polymer papers

Conformational structure of bisphenol A polycarbonate studied by infra-red spectroscopy

P. Schmidt and J. Dybal
Institute of Macromolecular Chemistry, Czechoslovak Academy of Sciences, 162 06 Prague 6, Czechoslovakia

and E. Turska and A. Kulczycki
Institute of Polymer Chemistry, Polish Academy of Sciences, Zabrze, Poland
(Received 16 March 1990; revised 12 June 1990; accepted 19 June 1990)

Infra-red spectra of amorphous and partly crystalline bisphenol A polycarbonate were measured. Based on the temperature dependences of the infra-red spectra of the polycarbonate and its model compound, diphenyl carbonate, infra-red bands sensitive to transitions between the *trans–trans* and *trans–cis* conformations of the carbonate group were determined. Using the spectral data obtained for the polycarbonate solution in chloroform, the enthalpy change ΔH for the *trans–cis* to *trans–trans* transition was estimated to be $\sim$0.5 kcal mol^{-1}. Infra-red spectra of solid polycarbonate suggest that the interchain forces in the crystalline state stabilize the less favoured conformation of the carbonate group, most probably the *trans–cis* structure.

(Keywords: bisphenol A polycarbonate; diphenyl carbonate; infra-red spectroscopy; conformations)

INTRODUCTION

The structure of bisphenol A polycarbonate (BPAPC) has been studied by many authors. Two sets of crystal data derived from the X-ray diffraction patterns together with proposed structural models have been reported[1,2]. Several published empirical[3–8] and *ab initio*[9,10] calculations were aimed at calculating conformational features of BPAPC. Conformational energies associated with the rotations of the phenyl groups and the energy difference between the *trans* and *cis* conformations of the carbonate group have been reported. Recently, Perez and Scaringe[11] have published a full helical parameter analysis of BPAPC supplemented by conformational energy calculations. They have found two idealized chain conformations consistent with existing fibre data on the crystalline polymer.

In this paper an infra-red (i.r.) spectroscopic study of the conformational structures of BPAPC in the solid state and in solution is presented. On the basis of the temperature dependences, conformationally sensitive bands in the i.r. spectra of BPAPC have been found. The analysis of the i.r. spectra of the BPAPC model, diphenyl carbonate (DPC), combined with the results of the published conformational energy calculations allowed us to propose an assignment of these bands to the specific chain conformations of BPAPC. (For possible conformations of DPC, see *Figure 1*.)

EXPERIMENTAL

Samples of bisphenol A polycarbonate (tradename Bistan AF) were crystallized by annealing at 190°C for a period of 230 h. Infra-red spectra of BPAPC and DPC in the solid state were measured in KBr pellets. For measurements at increased temperatures, a commercial heated cell (Perkin–Elmer) was used. The temperature dependences of the i.r. spectra of the solutions were measured by means of an RIIC cell.

Infra-red spectra were measured on a Perkin–Elmer 580B spectrometer, connected on-line with a TN-4000 multichannel data analyser. The crystallinity of BPAPC was determined on an HZG4A X-ray powder diffractometer (Präzionsmechanik, Freiberg, Germany) and on a Du Pont 1090B d.s.c. instrument.

RESULTS AND DISCUSSION

The degree of crystallinity of the commercial BPAPC samples determined from the X-ray diffractograms was 17%. After further crystallization, the degree of crystallinity increased to 22%. The i.r. spectrum of this partially crystalline sample is shown in *Figure 2c*. When the partially crystalline sample was annealed to 250°C, i.e. above the melting point of BPAPC, and then slowly cooled in air to room temperature, the degree of crystallinity decreased practically to zero according to the X-ray diffractograms and d.s.c.

From *Figure 2* it can be seen that the i.r. spectrum of the amorphous BPAPC sample obtained by melting and subsequent cooling of the original sample in KBr pellets differs considerably from the spectrum of the partially crystalline sample. Changes of band intensities and wavenumbers are more pronounced when the spectrum of the amorphous sample is compared with the spectrum of the pure crystalline form of BPAPC (*Figure 2d*). (This difference spectrum was obtained from the measured i.r.

