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FTIR spectroscopy of polymer films under uniaxial stretching

1. Atactic polystyrene

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SUMMARY

The results of FTIR studies of atactic polystyrene (aPS) film during uniaxial deformation at ambient conditions are presented. The frequency shifts of several IR bands at strains from 1% to 20% were analysed. The pure vibrations of benzene ring and the conformation sensitive modes behave differently over the entire deformation range. The obtained results are compared with the band shifts observed in aPS film on heating and under high pressure. The molecular mechanism of deformation of glassy polymer is discussed.

INTRODUCTION

The structural changes in polymers at the small strains are not well studied. This deformation region is of special interest for glassy polymers. It incorporates the molecular scale events which are the precursors of plasticity. The experimental detection and the interpretation of these small structural changes are very diffucult for amorphous polymers. FTIR spectroscopy because of its high sensitivity seems to be the technique to attack the above-mentioned problem. Vibrational spectroscopy was used for the studies of stress-induced effects in oriented polymers[1,2]. The spectral variations (frequency shifts and bandshape variations) have been interpreted by the intramolecular changes. The conformational and structural effects were found in the IR dynamic stretching experiments on different rubbers[3]. In the FTIR study of uniaxial deformation of atactic polystyrene film in rubbery state[4] the role of the conformational changes in plasticity formation was discussed. We have used FTIR spectroscopy for monitoring the behaviour of films of unoriented polymers during uniaxial stretching at ambient conditions. The mechanically-induced frequency shifts of various IR bands are analysed. The observed effects are compared with the bandshifts registrated in aPS film on heating and under high pressure. The IR changes during deformation of annealed aPS and iPS (isotactic polystyrene) films are also shown.

EXPERIMENTAL

The industrial aPS film (thickness 20 μm) was used in the experiments. Molecular weight characteristics of this polymer as revealed by GPC measurements are $M_w = 265000$ and $M_w/M_n = 3.5$. Anisotropy of mechanical behaviour of the film was detected, molecular orientation was not revealed, however, by IR dichroism measurements. Stretching in one of the directions leads to necking. Brittle fracture was observed during stretching in the perpendicular direction. Dumbell-shape samples (width and

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*Present address and address for offprint requests: Freiburger Metallforschungszentrum der Universität, Stefan-Meier-Strasse 31, W-7800 Freiburg, FRG length of narrow part - 5 mm and 20 mm) were cut out of film. The home-made tensile machine$^{5)}$ was installed in the sample compartment of the Bruker IFS-113v FTIR spectrometer. Rectangular masked IR beam (4 mm X 10 mm) was focused at the central part of a sample. The film was stretched (rate .01 min^{-1}) at room temperature. The slight IR beam heating induced necking in the centre of sample. IR interferograms (resolution 2 cm^{-1}, number of scans 50) and stress-strain data were collected simultaneously. Polymer film was covered with the thin layer of hydrocarbon or fluorocarbon oil (for measurements in the different spectral regions) in order to avoid interference patterns. Interferograms were converted to IR absorbance spectra. The obtained IR spectra were assigned to stress or strain corresponding to half-time of IR data aquisition.

Several measurements were carried out in stress relaxation mode. In these cases stretching was stopped at different strains and IR spectra (resolution 2 cm^{-1}, 200 scans) were collected after stress relaxed to definite level. The mechano-spectroscopic data are presented as the deformation difference spectra (DDS). They are the result of substraction the spectrum of undeformed film from the spectra measured at different strains. Coefficient of the substraction was determined from the condition of preservation of integral absorbance in the examined IR region. Spectral regions, which incorporate isolated bands, were prefereably used. Such approach excludes the consideration of intensity changes. The shifts down to 0.01 cm^{-1} can be determined from the FTIR difference spectra$^{6)}$. Lorentz band shape was used in the calculation of frequency shifts$^{7)}$.

The details of IR measurements of aPS film on heating and under high pressure (20 kbar) are indicated elsewhere$^{8,9)}$. In some experiments annealed aPS film and film of iPS were used. Annealing of aPS at 140C during 3 hr was followed by slow cooling (10 hr) to room temperature. Film of iPS (Polysciences Inc.) was casted from the boiling solution (1% wt.) in decalin. The known assignment of the IR spectra of polymers$^{10,11)}$ was used.

