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Rheo-optical FT-IR spectroscopy of Solid Poly(acrylic acid) films

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SUMMARY: This paper describes experimental work where the mechanical behaviour of relatively dry, solid poly(acrylic acid) films at room temperature was correlated with changes in hydrogen-bonding in the polymer. Hydrogen-bonding between the carbonyl and the hydroxyl groups was followed by FT-IR spectroscopy while the films were stretched uniaxially. Limited mobility of the polymer below its T_g led to small but detectable changes in bonding. A characteristic strain-hardening behaviour was observed if no bound water was detected in the samples.

Introduction

Poly(acrylic acid) [PAA] is a polymer used in a number of applications, e.g., to stabilise colloidal suspensions, in coatings and as a thickening agent in latices. The carboxylic group in PAA is known to take part in intra- as well as inter-molecular hydrogen bonding in the polymer. Most of the work carried out on PAA has been concerned with its properties in solution.

Recently, Dong *et al* have suggested three different forms of carbonyl groups in PAA1). In addition to the free form and the cyclic dimeric hydrogen-bonded carbonyl group, they also provided spectroscopic evidence (Infrared, Raman, Near-Infrared spectroscopy) for the existence of linear, "oligomeric" COOH groups resulting from hydrogen-bonding between C=O and OH groups. See Fig. 1 for a schematic depiction. The broad carbonyl band at ~ 1700 cm^{-1} corresponding in the C=O stretching vibration was resolved into four Gaussian peaks corresponding to the free form (monomer) (~1742 cm^{-1}), the oligomeric end group (~1727 cm^{-1}), the cyclic dimeric form (~1705 cm^{-1}, asymmetric stretching) and the internal oligomeric form (~1690 cm^{-1}). These assignments were based on other publications, on other assignments in the IR spectrum as well as their Raman and Near –Infrared Spectroscopy results1). However, there is one other issue: water. One cannot over-emphasise the influence of water.

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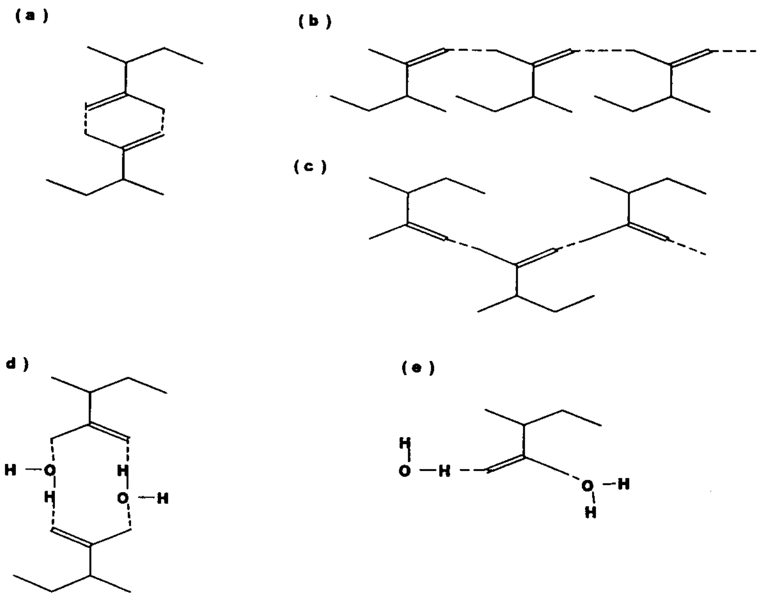

Fig.1. Schematic depiction of the various possible forms of hydrogen-bonding in PAA 1,2). (a) Cyclic dimeric form (b) Sideways oligomeric form (c) Face-on oligomeric form (d) Strongly bound water (e) Weakly bound water.

No mention at all was made of the H-O-H bending vibrations which also show up in the same region: ~1634 cm^{-1} in the case of unbound water and ~1672 cm^{-1} in the case of "non-freezing" or strongly bound water2). Possible structures arising from such interactions are shown in Fig. 1(d) and 1(e). Under the conditions employed by Dong et al1), and us, in order to dry the films, i.e. at relatively low temperatures to avoid anhydride formation, there is undoubtedly a small quantity of strongly bound water present in the polymer3). This factor affects, both, the interpretation of the spectra as well as the mechanical behaviour of the films.

Another band that would supply information on the hydrogen bonding would be the broad hydroxyl band in the region of ~3000 cm^{-1} corresponding to the O-H stretching vibrations. The overlap of this band with a number of other bands complicates the analysis of that region. Hence, analysis was restricted to the C=O stretching band.

The purpose of this work was to study the changes in intermolecular and intramolecular hydrogen-bonding in solid PAA induced by tensile stresses in the polymer. Solid PAA films were stretched uniaxially and simultaneous measurements of mechanical behaviour and Fourier Transform Infrared spectroscopic (FT-IR) changes in the polymer were recorded at room temperature. This technique has been applied to a number of systems$^{4)}$.

