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Raman spectroscopic study of a substituted poly(phosphazene)

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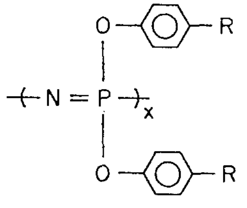
Summary

Polyphosphazenes present a range of unique and fascinating physical properties, including thermotropic behaviour, which are highly dependent both on the type of substitution at the P atom in the inorganic backbone, and the thermal history of the material. Recent technological advances have allowed us to study this group of polymers using vibrational spectroscopy. Fourier transform (FT) Raman spectra have been recorded from samples of poly[bis(4-methoxy-phenoxy)phosphazene] with different thermal histories. With the aid of spectral subtraction methods, differences observed between the spectra have been related to the crystalline and mesophase content of the materials.

Introduction

The polyphosphazenes are a family of inorganic polymers which possess a series of commercially interesting physical properties, notably biocompatibility and thermal stability (1,2). Recently there has been much interest in changes in the physical properties of these polymers in relation to substituent groups attached to the main chain, particularly in their thermotropic behaviour (3-6).

The semi-crystalline poly[bis(R-phenoxy)phosphazenes], possess three transition temperatures: the glass transition temperature Tg, the thermotropic crystal to mesophase transition T(1), and the isotropic melting transition Tm. However, in addition to these accepted fundamental transitions a series of interesting anomalies have been discovered which are heavily dependent on the thermal history and crystallisation conditions of the material, and which have intimated the existence of a number of crystalline and mesomorphic structures (7,8). Studies on the nature of the crystal to liquid crystal transition using solid state nmr, dsc and x-ray diffraction have indicated that the main structural determinant in the crystalline phase is the type and arrangement of the side groups around the inherently flexible P-N chain, and accordingly this explains many of the physical properties of the materials (9-11).



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Vibrational spectroscopy often provides important structural details, and has frequently demonstrated sensitivity to the morphology of polymeric materials (12,13). However, to our knowledge the only spectroscopic study on polyphosphazenes reported (14) was applied to poly(dichlorophosphazene) (PDP), the precursor of this family of polymers. The Raman spectrum could only be recorded from a freshly polymerised sample of PDP, up to a Raman shift of 1000 cm^{-1}, since the combined effects of sample decomposition in the laser beam and high levels of background scattering rapidly overwhelmed the Raman signals.

However, liquid crystalline behaviour and phase transitions have recently been succesfully studied using FT vibrational spectroscopic techniques (15,16). Consequently, we have approached a range of poly[bis(R-phenoxy)phosphazenes] using a near-infrared FT Raman interferometer and have obtained very high quality Raman spectra from samples studied both in their original form, and after thermal treatment. In this communication we report the FT Raman spectra of poly[bis(4-methoxyphenoxy)phosphazene] (PBMOPP), where R = OCH_3.

Experimental

The polymer PBMOPP was synthesised by a substitution reaction of thallium 4-methoxyphenoxide on PDP. Complete details of the preparation have been reported elsewhere (17). DSC thermograms were recorded on a Mettler TA 3000-DSC-30 differential scanning calorimeter, at a heating rate of 10°C/min. X-ray diffractograms were obtained using a Philips PW 1050/70 Geiger counter diffractometer. Diffractograms were recorded at a rate of 2°/min between 2θ = 5 and 30°, using Ni-filtered CuK_α radiation.

FT Raman spectra were recorded on a Perkin Elmer model 1710 FT-IR spectrometer which was modified to operate in the near-infrared as a Raman spectrometer. The instrumentation and sampling techniques have been described in detail elsewhere (18). A Nd^{3+}:YAG laser source was employed and in each case 800 mW of 1.064 μm radiation was incident upon the sample. No sample heating or photodegradation was evident. Spectra were recorded during 7 minutes (100 scans) at 6 cm^{-1} resolution. Data was collected and processed on a Perkin Elmer 7700 data station. All spectra were corrected for instrument, filter and detector characteristics. Spectral subtractions were performed using the interactive spectral difference routine, IDIFF, provided in the CDS-3 software.