RESULTS

The stress-strain curve of the aPS film (Fig.1) is characterized by the yield point near 4% strain followed by necking region. The mechano-spectroscopic behaviour of the 1602 cm^{-1}, 906 cm^{-1} and 539 cm^{-1} bands is presented in Fig.2A-2C and Fig.3A-3B. These data include the DDS, the strain dependences of the low frequency shift (1602 cm^{-1} and 906 cm^{-1} bands) and the differential spectral effect (539 cm^{-1} band). The low frequency shift of 1602 cm^{-1} band (C-C stretching symmetric vibration of monosubstituted benzyl ring) increases up to the yielding point. The symmetrical shape of the DDS indicates that this band shifts without shape variation. The band shift decreases in the strain region 5%-15%. However, the effects become complex because the IR information is collected from an area consisting from necked and pre-necked material. The high frequency shift of 1602 cm^{-1} band in the necked film was detected. It was also registrated after the stress release.

Different deformation behaviour was found for the 906 cm^{-1} band and for bands in the region 560 cm^{-1} - 530 cm^{-1}. The in-plane and out-of-plane deformation vibrations of benzyl ring mixed with backbone modes are situated between 1410 cm^{-1} and 810 cm^{-1}. The pure backbone vibrations are weak in IR spectrum, and the mixed modes are used to analyse the behaviour of polymer chain. The standing alone 906 cm^{-1} band is suitable for the band shift analysis. The low frequency shift of the 906 cm^{-1} band appearing at

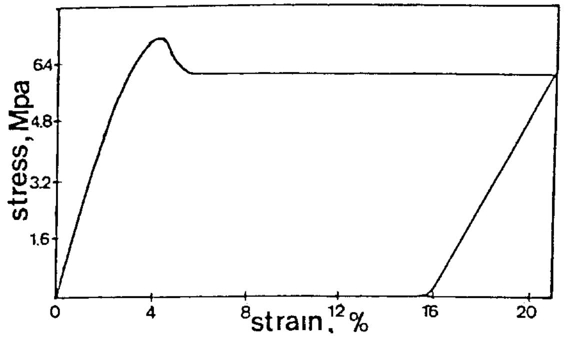
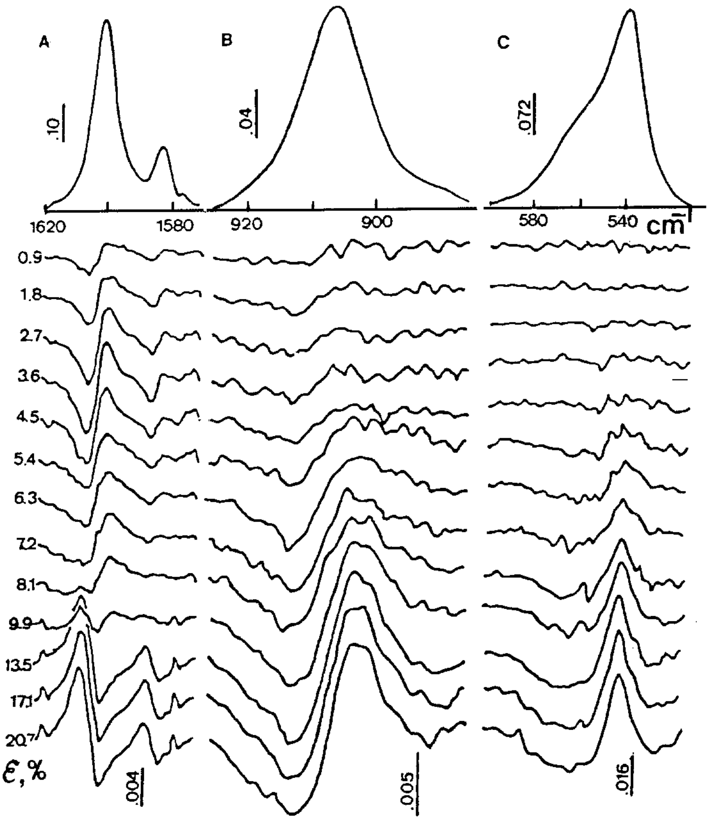
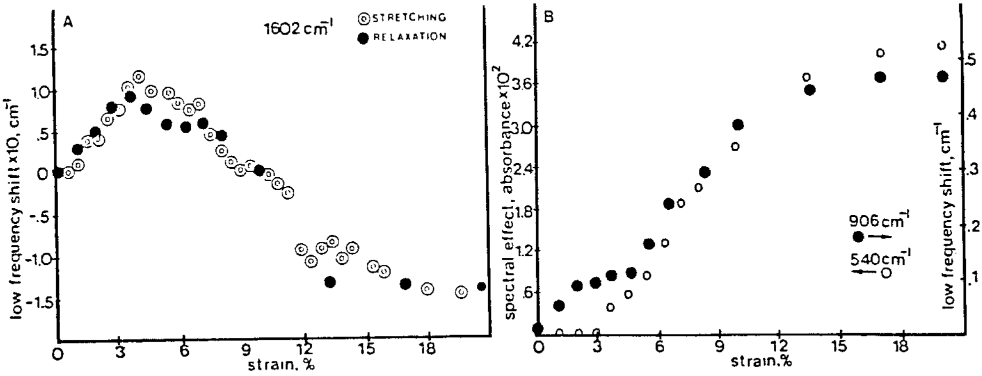


