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Temperature studies of polycarbonate using Fourier transform Raman spectroscopy

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Summary

The temperature dependence of the Fourier transform Raman spectrum of polycarbonate has been investigated. C-O-C stretching and C-H stretching modes were found to be temperature-sensitive. The changes noted indicate the presence of a *cis-trans* conformation for the crystalline polymer, while the *cis-cis* conformation predominates in amorphous polycarbonate.

Introduction

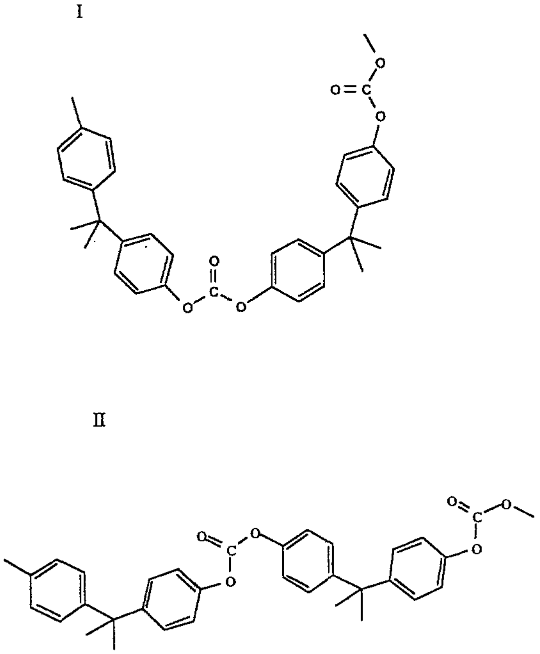
Polycarbonate (PC) is a high performance polymer with the useful properties of transparency and toughness, making this material suitable for the production of compact discs, for instance. Controlling the degree of crystallinity in PC is an important factor in maintaining suitable physical and mechanical properties of this polymer. Clearly, the thermal history of the polymer must be an important influence on the degree of crystallinity produced in PC and it is this factor which is investigated here.

The conformational sensitivity of the PC is associated with the ester group in the structural repeat unit of this polymer. Two stable conformations are possible, *cis-cis* and *cis-trans*, and these are illustrated in Figure 1. The *cis-cis* conformation is the lower energy conformation and for the amorphous regions of PC this conformation predominates, although the *cis-trans* conformation also may be the extended chain conformation of the amorphous phase. The crystalline regions are composed purely of the *cis-trans* conformational isomer.

Vibrational spectroscopy provides a useful means for examining the effect of temperature on PC at the molecular level. The infrared spectrum of PC is dependent on the physical environment of the polymer and the temperature dependence of the infrared spectrum of PC has been studied by Schmidt *et al.* [2]. Modes associated with the higher energy *cis-trans* conformation were found to increase in intensity at the expense of the *cis-cis* mode. Briscoe and co-workers [3] used Fourier transform infrared (FTIR) spectroscopy to examine the solvent induced morphological changes to PC due to xylene. Spectral components at 1245 and 1226 cm^{-1} were assigned to the *cis-cis* and *cis-trans* conformations, respectively, in PC prior to treatment. Exposure of the polymer to xylene produced an increase in the *cis-trans* component in the infrared spectra of PC, and thus an increase in the ordering of the polymer chains for the xylene plasticised system.

Raman spectroscopy has developed as a useful technique for investigating polymers and has been particularly useful for the study of polymer crystallisation [4]. A Fourier transform (FT) Raman study of the influence of xylene on the conformation of PC has been recently reported [5]. Changes to the FT-Raman spectrum of PC in the presence of xylene were believed to be due to an increase in the amount of the *cis-trans*

Figure 1. The structural conformations of PC: *cis-cis* (I) and *cis-trans* (II) conformation around the carbonyl group.



conformation produced in the polymer. It was proposed that xylene causes plasticisation of PC while inducing ordering in the polymer

In the present study the influence of temperature on the FT-Raman spectrum of PC is discussed. Examination of the spectra over a range of temperature allows the conformations of the polymer molecules in the amorphous and crystalline states to be deduced.

Experimental

Samples of amorphous bisphenol A polycarbonate (Makralon) were supplied by Display Developments Ltd, U.K. (glass transition temperature T_g = 145°C; melting temperature T_m = 250°C).

All of the FT-Raman spectra were recorded using a Bomem Ramspec 152 equipped with an indium gallium arsenide (InGaAs) photodiode detector and using approximately 1.0 W of 1064 nm radiation from a Quantronix Series 100 Nd:YAG laser. For each spectrum, 200 scans were co-added, apodised with a cosine function and Fourier transformed with a resolution of 4 cm^{-1}. The samples were mounted into the hot stage of a Linkam THMS 600 temperature cell. The sample was allowed to thermally equilibrate at the appropriate temperature for 5 min before a scanning time of 10 min at each temperature.