Experimental

Atactic poly(acrylic acid) [PAA] of molecular mass 450,000 g/mol was purchased from Aldrich Chemical Co., and used without further purification. Films were prepared by using a doctor blade and an ethanol solution of the polymer (2 wt%). Films (thickness ~ 3 - 5 μm) were cast on a clean polyethylene foil stretched across a smooth glass plate, which facilitated removal of the film. After drying in air, the films were stored under vacuum prior to measurements. The films were flushed with dry nitrogen overnight (in the spectrometer) prior to measurements. FT-IR spectra were recorded on a Bruker Equinox 55 FT-IR spectrometer with the help of a liquid nitrogen cooled MCT detector. 128 scans were averaged at a resolution of 4 cm^{-1}. The Happ-Genzel apodization function was used in the Fourier Transformation process.

Tensile measurements were carried out on a specially fabricated tensile tester that was mounted into the spectrometer. A calibrated Kulite load cell (BG 500G) was used to record the tensile forces acting on the film during measurements; the values were processed from the output of the load cell with a Labview program. The film was attached to the two halves of the tensile tester by gluing it with the help of cyanoacrylate adhesive and aligned carefully to avoid irregular straining of the sample. Deformation was induced with the help of the micrometer screw gauge and a stepping motor (rate 1 μm/sec). The gauge length of the films ranged between 5 and 10 mm. and the width of the films was 4 mm. Both, continuous as well as intermittent measurements of stress and IR spectra were carried out.

Results and Discussion

First of all, a note on reproducibility: the detected changes in the carbonyl region were rather small were rather small (less than 1%) due to the deformation being carried out in the glassy state. In the glassy state, the mobility will come predominantly from local movements in the chains. The changes in bonded or free species taking place will depend on the initial conformation of the molecules relative to the stretching direction. Under these conditions, it may be difficult to generalise the changes taking place. Besides, the amount of strongly or weakly bound water is crucial to the mechanical behaviour of the film as well as the interpretation of the spectra.

Weakly bound water (present when the highly hygroscopic polymer was not dried thoroughly) acts as a plasticiser, in that it induces plastic deformation in the polymer. We found that the polymer then displays a linear elastic region and a yield stress followed by a region of plastic deformation and necking (not shown). In this case, strain at yield is between 2 – 4%, whereas strain at break is about 10%. The elastic modulus is also lower (~1 GPa) on virtue of the fact that the weakly bound water weakens the intermolecular interactions. Besides, weakly bound water is continuously being liberated during the course of stretching under the nitrogen atmosphere in the spectrometer, which makes it difficult to separate changes induced by drying with those caused by stretching.

If only strongly bound water is present in the sample (when the concentration of water is low), brittle behaviour was observed. Deformations are then restricted to values in the region of only a few % (1 – 2%). Strongly bound water is usually intercalated between the hydrogen-bonded structures and acts as an effective crosslinker, responsible for increasing the modulus (~ 4 - 5 GPa). This behaviour matches the measurements of the relaxation behaviour of PAA reported in the literature – the sorption of water leads to a lowering of T_g and a secondary dispersion near –80°C, which is absent in the dry state6).

Fig. 2 shows typical transient force-displacement curves of a test carried out in the spectrometer. An interesting aspect of this measurement is that a small degree of strain hardening can be observed in the films throughout the course of the experiment. This behaviour This behaviour is not an artefact, since other materials with known properties were tested on the same apparatus and did not show this behaviour. One of the reasons for this could be stress-induced self-association, evidence for which we will give in due course. Stress-induced crystallisation can be ruled out on account of the atacticity of the polymer and the small extensions responsible for the phenomenon.

In most of the cases, we found that on stretching, the small but distinct mobility in the polymer led to the generation of more strongly-bound, cyclic dimeric species at the cost of more weakly bound oligomeric species. We propose that this could be an indication of the inducement of alignment in certain portions of the chains, which is needed for the formation of dimers. Since the changes detected by our initial experiments. are small, we do not as yet have clear evidence for this intuitive argument, i.e., the correlation between chain alignment and the generation of cyclic dimers. For this we will have to resort to another approach, e.g. the inducement of orientation with strong shear forces during processing and correlating this orientation (detected through a technique like birefringence or polarised FT-IR or Raman spectroscopy) to the formation of cyclic dimers detected by FT-IR in the same sample.

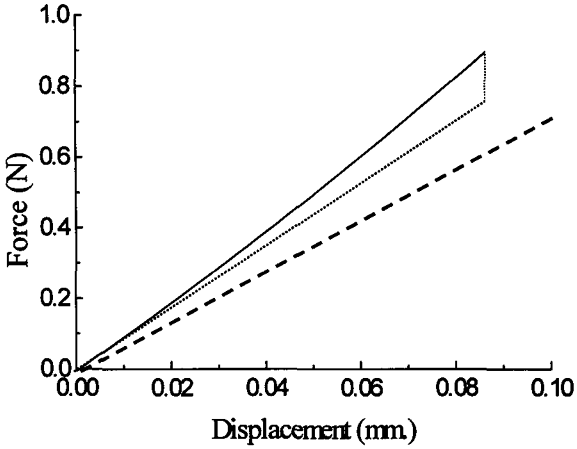

Fig.2. Typical force-displacement curve of solid PAA films: relatively dry (——), relatively wet (-----). The dotted lines (...) are shown to demonstrate the strain-hardening behaviour prior to failure in the dry films. The curve can be modelled by a quadratic equation ($y = 9.3 + 12.75\,x^2$).

