

# polymer papers

## FT i.r. investigation of structural modification of polycarbonate during thermodynamical treatments

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The effect of annealing and ageing on i.r. absorption spectra of polycarbonate are investigated. Annealing is accompanied by conformational rearrangements, visible through changes in *trans-trans* and *trans-cis* populations, whereas ageing entails only extremely local rearrangements. The connection between these observations and the concept of structural temperature is discussed. © 1997 Elsevier Science Ltd.

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### INTRODUCTION

Physical properties of polymers in the glassy state are well known to be sensitive to their thermomechanical history. After quenching from above the glass transition temperature  $T_g$ , a decrease in the yield stress and yield drop are observed<sup>1,2</sup>, and sub- $T_g$  exothermal plateaux appear on d.s.c. scans<sup>3</sup>. A quenched sample displays excess mechanical loss in two temperature ranges: a shoulder appears on the low temperature side of the glass transition loss peak (termed  $\alpha'$  loss), and an excess loss appears in a range above the secondary ( $\beta$ ) transition but well below the glass transition ( $\alpha''$  loss, approximately at room temperature in polycarbonate)<sup>1,4</sup>. Plastic deformation, or rejuvenation, appears as an extreme form of quenching, producing similar but more intense effects<sup>5,6</sup>. Annealing in a range below but close to the glass transition temperature produces an increase in the yield stress and yield drop<sup>2,7</sup>, and enthalpy relaxation observable in d.s.c. as an endotherm at  $T_g$  after annealing quenched samples<sup>7</sup>, or a shift to increasing temperatures of the onset of the exothermal plateau in rejuvenated samples<sup>5</sup>; annealing also gradually erases the  $\alpha'$  shoulder<sup>8</sup>. Ageing, at temperatures well below  $T_g$  but above the  $\beta$  transition, does not affect the yield stress<sup>2</sup> but hinders anelastic deformation at low stresses and strains, and hence slows down creep<sup>9–12</sup>. Ageing also gradually erases the  $\alpha''$  excess mechanical loss<sup>4,13</sup>; similar effects are observed in thermally stimulated discharge currents<sup>14</sup>. Ageing does not, however, affect d.s.c. behaviour.

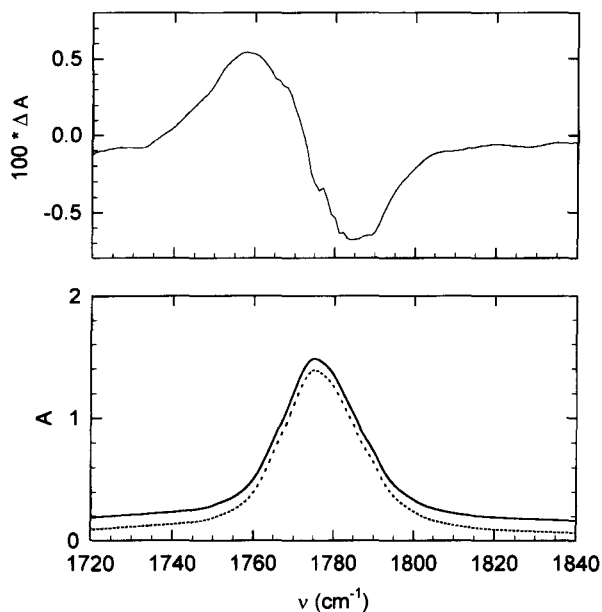
The formalism obtained from the concept of 'structural' or 'fictive' temperature has been shown to account quantitatively for the various effects produced by quenching, plastic deformation and annealing<sup>2,5,7,8,15,16</sup>. There are, however, some puzzling aspects in the concept of structural temperature, in particular the fact that the changes in structural temperature obtained from enthalpy and volume relaxation are different<sup>15</sup>. Ageing, on the other

hand, appears to occur at constant structural temperature, and is well described phenomenologically by assuming that some characteristic timescale increases with ageing time<sup>9–12</sup>.