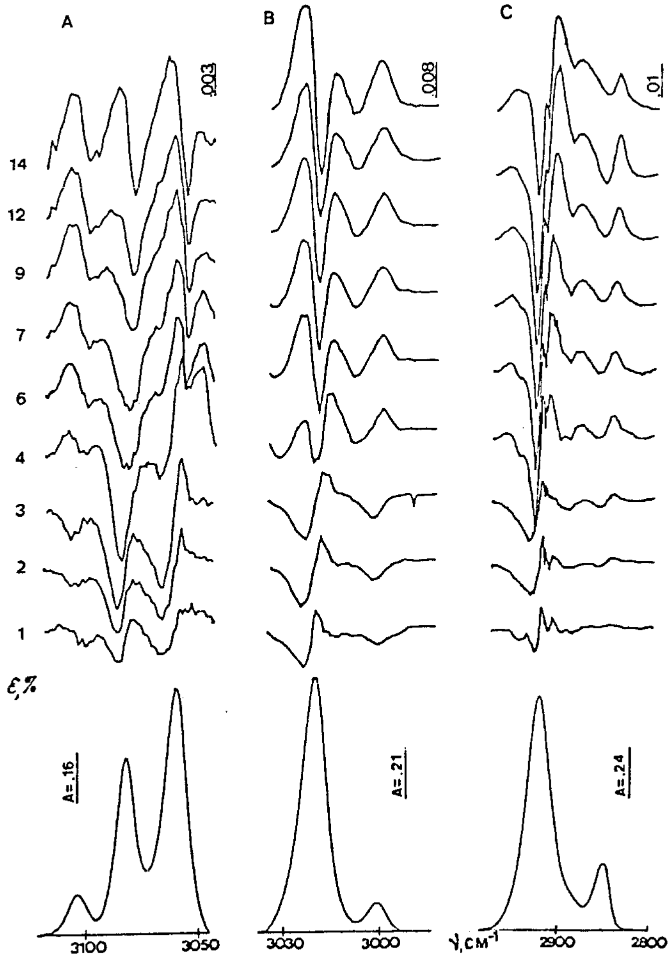
Figure 1.Stress-strain curve of aPS film (thickness 20μm) at ambient conditions. Uniaxial stretching was carried out with the rate 0.01 min^{-1}.



Figures 2A-2C. The FTIR spectra of aPS film (upper) and deformation difference spectra at different strains, ε(%), (below) in three spectral regions (A, B, C).



Figures 3A-3B. The strain dependences of low frequency shifts of the 1602 cm^{-1} and 906 cm^{-1} bands (A) and of the differential spectral effect near 540 cm^{-1} (B).