0032-3861/91/101862-05

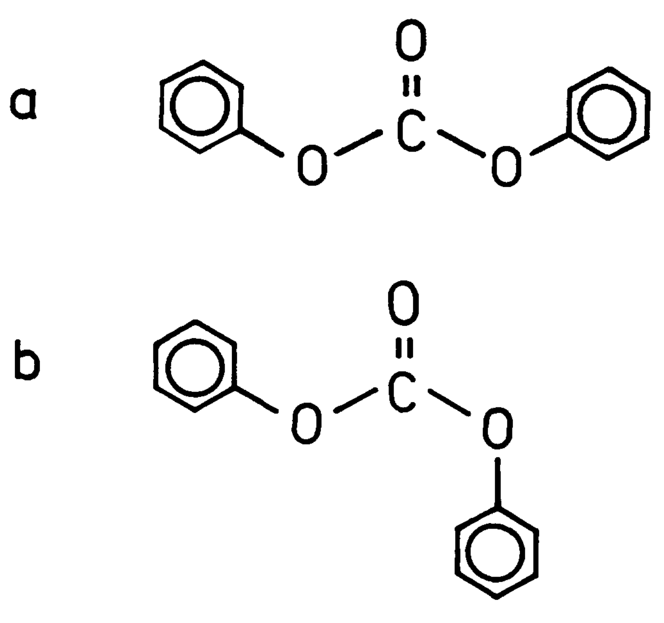

Figure 1 Possible conformations of diphenyl carbonate: (a) *trans–trans*; (b) *trans–cis*

spectrum of the partially crystalline sample by digital subtraction of the spectrum of the amorphous sample multiplied by the factor 0.78 corresponding to the content of the amorphous regions in the partially crystalline sample according to the X-ray results and d.s.c.)

The main differences between the spectra of pure crystalline and of amorphous BPAPC can be found in the bands corresponding[12,13] to the antisymmetric vibration of C–O–C, the skeletal vibration of the aromatic ring and the carbonyl band. In the spectrum of amorphous BPAPC the C–O–C antisymmetric vibration is characterized by a doublet with maximum at 1252 cm^{-1} and a shoulder at 1223 cm^{-1}. The skeletal vibration of aromatic ring exhibits a doublet with the component of slightly higher intensity at 1594 cm^{-1} and the second component at 1604 cm^{-1}. The broad carbonyl band of amorphous BPAPC has a maximum at 1767 cm^{-1} and a shoulder at 1785 cm^{-1}. In the spectrum of the pure crystalline phase of BPAPC, the analogous vibrations are characterized by the bands found at 1223, 1603 and 1785 cm^{-1}, respectively (see *Figure 2*). *Figure 2* also shows that, on measuring the spectra of amorphous BPAPC above T_g, the intensities