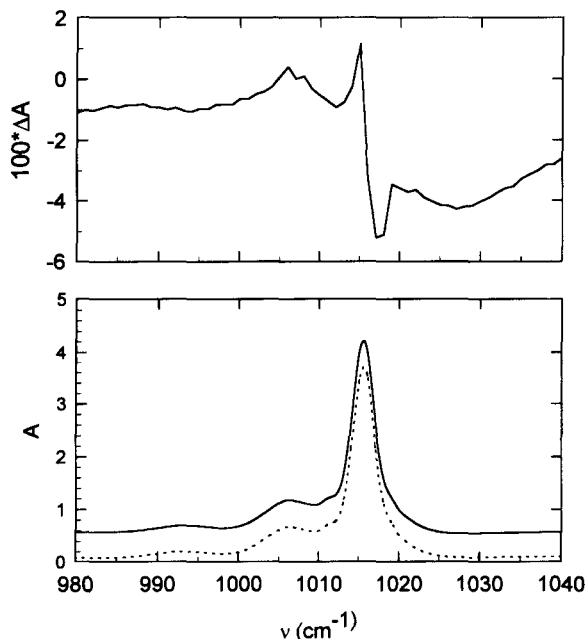
If changes in enthalpic content, or structural temperature, occur following plastic deformation or during annealing, it may be anticipated that some form of structural modification such as a change in population of *trans* or *gauche* sequences, should be apparent in the i.r. absorption spectrum of the polymer. Such modifications have been observed previously in various polymers at yield<sup>17,18</sup>. Changes occurring during ageing, on the other hand, would not be expected to affect these populations, since ageing does not affect the enthalpic content of the polymer. This work was therefore undertaken to investigate the effect of thermomechanical treatments on i.r. spectra of polycarbonate.

### EXPERIMENTAL

Thin films of bisphenol-A polycarbonate (PC) were obtained by casting a solution of PC in 1,2-dichloroethane onto a glass slide. Two concentrations were used: 3% (samples A) or 6% (samples B) by weight, yielding films of approximate thickness 10 (A) or 30 (B)  $\mu\text{m}$ . Samples A were heat treated at 165°C for 1 h and air-cooled, and subsequently annealed at 130°C or 140°C or aged at 30°C. Preliminary tests were carried out by annealing at the selected temperature, removing the sample from the environmental chamber and taking the i.r. spectrum at room temperature, then replacing the sample in the chamber for increasing lengths of time. It was found that this procedure led to wild scatter, probably attributable to indirect quenching effects, and subsequently a home-made environmental chamber was fitted in the sample compartment of a Perkin-Elmer 1725XFT i.r. spectrometer. During the thermal treatment, spectra were taken at regular intervals on a logarithmic time scale of factor 2, starting 5 min after



**Figure 1** Spectra obtained in  $1775\text{ cm}^{-1}$  region on a quenched film after annealing at  $130^\circ\text{C}$  for (a) 4460 min (full line); (b) 5 min (dotted line). Full line arbitrarily shifted. Top: difference  $a-b$



**Figure 2** Deconvoluted spectra in stress-sensitive region obtained on a cold rolled film after annealing at  $80^\circ\text{C}$  for (a) 9950 min (full line); (b) 10 min (dotted line). Full line arbitrarily shifted. Top: difference  $a-b$

introducing the sample into the chamber. Spectra were taken at  $4\text{ cm}^{-1}$  resolution, eight scans were accumulated for the first spectra and 32 scans were accumulated at annealing times longer than 2.5 h.

Samples B were deformed by cold rolling to obtain an increase in surface area of approximately 300%. This ratio was chosen in order to obtain sufficiently thin deformed films. The films were then annealed at  $80^\circ\text{C}$  and spectra were taken during annealing as for samples A.