Results and Discussion

The thermal transitions in PBMOPP, observed by dsc, have been reported previously (5). The glass transition, Tg, appears at 16°C, and a transition at 151°C is associated with the crystal-liquid crystal transition, T(1). No clear evidence of a transition from the mesophase to the isotropic melt could be detected by dsc, however, observations using polarised microscopy show the transition from liquid crystal-isotropic melt, Tm to take place at around 340°C. In order to investigate influence of the thermal treatment on the structure and

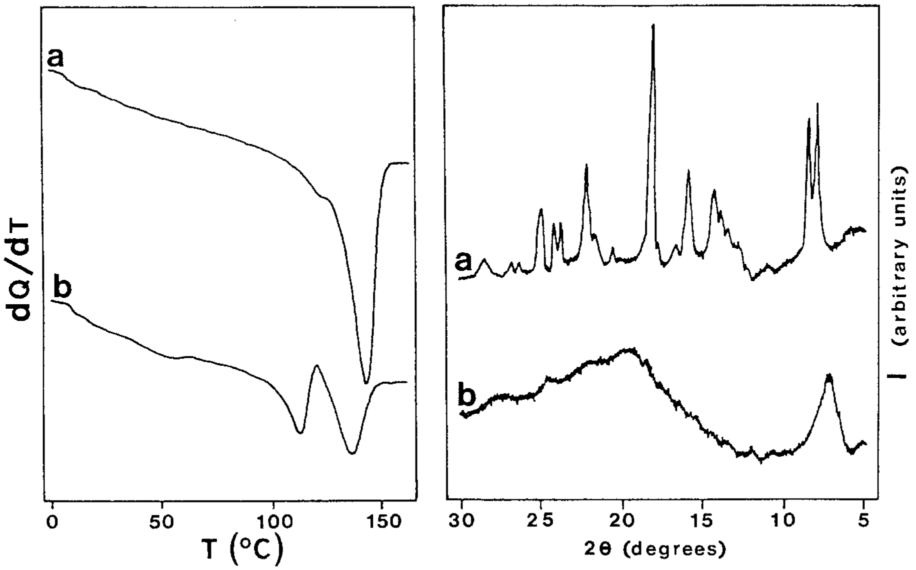

FIGURE 1: **DSC thermograms (left) and x-ray diffractograms (right) of PBMOPP, (a) after quenching from the mesophase at 170°C, and (b) in its "as polymerised" form.**

composition of the phases, we initially characterised samples with different thermal histories. Figure 1 presents DSC and x-ray scattering measurements taken from PBMOPP in both its original form, and after a thermal treatment which consisted of heating the material into the mesophase at 170°C, holding it at temperature for 5 minutes and then quenching into air at room temperature.

As can be observed from the x-ray diffractograms the original white gum-like material is essentially amorphous, however the appearance of a strong low angle reflection at $2\theta = 7.4°$ indicates a reasonable amount of mesophase content (5). On the other hand, the sample quenched from the mesophase presents a diffraction pattern typical of a highly crystalline material, in this case around 60% crystallinity, with well developed reflections associated with inter- and intra-molecular order in the crystal. In this diffractogram the low angle reflection due to the liquid crystalline phase is not apparent. However, it has been confirmed by optical microscopy that a very small amount of mesophase is present in the semi-crystalline sample (5). The dsc thermograms confirm that the "as polymerised" sample has a considerably lower crystallinity, whereas after thermal treatment the crystallisation endotherm becomes well developed, $\Delta H_{T(1)} \approx 35\ Jg^{-1}$. To summarise, the original material is of low crystallinity, and has a high mesophase content, whereas the quenched material is highly crystalline, with a negligible mesophase content.