Results and Discussion

The FT-Raman spectrum of untreated PC at 30°C was recorded and is shown in Figure 2. The Raman modes of PC sample were assigned with reference to the infrared mode assignments [2] and by comparison with assignments made in an earlier Raman study [5]. The assignments are summarised in Table 1. The spectrum in Figure 2 shows intense bands due to C-H stretching in the region near 3000 cm^{-1}. A series of weak bands in the region 2800-2400 cm^{-1} are attributed to overtone and combination bands. The C=O stretching mode of PC appears at 1781 cm^{-1}. At frequencies in the range below 1600 cm^{-1} there is a number of bands, but largely overlapped. The modes in this region are associated with stretching of the ester group or modes due to the phenyl rings.

Table 1. The assignment of the FT-Raman modes of PC.

frequency / cm^{-1}	assignment
637	phenyl ring vibration
706,735	C-H out-of-plane bending
772	O-C(O)-O stretching
830	phenyl ring vibration
888	O-C(O)-O stretching
919,939,1001	C-H in-plane bending
1022,1110,1179,1237,1295,1313	C-O-C stretching
1411,1450,1465	CH_3 deformation
1603	phenyl ring vibration
1781	C=O stretching
2800-2400	overtone and combination bands
2985,3002,3072	C-H stretching

The Raman spectra of PC were recorded over a range of temperature from 30 to 240°C. The spectrum recorded at 240°C is shown in Figure 3. Changes were noted to certain Raman modes of PC with increasing temperature. In particular, changes to the C-H stretching region of the Raman spectrum of PC are observed. Figure 4 illustrates the C-H stretching modes observed in the region 3030-2950 cm^{-1} at 30, 150 and 240°C. At 30°C the C-H stretching region is characterised by the doublet with peaks at 3002 and 2986 cm^{-1}. At 150°C, where the T_g of PC has been reached, the component at 3002 cm^{-1} decreases in intensity relative to the component at 2986 cm^{-1}. When the temperature of the sample reaches 240°C the 2986 cm^{-1} component is reduced in intensity even further and the lower frequency component, now observed at 2989 cm^{-1}, predominates.

Figure 2. The FT-Raman spectrum of PC at 30°C.

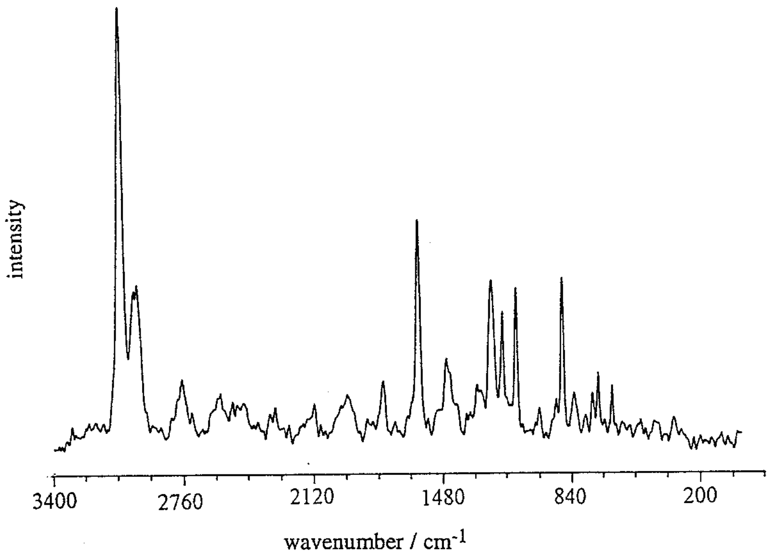


Figure 3. The FT-Raman spectrum of PC at 240°C.

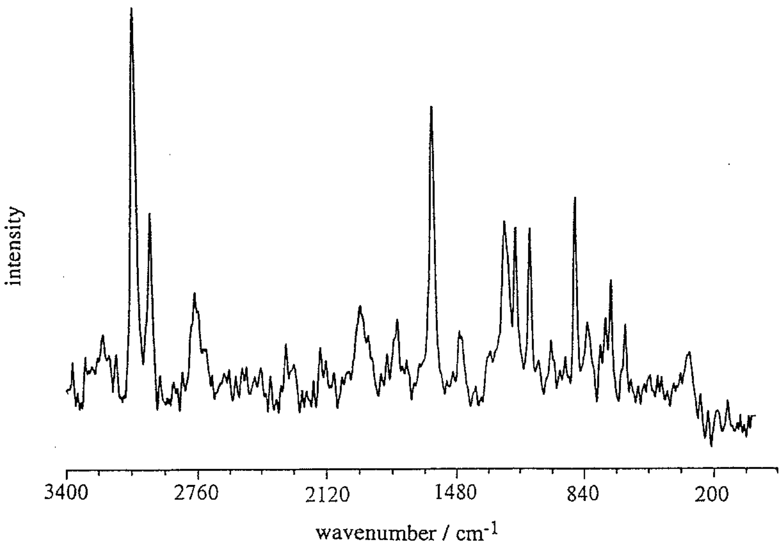


Figure 4. The temperature dependence of the C-H stretching region of the FT-Raman spectrum of PC.