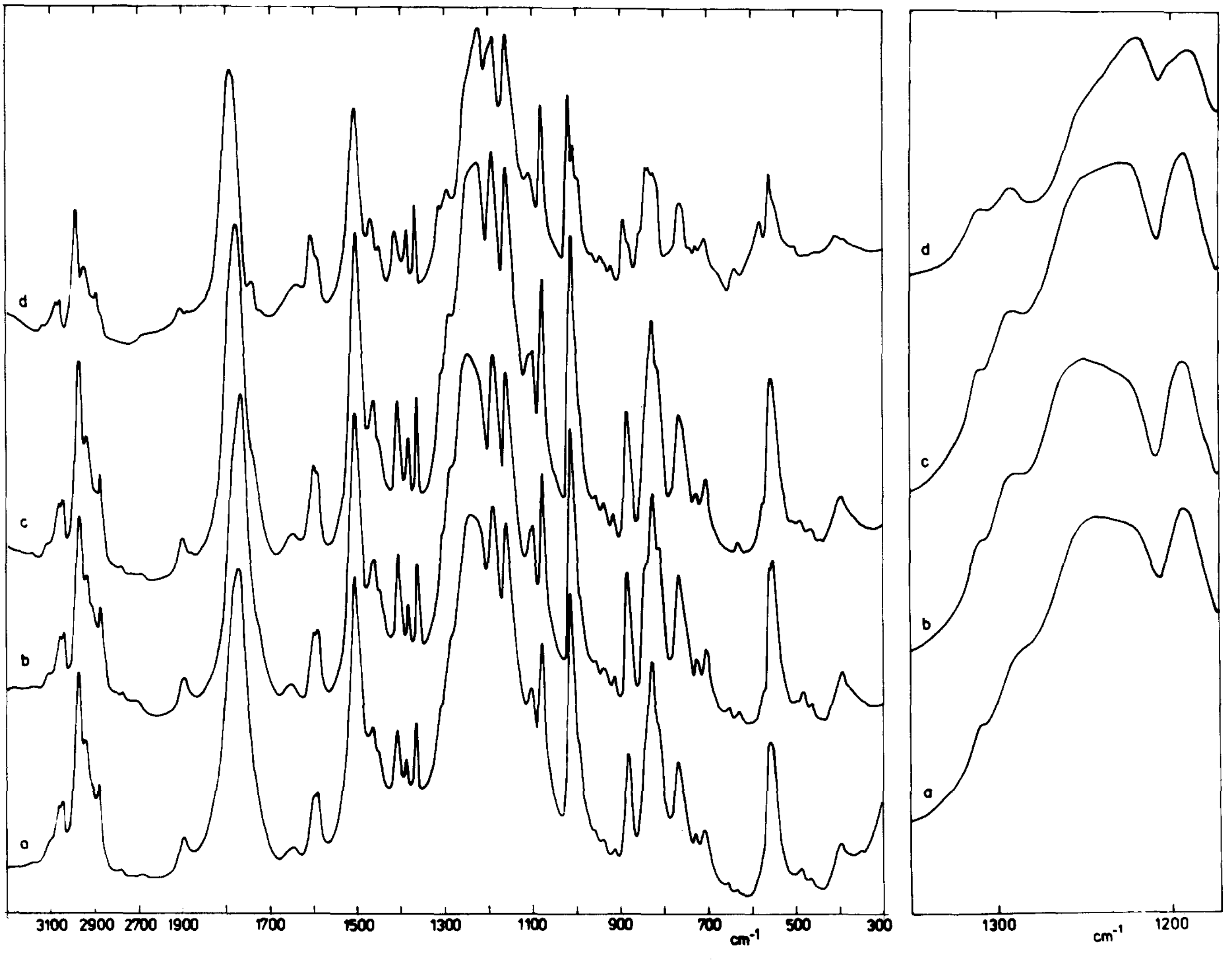

Figure 2 Infra-red spectra of polycarbonate: (a) melt ($t = 243$°C); (b) amorphous (after melting and subsequent cooling); (c) partially crystalline (original); (d) pure crystalline (difference (c) − 0.78 × (b))

of the absorption bands at 1223, 1603 and 1785 cm^{-1} increase with increasing temperature.

In the i.r. spectra of the solutions of BPAPC in chloroform and dimethylformamide, the wavenumbers and intensities of the bands described above correspond approximately to the spectrum of the amorphous BPAPC sample. Also the temperature dependence of the i.r. spectrum of BPAPC solutions shows similar behaviour as in the case of the amorphous BPAPC sample.

The described temperature behaviour of the doublets at 1252/1223 cm^{-1} and 1603/1594 cm^{-1} and of the carbonyl band at 1775 cm^{-1} and their changes during the transition of BPAPC from crystalline to amorphous state indicate that these bands are sensitive to conformational structure. The observed changes in the i.r. spectra can be explained by the presence of at least two conformational structures in the amorphous phase and in the solutions, and of a single conformation in the pure crystalline phase. According to the conformational energy calculations, accessible conformations of the BPAPC chain are generated by the restricted rotations of the phenyl groups and by the transitions between *trans–trans* and *trans–cis* structures of the carbonate group.

The bands in the i.r. spectra of BPAPC in solution and of amorphous BPAPC, the intensities of which increase with increasing temperature, i.e. the bands at 1223 and 1603 cm^{-1} and the higher-frequency component of the carbonyl band, correspond to the energetically less favoured chain conformation. From the comparison of the spectra of amorphous and crystalline BPAPC, it can be concluded that this energetically less favoured structure is stabilized in crystalline BPAPC, regardless of the assignment of the conformationally sensitive bands to specific conformations.

In order to determine which conformational transitions are manifested in i.r. spectra of BPAPC, we have measured i.r. spectra of the BPAPC model compound, diphenyl carbonate (DPC). In crystalline DPC the *trans–trans* conformation of the carbonate group is present, according to the X-ray study[4]. In the i.r. spectra of DPC in various solutions (chloroform, chloroform-d_3, tetrachloromethane and acetonitrile), analogues of the conformationally sensitive bands of BPAPC can be observed in the C=O stretching and the C–O–C stretching regions, and they exhibit similar temperature dependences. Therefore, it is assumed that these bands are sensitive to the structure of the carbonate group (*trans–trans* and *trans–cis* conformations). As the carbonyl band is probably complicated by Fermi resonance[14,15], we have mathematically analysed only the doublet in the region 1250–1200 cm^{-1}. The overlapped bands were separated into Lorentzian components by the least-squares method. Reliable results were obtained only for the spectrum of the DPC solution in CCl_4 shown in *Figure 3*, where the bands are sufficiently well resolved.