Since PC absorbs strongly in the i.r., it was found that several interesting regions of the spectra tended to saturate, even in films of only  $10\text{ }\mu\text{m}$  thickness. Several

attempts were made to obtain attenuated total reflection (ATR) spectra; however these spectra are extremely sensitive to the pressure with which the sample is applied to the ATR accessory, and compulsory use of this accessory at room temperature meant that annealing treatments were necessarily interrupted; hence two sources of experimental scatter were accumulated and it was found that no useful information could be obtained from these spectra.

## INTERPRETATION OF I.R. SPECTRA

Five regions of the i.r. spectrum of PC are of interest in connection with structural modifications which might occur due to thermomechanical modifications. The bands having their peaks at approximately  $1775\text{ cm}^{-1}$ ,  $1235\text{ cm}^{-1}$  and  $1600\text{ cm}^{-1}$ , corresponding respectively to C=O stretching, C-O-C antisymmetric stretching and C-C aromatic in-plane stretching, have been identified by Schmidt *et al.*<sup>19</sup> as doublets, containing contributions from *trans-trans* (*t-t*) conformers at  $1767\text{ cm}^{-1}$ ,  $1252\text{ cm}^{-1}$  and  $1594\text{ cm}^{-1}$ , and from *trans-cis* (*t-c*) conformers at  $1785\text{ cm}^{-1}$ ,  $1223\text{ cm}^{-1}$  and  $1604\text{ cm}^{-1}$  respectively. (The terms *trans-trans* and *trans-cis* refer to the conformation of the carbonate group.) The frequencies of the C-C-C aromatic bending vibrations at  $1083\text{ cm}^{-1}$  and  $1015\text{ cm}^{-1}$  were found to be stress sensitive by Levy and Wool<sup>20</sup>. These regions of the spectra were therefore investigated systematically. No visible modifications were found in other spectral regions.

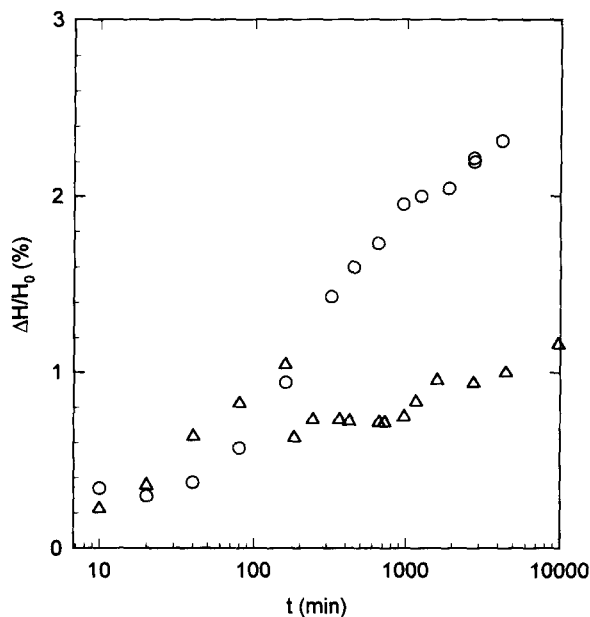
In films  $10\text{ }\mu\text{m}$  thick, the  $1600\text{ cm}^{-1}$  band is rather weak, and modifications, if any, are difficult to measure quantitatively. On the other hand, the  $1235\text{ cm}^{-1}$  band saturates in films of this thickness, so that modifications, if found, are not meaningful. Therefore only observations of conformational rearrangements obtained from the  $1775\text{ cm}^{-1}$  band are given below.