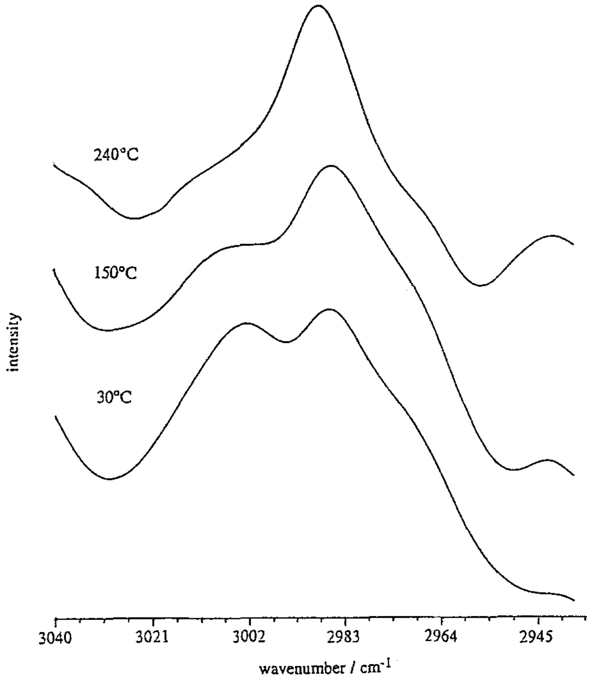
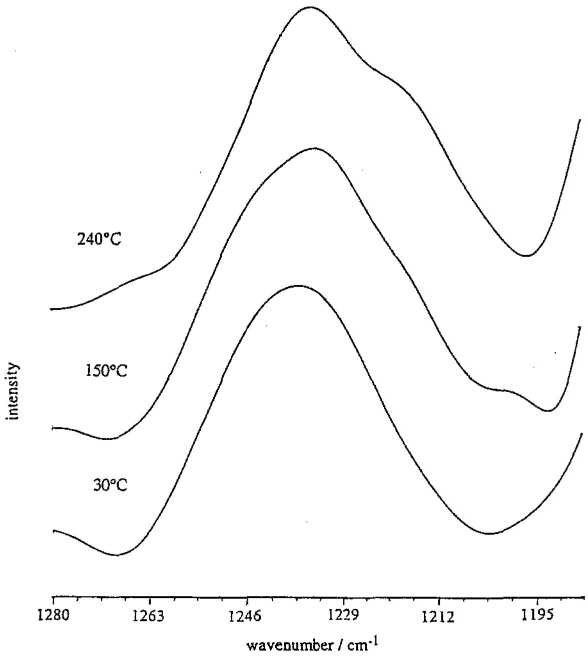


Figure 5. The temperature dependence of the C-O-C stretching region of the FT-Raman spectrum of PC.



The C-O-C stretching mode which appears in the range 1270-1200 cm^{-1} is also sensitive to an increase in temperature. Figure 5 illustrates this region at the temperatures 30, 150 and 240°C. At 30°C one broad band is observed in this region, with a maximum intensity at 1237 cm^{-1}. At 150°C, the maximum of this mode is shifted slightly to 1234 cm^{-1} and a shoulder has appeared at about 1218 cm^{-1}. At 240°C this mode exhibits a doublet with a component of higher intensity at 1235 cm^{-1} and the shoulder at 1218 cm^{-1} is more distinct.

The changes to both these modes with increasing temperature show a common trend. A higher frequency component observed in the amorphous polymer decreases in intensity while a lower frequency component increases in intensity as the crystalline polymer is formed. The higher frequency component may be attributed to the more favourable conformation, the *cis-cis* conformation, while the lower frequency component may be assigned to the higher energy *cis-trans* conformation (Figure 1). These observations are supported by the reported vibrational spectroscopic studies of PC [1-3]. Schmidt *et al.* [2] investigated the temperature dependence of an asymmetric C-O-C stretching mode in the infrared spectra of PC films and solutions. They noted that the less energetically favoured *cis-trans* conformation could be assigned to the lower frequency spectral component, while the more energetically favourable *cis-cis* conformation of amorphous PC is observed at a higher infrared frequency.

Conclusions

The observations made here support the theory that the *cis-cis* conformation predominates in the amorphous polymer, while for the crystalline polymer the *cis-trans* conformation is observed. The study has demonstrated the effectiveness of FT-Raman spectroscopy as a technique for the investigation of polymer crystallinity. The results obtained also support those findings made as a result of a FTIR spectroscopic study, emphasising the usefulness of combining these complimentary techniques.

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