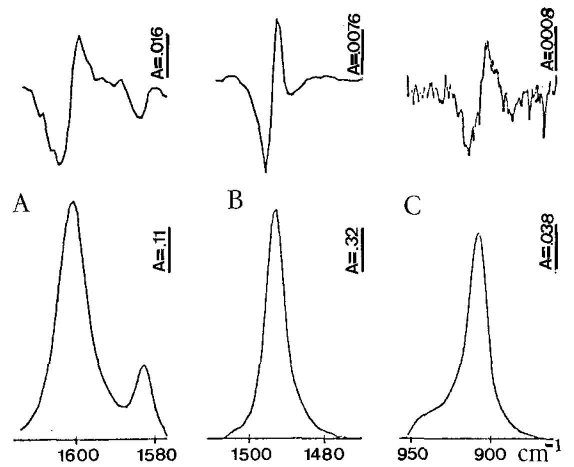
Figures 4A-4C. The FTIR spectra of aPS film (lower part) and deformation difference spectra at different strains, ℰ(%), (upper part) in three spectral regions (A, B, C).

small deformations (1%-3%) sharply increases at the strains higher than 6% and saturates in the neck. The conformational sensitive bands - 556 cm^{-1} (gauche) and 539 cm^{-1} (trans) assigned to out-of-plane deformation vibrations of benzyl ring lie in the spectral region 560 cm^{-1} - 530 cm^{-1}. They are sensitive to conformational order of the chain segments consisting of 4 and more monomer units[12)]. The temperature difference spectra of aPS in this region (see below Fig.5B) are very similiar to the DDS presented in Fig.2C. These spectra can be explained as the superposition of the low frequency shift effects of two conformational bands[9)]. However, we will use the differential spectral effect (the distance between negative and positive peaks) to describe these spectral changes. This effect originates near the yield point, increases at 5%-15% strains and then saturates. Thus, the low frequency shift of conformational sensitive bands is observed in necked material. It becomes smaller after unloading.

The DDS of other bands will be useful in the discussion of the molecular changes during stretching. It was found that the C-C stretching modes of benzyl ring (1584 cm^{-1}, 1493 cm^{-1} and 1453 cm^{-1}) behave similiar to the 1602 cm^{-1} band. The DDS in the region of the C-H stretching vibrations are shown in Fig.4A-4C. The C-H bands of benzyl ring (3100 cm^{-1}- 2950 cm^{-1}) show the same tendency as the C-C stretching modes. They shifted to lower frequencies in the prenecked material and to higher ones in the necked polymer. The low frequency shift in the prenecked material at small deformations (up to 5%) is observed for the 2845 cm^{-1} band (C-H stretching mode of CH_2 group). However, the DDS at higher deformations are difficult to interprete due to the interference of the intensive 2922 cm^{-1} band. The DDS obtained in the stress relaxation experiments show not much differences with those registrated during stretching (Fig.2A-2C). The shifts near the yield point are smaller which can be explained by lower stress (at identical strains) in the relaxation experiments. The general character of mechano-spectroscopic results was also proved in experiments with temperature annealed aPS film and film of iPS. However, these films are brittle and the results (Fig.5A-5C) reflect the changes occuring only in the elastic and inelastic regions (up to 5% deformation). The DDS show low frequency shifts of 1602 cm^{-1}, 1492 cm^{-1} and 906 cm^{-1} bands. The maximal shift of the 1602 cm^{-1} band in the annealed film was observed near 4% deformation prior to fracture.

The small spectroscopic changes in stretched films are difficult to analyze. The frequency shifts in polymer film occuring on heating and under high pressure can be useful for the understanding the presented results. The temperature difference spectra of aPS (Fig.6A-6B) show that the bands shift to lower frequencies on heating. However, the temperature coefficients of shifts (Fig.7) are different for various modes. The presented results were obtained with the aPS film used in the previous experiments[9)]. The temperature dependences of the 3027 cm^{-1}, 1493 cm^{-1}, 1602 cm^{-1} and 1027 cm^{-1} bands shifts show no changes when the film is heated through the glass transition region. The lower frequency bands, 906 cm^{-1} and 845 cm^{-1}, in rubbery state exhibit higher temperature coefficients of frequency shifts. This effect is pronounced for the 556 cm^{-1} and 539 cm^{-1} bands which are sensitive to segmental order. Their behaviour in the glass transition region is dependent on the thermal history[9)].