Fig. 3 is an FT-IR spectrum of solid PAA with the relevant assignments. In order to detect changes in H-bonding induced by stretching, we used difference spectra in the carbonyl region and a knowledge of the assignments of the various forms of the carbonyl group, and that of the H-O-H bending vibrations in the same region. The spectrum of the final stage (prior to failure) was subtracted from the initial stage. This resulted in the characteristic W-shaped curve shown in Fig. 4, provided that the difference spectra did not give changes in the amount of bound water (~1672 or 1634 cm^{-1}) on stretching. If this was the case, the resulting spectrum was too complex for interpretation. The W-shape indicates an increase of the dimeric species (~ 1710 cm^{-1}) at the cost of the oligomeric species (~1690

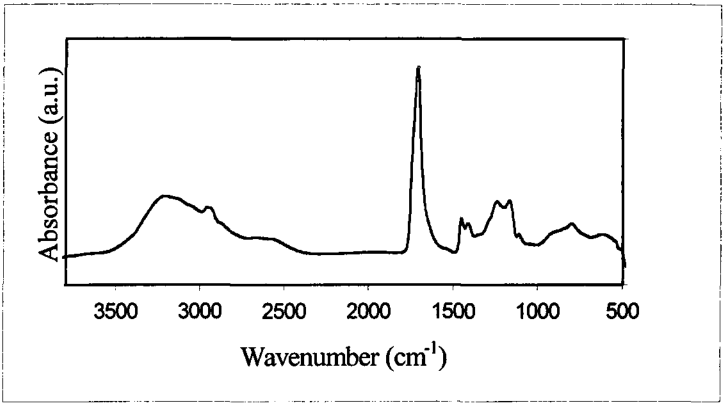

Fig.3. FT-IR spectrum of solid PAA. The following is a list of relevant assignments[1] (wavenumbers in cm^{-1}): 3100 (broad O-H stretching band), 2900 (CH_2 or CH stretching), 2700-2500 (overtones of bands near 1413 and 1248 enhanced by Fermi resonance by the band at 3100, 1700 (C=O stretching and H-O-H bending), 1450 (CH_2 deformation), 1415, 1242 and 1170, (C-O stretching coupled with O-H in-plane bending), 1112 (C-CH_2 stretching), 902 (broad O-H out of plane bending band of the dimeric species), 800 (CH_2 twisting and C-COOH stretching).

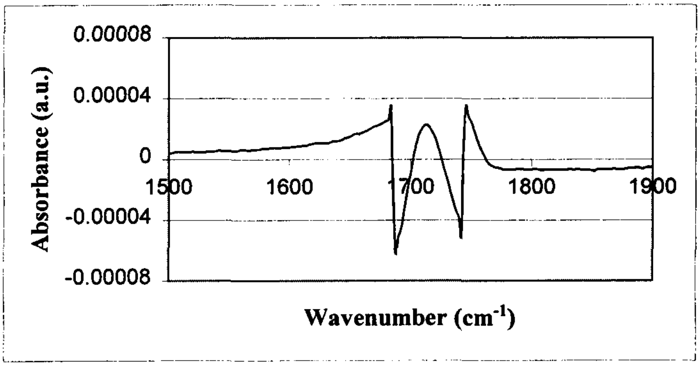

Fig.4. Difference spectrum between the final and initial stages of stretching of a PAA film (the 1700 cm^{-1} region) shwoing the characteristic W-shaped curve.

cm^{-1} and free species (~1747 cm^{-1}). In order to be more quantitative about the changes taking place, it is essential to estimate the absorption coefficients of the various species, by no means a trivial matter. We attempted to monitor the changes with curve-fitting, but the changes were generally too small to provide a definite trend on which we could base our calculations. In such a case, any attempts at quantifying the changes by numerical analysis would be prone to errors. However, where the changes are significantly larger than the errors of the curve-fitting procedure, it may be possible to quantify the changes by using the Beer – Lambert law.

Concluding Remarks

We have shown that on stretching PAA films at room temperature, small changes in hydrogen-bonding can be detected. Before drawing conclusions, one needs to be sure about the influence of weakly or strongly bound water. Although at this stage it is difficult to generalise the changes induced by stretching, it seems that molecular rigidity is gradually increased in the polymer due to an increase in the concentration of the cyclic dimeric species. This is reflected in a gradual strain-hardening effect in the force-displacement curve. Other interesting aspects of these changes would be rate effects and reversibility, which need to be looked into.

Acknowledgements

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