## RESULTS

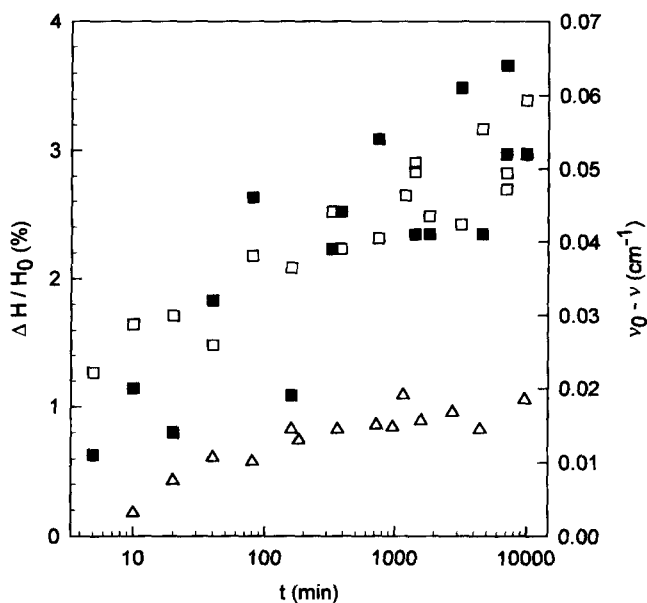
### Data analysis

The difference between the spectrum obtained after annealing time  $t_a$  and the reference spectrum obtained immediately after cooling from  $165^\circ\text{C}$  displays a characteristic shift from the  $1785\text{ cm}^{-1}$  to the  $1767\text{ cm}^{-1}$  component, indicating an increase in *t-t* population during annealing. A typical example is given on *Figure 1*. The modification is characterized by the normalized height of the difference peak  $\Delta H/H_0$ , where  $H_0$  is the initial height of the peak, obtained taking a linear baseline between  $1720$  and  $1840\text{ cm}^{-1}$ , and  $\Delta H$  is the difference between the maximum at  $1767\text{ cm}^{-1}$  and the minimum at  $1785\text{ cm}^{-1}$ . Changing the baseline limits does not significantly alter the results.

Modifications of the stress-sensitive peaks at  $1083$  and  $1015\text{ cm}^{-1}$  are difficult to detect on the raw spectra, therefore these spectral regions were self-deconvoluted taking a Lorentzian with  $\text{FWHM} = 7\text{ cm}^{-1}$  and Gaussian apodization with  $\sigma = 3\text{ cm}^{-1}$ . Difference spectra obtained from deconvoluted peaks display the zigzag shape characteristic of frequency shifting, shown in *Figure 2*. Results are plotted again as  $\Delta H/H_0$ . It was also attempted to determine frequency shifts directly by 9 point interpolation; however, this method is less sensitive to small shifts than the difference spectra. A



**Figure 3** Relative change of height of difference peak at  $1775\text{ cm}^{-1}$  in polycarbonate during annealing at  $130^\circ\text{C}$  (triangles) and  $140^\circ\text{C}$  (circles)

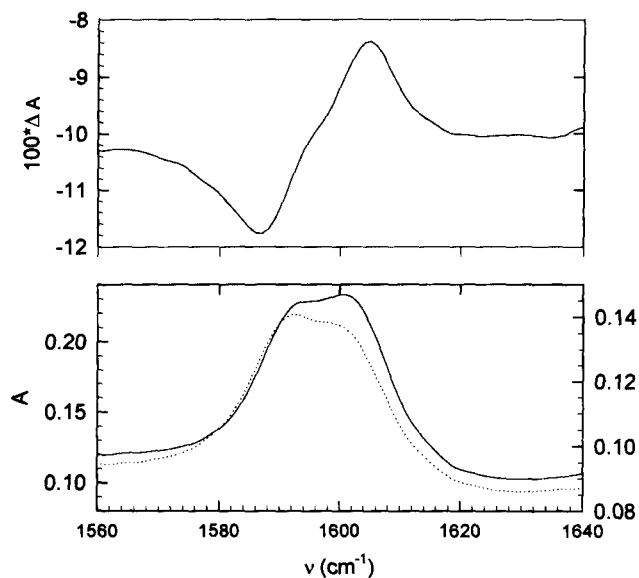


**Figure 4** Relative height of difference peak at  $1015\text{ cm}^{-1}$  in polycarbonate during annealing: open squares: cold rolled film annealed at  $80^\circ\text{C}$ ; open triangles: quenched film annealed at  $130^\circ\text{C}$ . Frequency shift measured by 9-point interpolation while annealing cold rolled film at  $80^\circ\text{C}$ : filled squares