The population of the *trans–trans* and *trans–cis* conformers in the DPC solution at various temperatures is proportional to the ratio of the absorbances of the bands due to these conformers. By applying the equation:

$$\ln K = \Delta H/RT - \Delta S/R$$

where ΔS is the entropy change and K is the ratio of the absorbances, the enthalpy difference ΔH can be determined from the plot of ln K *versus* $1/T$. It is assumed that ΔH is not a function of temperature. The ratio of the integrated absorbances of the bands at 1240 and 1227 cm^{-1} obtained by the least-squares separation is plotted in *Figure 4* as a function of $1/T$. A value of 1.1 ± 0.1 kcal mol^{-1} for ΔH was obtained based on the slope of the plotted line.

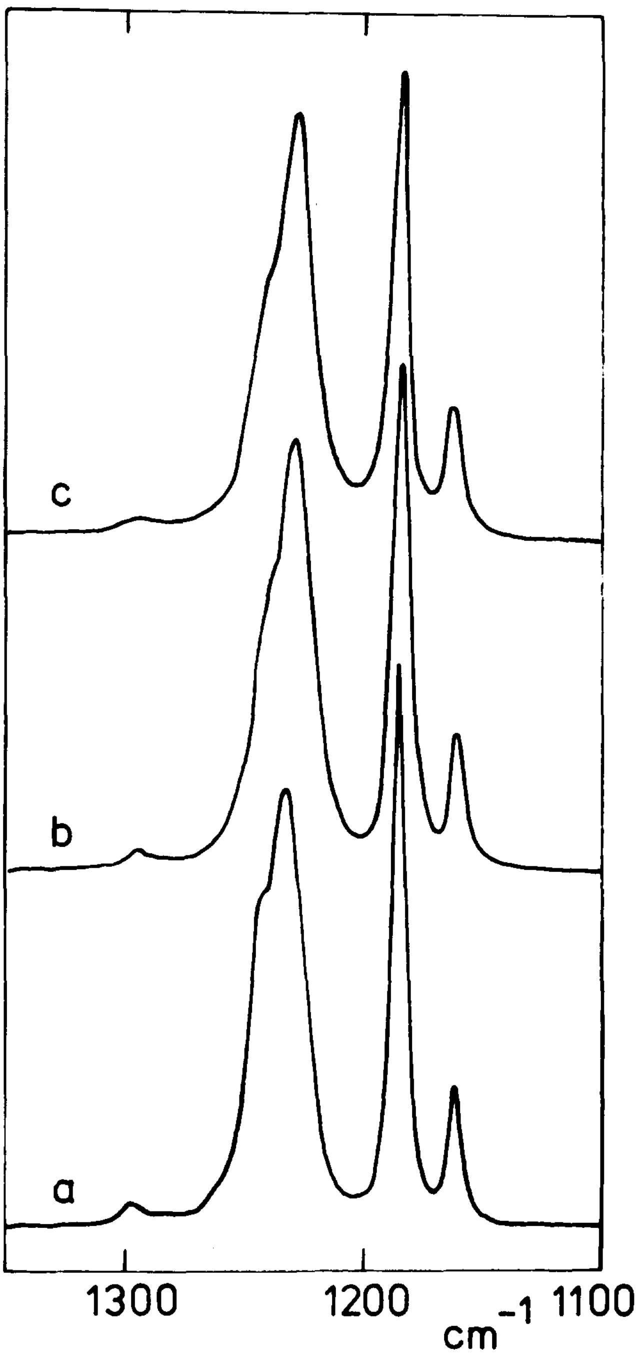

Figure 3 Infra-red spectra of diphenyl carbonate solution in CCl_4: (a) $t = -21$°C; (b) $t = 30$°C; (c) $t = 59$°C

This experimental result is close to the values of the conformational energy differences reported in different theoretical studies on DPC[4,5,9,10], according to which the *trans–trans* conformation is favoured over the *trans–cis* conformation. Based on the given data the lower-frequency band at 1227 cm^{-1} can be assigned to the less stable *trans–cis* conformer. This assignment is consistent with the empirical theorem[16] saying that the band corresponding to the conformer with higher dipole moment (*trans–cis* conformer in the case of DPC[14]) is higher in wavenumber in the C=O stretching region. It

