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An investigation of glass formation and physical ageing in poly(ethylene terephthalate) by FT-IR spectroscopy

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Abstract

FT-IR spectroscopy has been used to follow changes in chain conformation of poly(ethylene terephthalate) (PET) which occur during glass formation and physical ageing. It has been shown that there is an increase in the population of *gauche* ethylene glycol conformation at the expense of the *trans* on cooling the liquid and on physical ageing. This is contrary to a previous interpretation and it is implied that the *trans* has the higher energy of the two conformations since it is considered to produce less well packing of the polymer chains. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: FT-IR spectroscopy; Poly(ethylene terephthalate); Conformation

1. Introduction

The transformation of a liquid to a glass is kinetic in nature, such that the glass is not in equilibrium but gradually relaxes to the liquid when it is kept at a temperature close to but beneath the glass transition temperature. As a result storage below the glass transition temperature results in a decrease in volume [1], enthalpy [2] and a change in physical and mechanical properties [3–5]. The rate at which this relaxation occurs is dependent on the temperature and the thermal history of the sample [6] and results in a reduction in the free volume of the glass [7].

Differential scanning calorimetry (DSC) has been widely used to follow the kinetics of physical ageing from which it has been concluded that physical ageing is an extension of the glass forming process to lower temperatures and slower rates. It is the purpose of the present work to investigate whether glass forming and physical ageing processes can be detected by using FT-IR spectroscopy and whether they involve the same changes in molecular conformation.

2. Experimental

Thin films of poly(ethylene terephthalate) (PET) (6 μm thick) were supplied by Goodfellows Ltd, Cambridge. The films were oriented and before being used, the orientation was removed by heating to 280°C in a hydraulic press under load. The films were quenched in ice/water to keep them amorphous and dried in vacuum.

IR spectra were recorded on a Nicolet Magna-IR 760 ESP spectrometer. Each spectrum was made from an average of 100 scans at a resolution of 1 cm^{-1}. The films were analysed in the spectrometer mounted vertically in the furnace of a hot-stage of a microscope, supplied by Linkam Ltd, model TH600, with a temperature programmer, model PR600. The aperture of the furnace was aligned to produce a maximum signal in the IR detector. Samples were loaded into the furnace without altering its position by the use of a spring-loaded sample holder.

3. Results and discussion

The vibrational spectrum of PET has been well characterised [9] and several absorption bands change progressively with crystallinity. In a previous study [10] it has been shown that the intensities of two absorption bands at 898 and 973 cm^{-1} change with temperature in line with the glass transition and also with the development of physical ageing. These particular absorption bands correspond to the "wagging" of the oxy-ethylene group and to their *gauche* and *trans* conformations, respectively. The conclusions drawn, based on transmission rather than absorbance, were incorrect and g*auche* conformation increases on cooling and on ageing.

The IR spectrum of a quenched sample of PET at 45°C is

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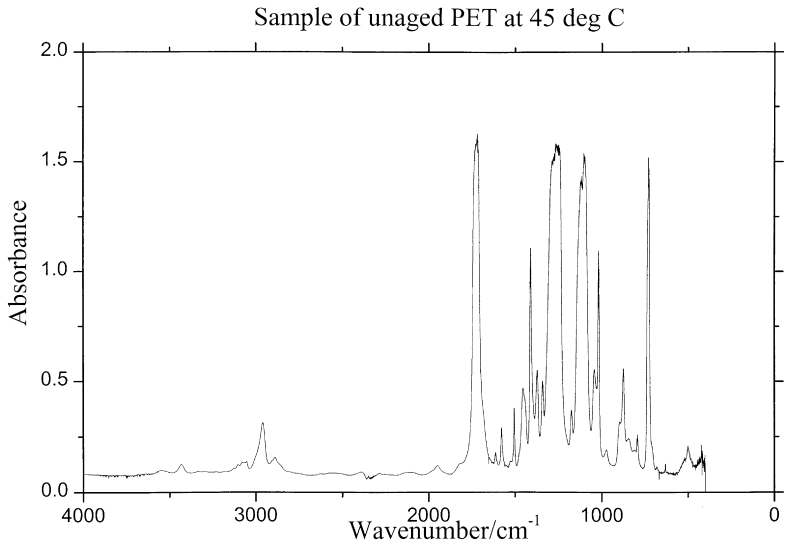

Fig. 1. The IR spectrum of PET at 45°C.

shown in Fig. 1. Absorption bands at 1340 and 1370 cm^{-1}, corresponding to the wagging of the ethylene units in *trans* and *gauche* conformations [8] are present. These absorption bands exhibited a greater change in intensities on crystallisation (see Fig. 2) and with temperature than those at 973 and 898 cm^{-1}. The large change in absorbance of the 1340 cm^{-1} band on crystallisation also confirmed the assignment to the *trans* isomer. These bands were used to follow the changes in molecular structure on ageing.