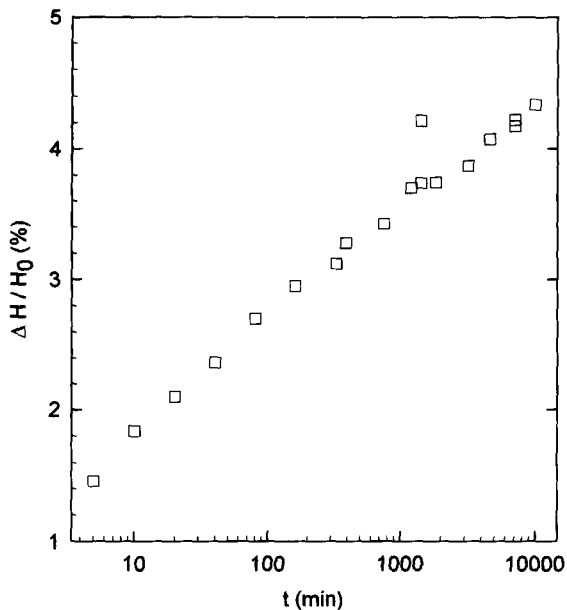
typical example is given in *Figure 4*, where it can be seen that direct determination of frequency shifts (filled squares) shows the same trend but more scatter than results obtained from difference spectra (empty squares).

#### Annealing quenched films

*Figure 3* shows that in the course of sub- $T_g$  annealing, the population of  $t-t$  sequences gradually increases at the expense of higher energy  $t-c$  sequences. At  $130^\circ\text{C}$  no saturation is observed on the timescale of the experiment. At  $140^\circ\text{C}$  some indication of stabilization of the concentration of conformers is observed after several days; this timescale is much longer than the timescale for



**Figure 5** Spectra obtained in  $1600\text{ cm}^{-1}$  region (a) a cold rolled film (full line, left axis); (b) a quenched film (dotted line, right axis). Top: difference a-2.4b



**Figure 6** Relative change of height of difference peak at  $1775\text{ cm}^{-1}$  in polycarbonate during annealing cold rolled films at  $80^\circ\text{C}$

enthalpy relaxation, where equilibrium is reached after only a few hours at  $140^\circ\text{C}$ <sup>16</sup>.

The stress-sensitive peak at  $1015\text{ cm}^{-1}$  was found to shift slightly to lower frequencies during annealing, indicating an increase of tensile stress. This modification, shown in *Figure 4*, was observed to saturate after a few hours.

#### Annealing after rejuvenation

Rejuvenation by cold rolling is observed to produce a large increase in  $t-c$  sequences, as shown in *Figure 5* by comparison of the  $\text{C}=\text{C}$  aromatic stretching region is undeformed and cold-rolled films. (The carbonate band saturated in the undeformed film and could therefore not be compared with the deformed film.) This increase is compatible with the high structural temperature of rejuvenated polycarbonate, as found previously<sup>5</sup>.