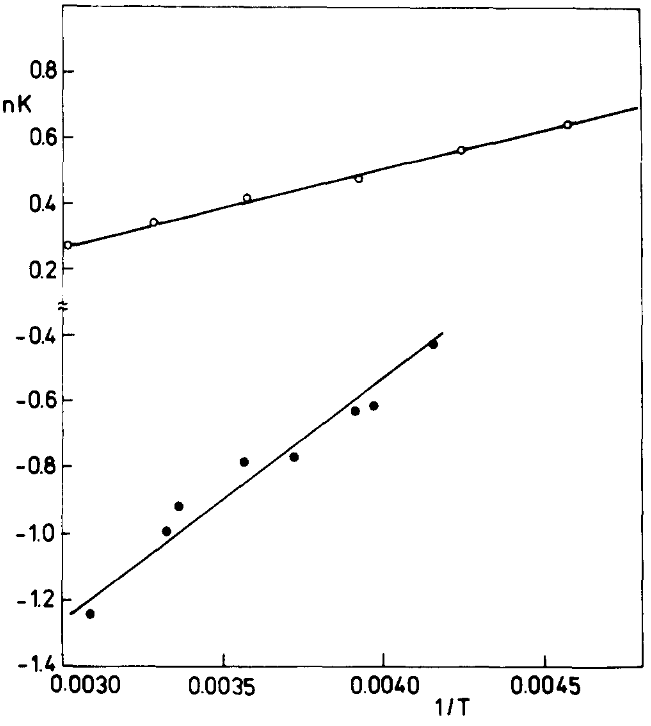

Figure 4 Temperature dependences of the band absorbance ratios: (○) polycarbonate in $CDCl_3$, $K = A_{1252}/A_{1223}$; (●) diphenyl carbonate in CCl_4, $K = A_{1240}/A_{1227}$

corresponds to the band lower in wavenumber in the C–O–C region according to the temperature behaviour.

As BPAPC is not soluble in CCl_4, the analysis of the doublet at 1252 and 1223 cm^{-1} was performed for the spectra of BPAPC solution in $CDCl_3$ measured at temperatures ranging from −54 to +59°C (*Figure 5*). The plot of ln K as a function of the reciprocal of the absolute temperature is shown in *Figure 4*. For ΔH a value of 0.46 ± 0.02 kcal mol^{-1} was obtained. Based on the conclusions of the DPC analysis, the band lower in wavenumber in the 1252/1223 cm^{-1} doublet is assigned to the higher-energy *trans–cis* conformation of the carbonate group in the BPAPC chain. The band at 1603 cm^{-1} and the higher-frequency component of the carbonyl band exhibit similar temperature behaviour in the i.r. spectra. Therefore, they probably correspond to the less favoured *trans–cis* conformation, too. The experimental value of 0.46 kcal mol^{-1} for the energy difference between the *trans–cis* and the *trans–trans* conformation is somewhat lower than the published calculated values (1.1–1.8 kcal mol^{-1})[4,5,9,10]. However, the experimental value obtained for the BPAPC solution in $CDCl_3$ is affected by the solute–solvent intermolecular interactions not taken into account in the theoretical studies.

As shown earlier, i.r. spectra suggest that population of the less favoured conformation of the BPAPC chain is increased in crystalline BPAPC compared to amorphous BPAPC. Our analysis of i.r. spectra supports the results of the theoretical studies, which favour the *trans–trans* conformation over the *trans–cis* conformation of the carbonate group, for both DPC and BPAPC. Whereas crystalline DPC is formed by the *trans–trans* structure[4], in crystalline BPAPC the interchain forces stabilize the less favoured *trans–cis* conformation. Consequently, one of the two idealized conformational structures of BPAPC[11] consistent with existing fibre data on crystalline polymer is favoured by our result.