The FT Raman spectra of PBMOPP are presented in figure 2, and from these, several general points can be made. Skeletal vibrations of the chain are relatively weak when compared to the high scattering cross-section of the aromatic groups, which dominate the spectra. In this case the spectrum of PBMOPP is similar to those of anisole and 4-methoxyphenol, in that characteristic modes due to the methyl and para-substituted phenyl moieties appear at similar frequencies in the Raman spectra of the polymer. We have found this observation to be universal for a wide range of polyphosphazenes (19). The strongest band in the FT Raman spectrum arises from the totally symmetrical aromatic ring breathing mode, ν_2 (Herzberg numbering), at 817 cm^{-1}, far removed from its corresponding frequency in benzene, firstly because the substituents load the ring with added mass, and secondly, due to the lower local symmetry the ring breathing mode interacts with other modes, thus changing the frequency of vibration. C-H deformation vibrations of the methyl group characteristically appear between 1400 and 1470 cm^{-1}, and the methyl C-H stretching vibrations at between 3015 and 2835 cm^{-1}. The $O-CH_3$ stretch is weakly observed at 1030 cm^{-1}. We observe a weak P-N-P deformation mode at around 450 cm^{-1}, but the P-N stretching vibrations, which appear between 1250 and 1300 cm^{-1} (1) are not clearly resolved since they are mixed with bands due to the aromatic nucleus.

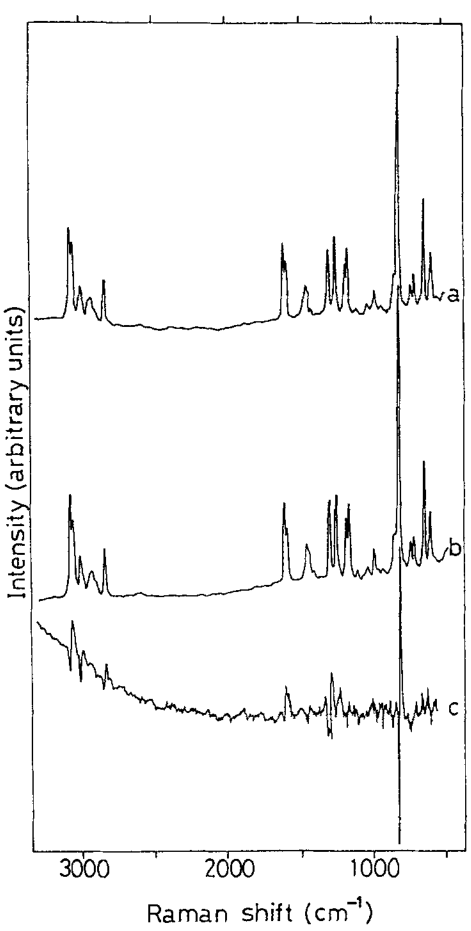

FIGURE 2: FT Raman spectra of PBMOPP, (a) after quenching from the mesophase, (b) in its "as polymerised" form, and (c) a spectral subtraction of a-b.

Figures 2a and 2b show the FT Raman spectra of PBMOPP after quenching from the mesophase, and in its original form respectively. Differences between a number of relative spectral band intensities are observed. For example, the following ratios; 1595/1605 cm^{-1} (C=C stretching vibrations, ν_{16a} + ν_{16b}); 711/737 cm^{-1} ; and 1297/1252 cm^{-1}, all increase after quenching the sample from the mesophase. The relative intensities of ν_{16a} and ν_{16b} have been shown to be sensitive to both composition and crystallinity in some aromatic polymers where the ring forms part of the polymer chain (20,21). The increase in the 1595/1605 ratio agrees with the observed increase in crystallinity of the sample of PBMOPP, which is consistent with the view that it is the characteristics of the substituent groups which determine the nature of the material.Other bands which demonstrate an increase in intensity may also be related with the crystallinity of the material. These and other changes become clearer when we consider figure 2c, which represents the spectral subtraction "b-a", normalised on the aromatic C=C stretching mode at 1605 cm^{-1}. Although the noise in the difference spectrum is high, some key features can be noted. We observe bandshifts in the ring breathing mode, ν_2, which moves to lower frequency in the crystalline material, as does the C-H stretching mode, ν_5, at 3031 cm^{-1}. These bandshifts may reflect the reduction of mobility of the aromatic rings in the crystallised material. Displacements to lower frequency can also be observed for the symmetric and anti-symmetric in-plane CH_3 stretching vibrations at 2837 and 3012 cm^{-1} respectively, and a negative band corresponding with the latter also appears, which may be associated with some form of conformational change when the liquid crystalline structure crystallises. The C-H stretch ν_1 at 3059 cm^{-1} displays an increase in intensity which may also be related to the increase in crystallinity. More complex changes are observed in the 1350 to 1200 cm^{-1} region, which contains a number of closely spaced bands which arise from both the inorganic chain and the aromatic nucleus. Once more a negative band appears at around 1300 cm^{-1}, and there is an increase in the intensity of the band at 1252 cm^{-1} relative to ν_{16a}, which may be related with mesophase and crystalline structures in the polymer respectively.