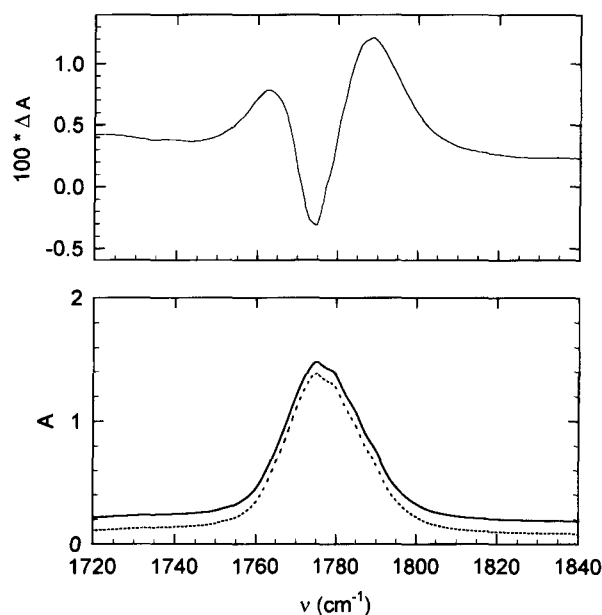


Figure 7 Spectra obtained in  $1775\text{ cm}^{-1}$  region (a) film aged 33 months at room temperature (full line); (b) freshly quenched film (dotted line); full line arbitrarily shifted. Top: difference a-b

Annealing the deformed film at  $80^\circ\text{C}$  produced a decrease in the fraction of  $t$ - $c$  sequences, characterized as above by the change in relative height  $\Delta H/H_0$  shown in Figure 6.

The stress-sensitive peak at  $1015\text{ cm}^{-1}$  shifted continually to lower frequencies during annealing; as shown in Figure 4, this change is much larger than in the case of quenched films, as would be expected if internal stresses due to cold rolling are relaxing during the thermal treatment. Figure 4 also shows that direct determination of frequency shift leads to much larger scatter than measuring the height of the difference peak. It is noteworthy that frequency shifts are small compared with differences between individual samples, and also that no systematic modification of the peak at  $1080\text{ cm}^{-1}$  could be observed.

#### Ageing at or near room temperature

The  $1775\text{ cm}^{-1}$  band obtained on a film aged 33 months at room temperature is compared with a freshly quenched film in Figure 7. There is little shift in emphasis between  $t$ - $t$  and  $t$ - $c$  sequences. However, there is clearly a change in shape of the C=O absorption band: the intensity increases during ageing at  $1764\text{ cm}^{-1}$  and  $1789\text{ cm}^{-1}$  and decreases at  $1775\text{ cm}^{-1}$ . This can be interpreted as a narrowing of each component of the band, with little or no change in relative  $t$ - $t$  and  $t$ - $c$  population. A plot of the relative height of the difference peak against ageing time at  $30^\circ\text{C}$  is given in Figure 8. These measurements were complicated to some extent by interference with a slight increase in  $t$ - $t$  content, leading to an increasingly asymmetric difference pattern. When the difference peak was asymmetric,  $\Delta H$  was taken as the absolute difference between the height at  $1775\text{ cm}^{-1}$  and the average of heights at  $1764\text{ cm}^{-1}$  and  $1789\text{ cm}^{-1}$ .

## DISCUSSION

### Annealing quenched samples

The present results all show that any thermomechanical treatment that is liable to increase the 'structural

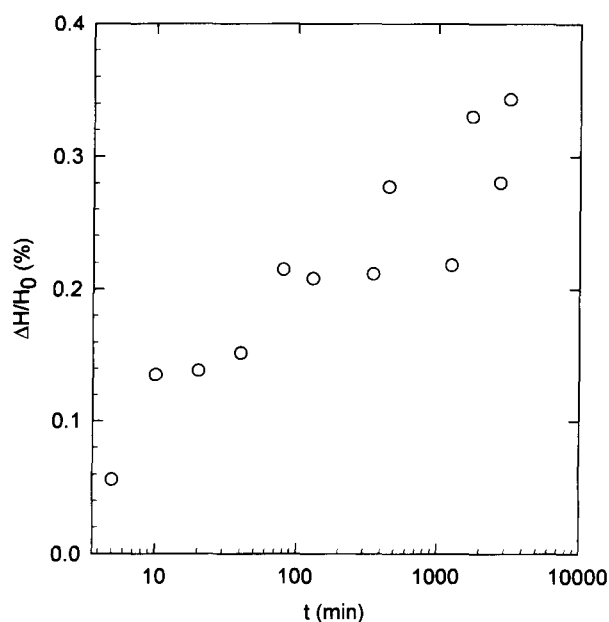


Figure 8 Relative height of difference spectrum during ageing at  $30^\circ\text{C}$

temperature' of the sample also increases the  $t$ - $c$  population. On the contrary, annealing, which decreases the structural temperature, is accompanied by a decrease in  $t$ - $c$  population.