The PET film was then cooled from 95 to 45°C, and a spectrum taken at 5°C intervals. The change in absorbance of both bands corresponding with the relative concentrations of *trans* and *gauche* isomers with temperature can be seen in Fig. 3a and b. The amount of *trans* conformation decreased with decreasing temperature, and the *gauche* increased. There was a sharp change in the temperature dependence of the *trans* absorbance at about 70°C that corresponded closely to the onset of the glass transition [11].

If the temperature dependence of the equilibrium liquid line is extrapolated to below the glass transition temperature, an estimate of the equilibrium absorbance for the *trans* conformation can be made. A film sample was aged at 55°C for 72 h, and its IR spectrum measured at 55°C. The measured change in absorbance closely matched that found by extrapolation. To normalise the spectra obtained, eliminate sample thickness effects and compare results directly between samples the ratio of the intensities of the

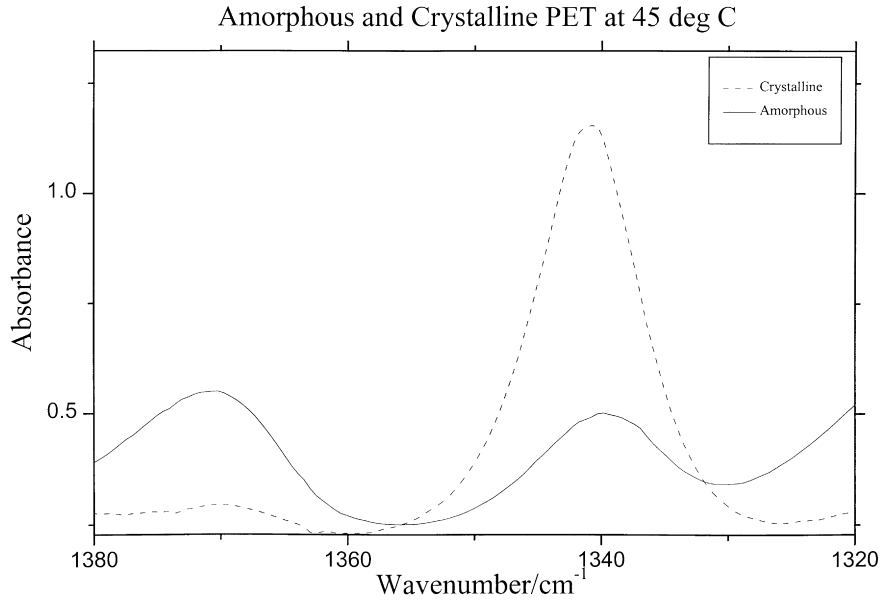

Fig. 2. The change in absorbance of the 1340 and 1370 cm^{-1} bands in quenched and crystalline PET.

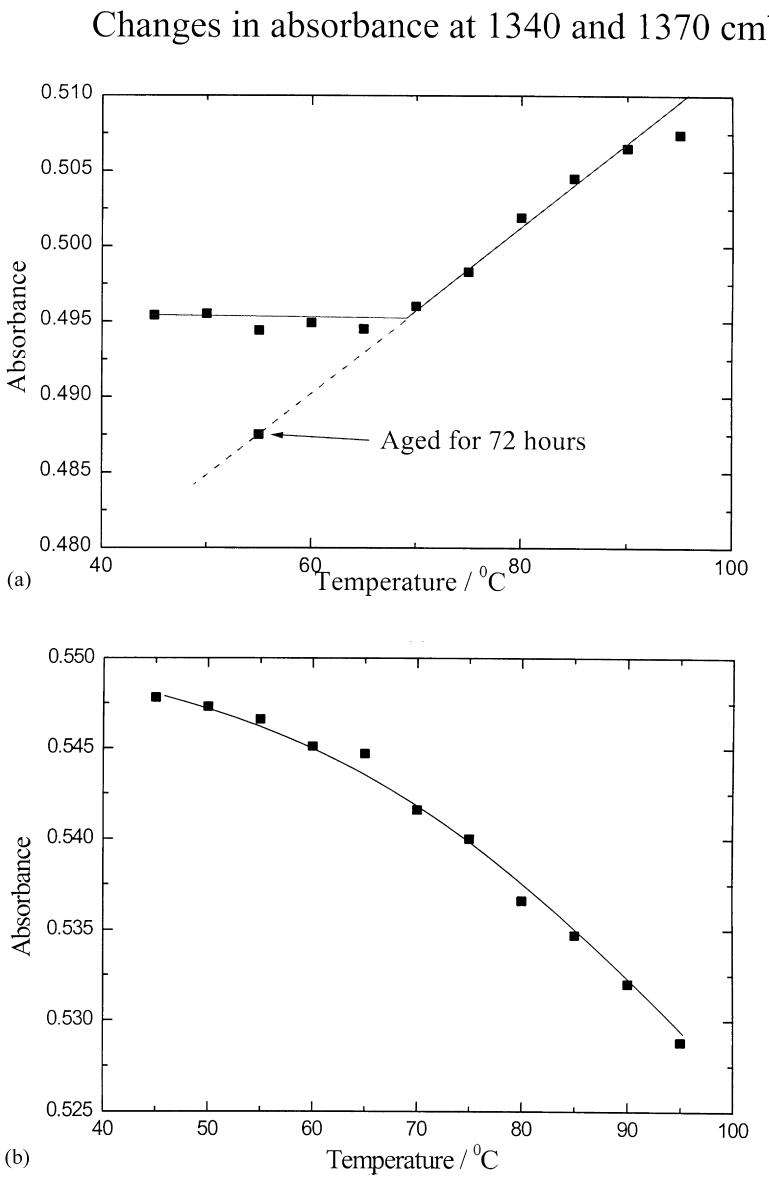

Fig. 3. Change in absorbance of the (a) 1340 and (b) 1370 cm^{-1} bands with temperature.

trans and *gauche* configuration bands was used. This is shown in Fig. 4.