Tendency of IR bands to shift to lower frequencies due to stretching and heating is identical, however there are some differences. The values of shifts of the 1602 cm^{-1}, 906



Figures 5A-5C. The FTIR spectra of iPS film (lower) and the difference spectra at strain before brittle fracture (upper) in different regions (A, B, C).

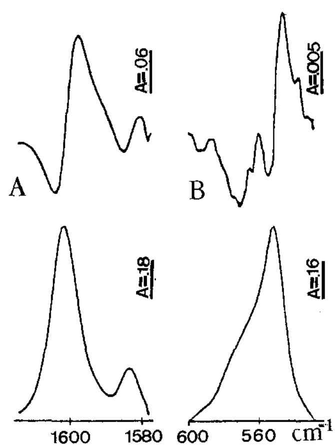


Figure 6 The 1602 cm^{-1}(A) and 540 cm^{-1} (B) bands of aPS at T=25C (lower) and difference spectra at T=85C and T=25C (upper).

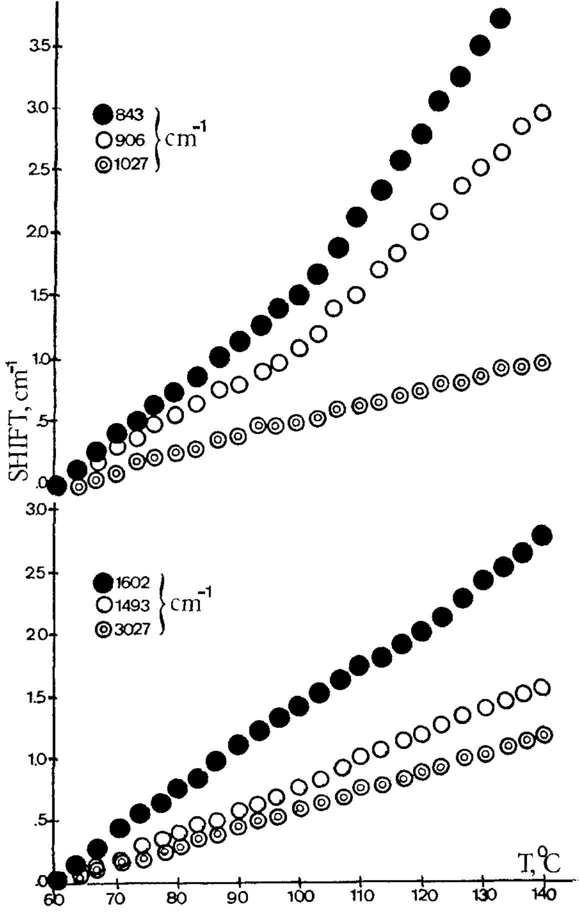
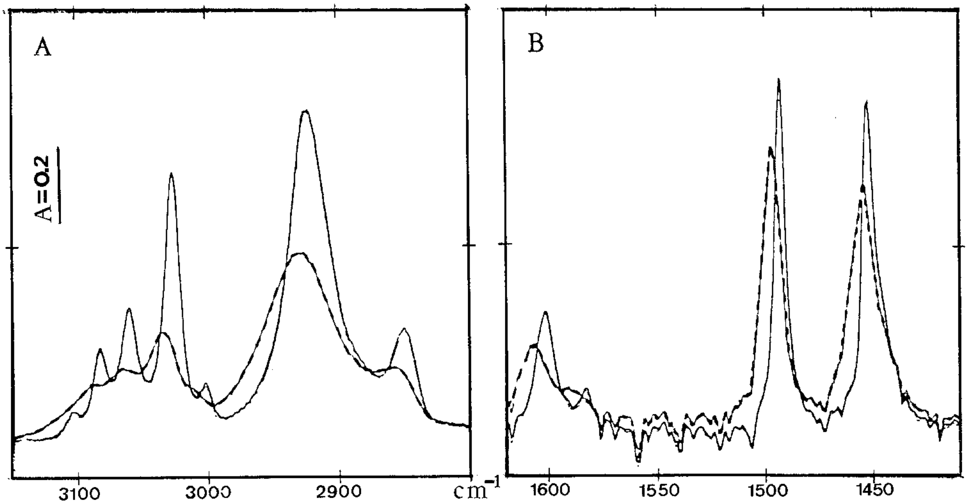