This modification is compatible with various effects found to accompany annealing. Evidence for structural modification during annealing was found by Mitchell and Windle<sup>21</sup>, who noted that a  $0.14\text{ nm}$  peak appears in WAXS on annealing between  $110$  and  $150^\circ\text{C}$ . This peak was observed by Mitchell and Windle to be meridional, and hence was assumed to be due to interchain correlations; the scattered intensity was assumed to be sensitive to interchain correlations. Schubach and Heise<sup>22</sup>, however, found the peak contained two close contributions, one from interchain, the other from intrachain correlations. The peak first increases in intensity before disappearing after prolonged annealing. Mitchell and Windle attributed this behaviour to a local nested structure, leading to correlations between neighbouring chains. Disappearance of the diffraction peak was attributed to a second layer, shifted by half a repeat unit; this shift would eliminate the scattering. 'Bundles' were also suggested by Lani-Lee *et al.*<sup>23</sup>, and deuterium magnetic resonance has convincingly demonstrated the existence of orientational coupling between neighbouring chains in strained rubbers<sup>24</sup>. If local ordered regions exist, they must be extremely limited in size, since annealing below  $T_g$  does not affect depolarized light scattering of PC<sup>25</sup>. Červinka *et al.*<sup>26</sup>, by comparing simulated diffraction patterns with experimental neutron scattering results, concluded that linear chains (i.e. extended chain structures) do not exist in amorphous polycarbonate, but that ordered regions are possible with bent chains (i.e.  $t$ - $t$  sequences leading to banana-shaped structures). Pietralla and Pieper<sup>27</sup>, on the other hand, propose a densified amorphous structure having some local order on the scale of a few chains, in which different conformations typical of the various possible crystalline (i.e. periodic and hence non planar) structures exist along a single chain. Some interesting results were obtained by Hutnik *et al.*<sup>28</sup> who, by modelling chain dynamics, found that the  $t$ - $c$  and  $t$ - $t$  energy minima are flat, that

conformations that are neither  $t-t$  nor  $t-c$  are frequent, and that the majority of carbonate groups are not planar. The present results indicate that, if ordered regions exist at all, they are probably favoured by  $t-t$  conformations, thus confirming Červinka *et al.*'s conclusions rather than Pietralla and Pieper's.

#### Ageing near room temperature

A comparison of a well aged sample with a freshly quenched one (Figure 7) shows little shift from  $t-c$  to  $t-t$  sequences. However, there is an observable narrowing of each component of the  $C=O$  absorption band. Ageing is known to affect the high temperature tail of the secondary ( $\beta$ ) relaxation, both in thermally stimulated discharge measurements<sup>14</sup> and in mechanical relaxation<sup>29</sup>. This relaxation has been identified as being associated with phenyl group  $\pi$  flips accompanying carbonate group reorientations<sup>30</sup>, although  $\pi$  flips cannot induce mechanical relaxation, but can act as an indicator for it<sup>30,31</sup>. These motions have also been shown to be linked with diffusion of  $t-c$  sequences along a chain<sup>32</sup>. Thus, local reorganizations are possible without necessarily implying a modification of the  $t-t$  population. These reorganizations do not require cooperative motion of several main-chain links, and, as such, can be qualified as 'local' even though their consequences may be felt further along the chain as a result of diffusion of  $t-c$  sequences. Such motions would simply allow the chain to settle into a 'more comfortable' structure, and to approach the local minima corresponding to  $t-t$  and  $t-c$  conformations more closely (i.e. the carbonate groups would approach a planar conformation). Since, according to simulations by Hutnik *et al.*<sup>28</sup>, the local minima are extremely flat, these rearrangements would not lead to a modification of the internal energy or 'structural temperature' but rather to a redistribution of internal energy.