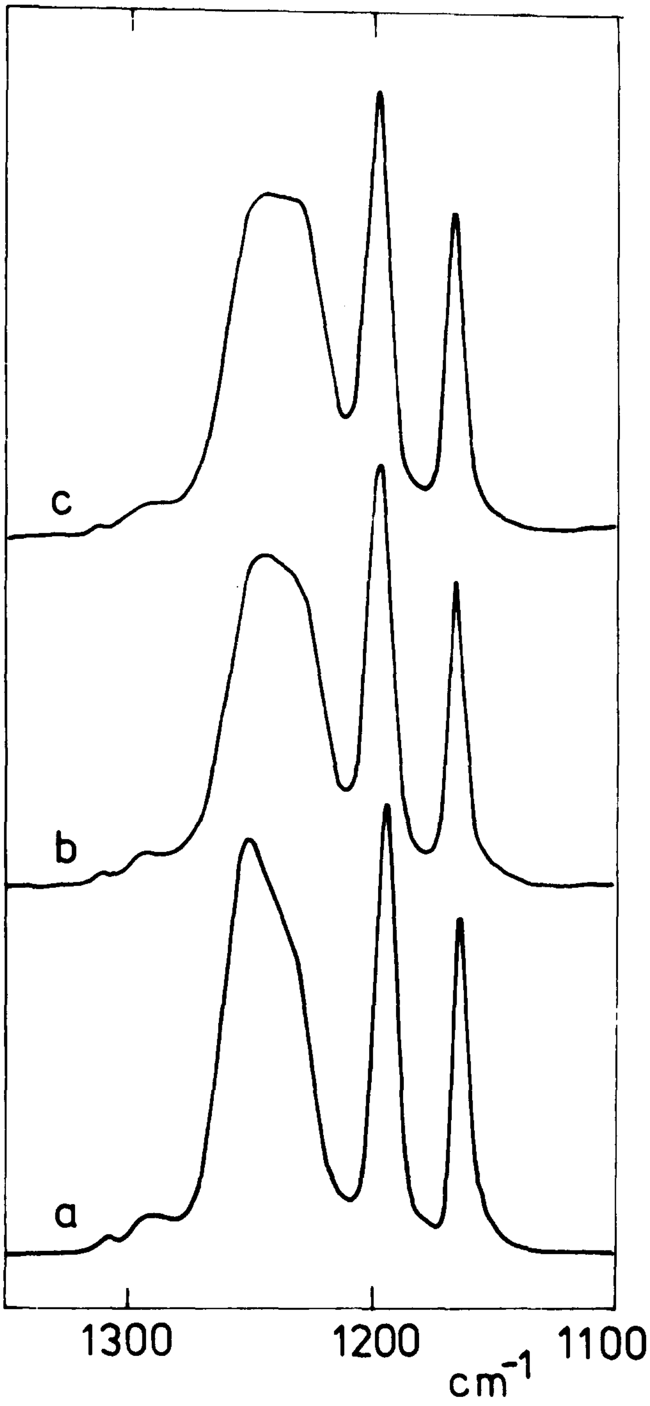

Figure 5 Infra-red spectra of polycarbonate solution in $CDCl_3$: (a) $t = -54°C$; (b) $t = 30°C$; (c) $t = 59°C$

ACKNOWLEDGEMENT

The authors wish to thank Dr J. Baldrian for the X-ray diffraction measurements.

REFERENCES

1 Prietschk, A. *Kolloid-Z.* 1958, **156**, 8
2 Bonart, R. *Macromol. Chem.* 1966, **92**, 149
3 Tonelli, A. E. *Macromolecules* 1972, **5**, 558
4 Erman, B., Marvin, D. C., Irvine, P. A. and Flory, P. J. *Macromolecules* 1982, **15**, 664

5 Tekely, P. and Turska, E. *Polymer* 1983, **24**, 667
6 Sundararajan, P. R. *Can. J. Chem.* 1985, **63**, 103
7 Sundararajan, P. R. *Macromolecules* 1987, **20**, 1534
8 Sundararajan, P. R. *Macromolecules* 1989, **22**, 2149
9 Bicerano, J. and Clark, H. A. *Macromolecules* 1988, **21**, 585
10 Laskowski, B. C., Yoon, D. Y., McLean, D. and Jaffe, R. L. *Macromolecules* 1988, **21**, 1629
11 Perez, S. and Scaringe, R. P. *Macromolecules* 1987, **20**, 68
12 Schnell, H. 'Chemistry and Physics of Polycarbonates', Wiley–Interscience, New York, 1964
13 Kulczycki, A. *Spectrochim. Acta (A)* 1985, **41**, 1427
14 Oki, M. and Nakanishi, H. *Bull. Chem. Soc. Japan* 1971, **44**, 3419
15 Guiheneuf, G. and Laurence, C. *Spectrochim. Acta (A)* 1978, **34**, 15
16 Bellamy, L. J. and Williams, R. L. *J. Chem. Soc.* 1957, 4294