An attempt was made to follow the extent of physical ageing with time from this ratio but the changes observed were too small for accurate measurement and any changes in the background spectrum masked the trend.

Schmidt [12] has studied the effect of orientation on the IR spectrum of PET and found that both the *trans* and the *gauche* forms in the amorphous phase of the material changed with degree of orientation. Physical ageing, as can be seen above, also resulted in a decrease in the amount of *trans* conformation. In rotational isomerisation, the *trans* form is normally taken to be the lower energy conformation, and should lead to the amount of *trans* increasing with decreasing temperature, the reverse appears to be the case in PET. However, as a glass physically ages there is a decrease in enthalpy of the material, which can be considered as being composed of both inter- and intramolecular contributions. Other changes along the polymer chain (i.e. the movement of other chain substituents e.g. the phenyl ring) resulting from the *trans–gauche* equilibrium will have a role in determining which of the two conformations is the most favourable. In the *gauche* form, easier packing of the polymer chain can be achieved and this is the driving force that makes the *trans* form the higher energy of the two conformations in this instance. The quenched glass contains a non-equilibrium concentration of *trans* groups because when the polymer was cooled from the liquid phase, there was a departure from the equilibrium ratio of *trans* to *gauche* which resulted in the population being “locked”. Physical ageing is a relaxation of this population towards

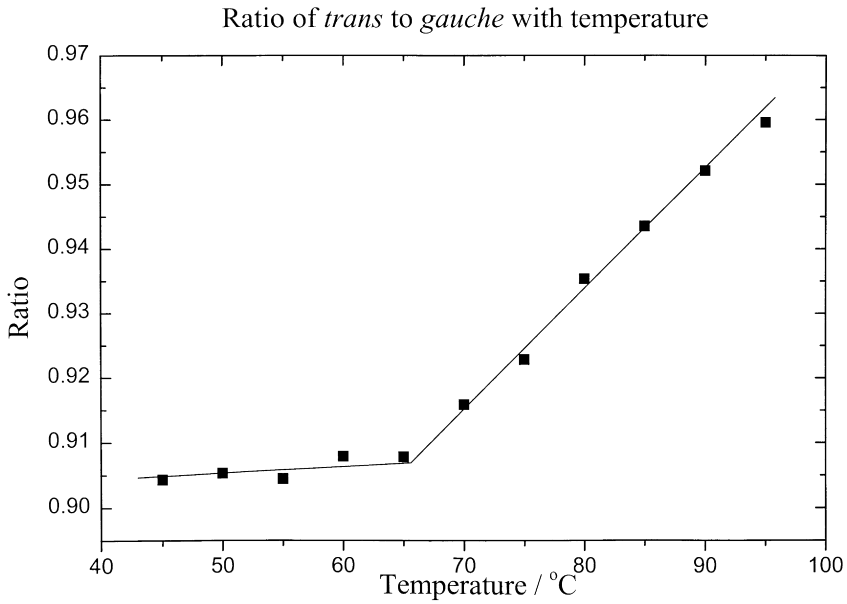

Fig. 4. Changes in ratio of the *trans* to *gauche* conformations with temperature.

equilibrium at the ageing temperature, which results in the number of *trans* species decreasing.

From statistical thermodynamics, the ratio of the *trans* to *gauche* is governed by the free energy difference, ΔG, between the two conformational isomers, shown by the following equation:

$$\frac{n_t}{n_g} \propto \exp\frac{-\Delta G}{RT} \quad (1)$$

where n_t and n_g are the number of units in the *trans* and *gauche* conformations, respectively. It should be noted that n_g is the summation of the two *gauche* forms, and ΔG is the free energy difference between the *trans* and *gauche* forms. A plot of the log of the ratio of the two conformations against $1/T$, gave a value of 2.30 ± 0.25 kJ mol^{-1} for the liquid.

4. Conclusions

The ageing and glass forming processes in PET are detectable by IR spectroscopy. They involve those changes in the conformation of the chain that occurs on cooling the liquid. The only difference is the time scale over which these changes occur—in the liquid the molecular rearrangements are fast and equilibrium populations are achieved within the timescale of cooling the sample. In the glass, equilibrium is only reached slowly over extended time periods dependent on temperature. One structural alteration that occurs on cooling and also on ageing is the change from *trans* to *gauche* conformations of the ethylene units in PET. This is at variance with the results reported by Aref-Azar et al. [10].

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