These modifications are compatible with observations of the endotherm at the onset of the exothermal plateau in d.s.c. scans of rejuvenated samples<sup>5</sup>. The predicted change in structural temperature during the scan does not provide for the existence of such an endotherm; the presence of the endotherm is, however, compatible with the existence of a distribution of structural temperature, or of enthalpy. The present results suggest that this distribution narrows during ageing, with little change of average enthalpy. This implies that ageing occurs by a mechanism similar to that responsible for the  $\beta$  relaxation, and can therefore only occur in the range of the high-temperature tail of this relaxation. The fact that there is a slight modification of  $t-t$  content during ageing is compatible with observations by Othmezzouri-Decerf<sup>33</sup> that ageing at room temperature not only affects the  $\alpha''$  excess loss, but also has a slight effect on the  $\alpha'$  loss.

#### Annealing cold rolled samples

The cold-rolled samples were treated at 80°C, i.e. well below the annealing range of undeformed PC. However, the 'structural temperature' description of thermomechanical modification of polymers predicts that, due to its high initial value, the structural temperature of a deformed sample should decrease during a thermal treatment in this range<sup>5</sup>. The shape of difference pattern observed is similar to that observed during sub- $T_g$  annealing of quenched samples, demonstrating that the same mechanism is operative. It is quite logical that

cold rolling should increase the  $t-c$  content in PC, since all extended-chain structures proposed for PC contain a significant proportion of  $t-c$  sequences. Figure 6 also shows that recovery of the  $t-t$  population at 80°C after cold rolling proceeds faster than annealing at 140°C after a quench. This means that the increase in structural temperature after cold rolling produces an acceleration of diffusion processes, extending the annealing range to lower temperatures as predicted by Bauwens-Crowet and Bauwens and observed in d.s.c.<sup>5</sup>. This acceleration of recovery after plastic deformation is compatible with observations by Pixa *et al.*<sup>34</sup> of acceleration of volume recovery of polycarbonate at room temperature after cold drawing: although the specific volume of the deformed samples was lower than that of annealed samples, volume contraction was observed at a higher rate than for quenched samples.

The shift of the 1015  $\text{cm}^{-1}$  peak to lower wavenumbers indicates an increase in tensile stress. This increase can be attributed to recovery of internal stresses induced by the plastic deformation. The measurements were not calibrated against stress. Levy and Wool<sup>20</sup> gave the stress sensitivity of the 1080  $\text{cm}^{-1}$  band as  $-0.0072 \text{ cm}^{-1}/\text{MPa}$  but did not give a value for the 1015  $\text{cm}^{-1}$  band. Here, no clear modification of the 1080  $\text{cm}^{-1}$  band was found; difference spectra did not show the zigzag pattern typical of frequency shifts and frequencies obtained by 9 point interpolation showed scatter with no trend one way or the other.

## CONCLUSIONS

Molecular rearrangements occurring during thermomechanical treatments have been observed in polycarbonate by FTi.r. This work shows that the effect of annealing is primarily a modification of  $t-t$  and  $t-c$  population of the carbonate group, leading to a more stable structure having a lower internal energy, whereas ageing proceeds mainly by extremely local rearrangements compatible with a densified structure; ageing is, however, accompanied by a slight change in conformational populations, compatible with observations that ageing can affect the  $\alpha'$  mechanical loss. This means that the  $\alpha'$  loss is linked with conformational rearrangements typical of the glass transition mechanism, whereas the  $\alpha''$  loss is linked with extremely local rearrangements typical of the  $\beta$  relaxation.

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