "Dynamic Infrared of Polymers," Applications of Polymer Spectroscopy, ed. by E.G. Brame, Jr., Academic Press, Inc., New York, (1978)
8. ZHURKOV, S.N., et al., Proceedings of the Second International Conference on Fracture, Brighton, Great Britain; Chapman and Hall, London, 545, (1969)

*Received and accepted August 4, 1980*