This preliminary data is very promising, and has clearly demonstrated that information on the vibrational structure of this type of material is now easily accessible. The FT Raman spectra are of high quality, and can be obtained without the need for any complicated sample purification or experimental procedures. Further work is already underway, including a spectroscopic study monitoring each phase and phase transition, with temperature, for a wide range of poly[bis(R-phenoxy)phosphazenes] in order to determine the origin of, and distinguish between, the spectroscopic structures which are observed, in relation to the chemical nature, thermal history and morphology of these materials.

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References

1. Allcock, H.R., "Phosphorus-Nitrogen Compounds" (1972) Academic Press, New York.
2. "Inorganic and Organometallic Polymers", eds. Zeldin, M; Wynne K.J; Allcock, H.R. (1988) ACS Symposium Series, 360
3. Kojima, M; Magill, J.H. (1989) **Polymer, 30**, 579
4. Allcock, H.R; Connolly, M.S; Sisko, J.I; Al-Shali, S. (1988) **Macromolecules, 21**, 323
5. Gómez, M.A; Marco, C; Fatou, J.G; Bowmer, T.N; Haddon, R.C; Chichester-Hicks, S.V. (1990) **Macromolecules** (accepted)
6. Gómez, M.A; Marco, C; Fatou, J.G; Chichester-Hicks, S.V; Haddon, R.C. (1990) **Polymer Commun., 31**, 308
7. Meille, S.V; Porzio, W; Allegra, G; Audisio, G; Gleria, M. (1986) **Makromol. Chem. Rapid Commun., 7**, 217
8. Kojima, M; Magill, J.H. (1989) **Polymer, 30**, 1856
9. Tanaka, H; Gómez, M.A; Tonelli, A.E; Chichester-Hicks, S.V; Haddon, R.C. (1988) **Macromolecules, 21**, 2301
10. Tanaka, H; Gómez, M.A; Tonelli, A.E; Chichester-Hicks, S.V; Haddon, R.C. (1989) **Macromolecules, 22**, 1031
11. Young, S.C; Magill, J.H. (1989) **Macromolecules, 22**, 2551
12. Glotin, M; Domszy, R; Mandelkern, L. (1983) **J. Polym. Sci. Polym. Phys. Ed., 21**, 285
13. Tadokoro, H. (1984) **Polymer, 25**, 147
14. Coleman, M.M; Zarian, J; Painter, P.C. (1982) **Applied Spectroscopy, 36**, 277
15. Benedetti, E; Galleschi, F; Chiellini, E; Galli, G (1989) **J. Polym. Sci. Polym. Phys. Edn., 27**, 25
16. Ellis, G; Marco, C; Gómez, M.A; Fatou, J.G. (1990) **Abs. II Congr. Lat. Amer. Polímeros**, 380
17. Haddon, R.C; Chichester-Hicks, S.V. (1989) **Macromolecules, 22**, 1027
18. Ellis, G; Hendra, P.J; Hodges, C; Jawhari, T; Jones, C.H; Le Barazer, P; Passingham, C; Royaud, I.A.M; Sanchez, A; Warnes, G. (1989) **Analyst, 114**, 1061
19. Ellis, G; Gómez, M.A; Marco, C; Fatou, J.G. (in preparation)
20. Ellis, G; Sánchez-Blázquez, A; Hendra P.J; Willis, H.A; Chalmers, J.M; Eaves, J.G; Gaskin, W.F; Krüger, K.-N. (1990) **Vibrational Spectroscopy** (accepted)
21. Louden, J.D. (1986) **Polymer Commun., 27**, 82

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