Figure 7. Temperature dependences of low frequency shifts for different spectral bands in the FTIR spectra of aPS film.

cm^{-1} and 539 cm^{-1} bands observed at 5% strain, for example, were found at various temperatures. The temperature and stretching effects are different for the 2845 cm^{-1} band (C-H stretching mode of CH_2). The C-H stretching bands of methylene group do not shift on heating. However, DDS show the low frequency shift of the 2845 cm^{-1}.

The IR bands in the region 3200 cm^{-1} - 600 cm^{-1} exhibit high frequency shifts when high hydrostatic pressure was applied to aPS film[13)]. The magnitudes of the shifts were dependent on the band nature and pressure value. The general correlation between high frequency shift and the density increase was discussed. Similiar pressure effects we have observed in the high pressure experiments with our film. In Fig.7A-7B the spectral differences induced by high pressure are presented in the two regions. All the bands become broader and shift to high frequencies under high pressure.



Figures 8A-8B. The FTIR spectra of aPS film at ambient conditions (full lines) and under high hydrostatic pressure, 20 kbar, (dotted lines) in the two spectral regions (A, B).

DISCUSSION

The perturbations of polymer structure induced by different physical causes (temperature changes, high pressure, stretching) are accompanied by shifts of IR bands. It is reasonable to assume that these changes reflect first of all intermolecular effects and can be generally correlated with density variations. The changes of distances between neighbouring atoms lead to changes in the anharmonic interatomic potentials. As a consequence, the frequencies of vibrational bands will change. The theoretical description of band shift phenomenon is under the way. It can be predicted, however, that the main differences in spectral responses to stretching and high pressure are due to different contributions of shear and hydrostatic components. The correlation between high pressure induced shifts and density changes[13)] shows that the volume changes play an important role in the origin of these spectral effects. The situation is more complex during temperature changes when the kinetic energy effects should be considered also. Some details of mechanical and temperature influences on polymer structure can be discussed on the basis of the behaviour of different vibrational modes. The internal modes are sensitive to local volume changes in the close vicinity of a specific group, while the conformational sensitive bands are influenced by larger scale volume effects. The study of the temperature and pressure effects on Raman bands of liquid toluene14) shows that the symmetric vibrations of benzene ring (6b-mode) appeared to be more sensitive to these parameters than assymetric ones (6a-mode). The possible reason is the different local volume required for two types of vibrations. It was shown that the volume changes for the toluene 6a and 6b modes are .01% and .67% correspondingly15).

Some of presented comments were used for the tentative explanation of mechanospectroscopic data of aPS film. In the elastic and inelastic regions of deformation the low frequency shift observed for different C-C and C-H modes of benzene ring reflects density decrease. The most sensitive 1602 cm^{-1} band represents symmetric C-C mode. The rearrangement of benzyl groups of aPS during stetching is not unexpected. The fluorescence data of eximer formation in films of aPS16) indicate that benzene rings in this polymer are situated close to each other. The changes of conformational sensitive bands were not observed up to the yielding point. The structural rearrangement detected by these bands, perhaps, needs more additional volume which can be accumulated during stretching in elastic region. No residual spectral changes have been detected after unloading the polymer film stretched to the yield point. However, the existence of small structural changes can not be excluded even at these deformations. Such changes, perhaps, take place during fatigue experiments17).

The neck formation is followed by more substantional structure changes than the above-mentioned ones. This process is accompanied by molecular orientation and conformational changes. The high frequency shift of benzene modes reflects the increase of density in the necked part. This conclusion is in the accordance with the comparative density measurements of original film and necked material. The differential spectral effect of conformational sensitive bands in the necked aPS indicate their low frequency shift. This behaviour, perhaps, reflects the new structural environment of molecular segments induced by the conformational changes.

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