The Laser-Raman Spectra of some Nylons

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Summary Good quality laser-Raman spectra have been obtained for some nylons.

STUDY of the molecular vibrations of the nylons has been confined to the recording and interpretation of their i.r., and to a lesser extent their far-i.r. spectra.[1–3] Apart from a spectrum of nylon 66 in a review,[4] no Raman spectra for this class of polymer are available. Predictions regarding their Raman spectra have, however, been made on occasion.[5]

The general features of the i.r. spectra may be summarised as follows:

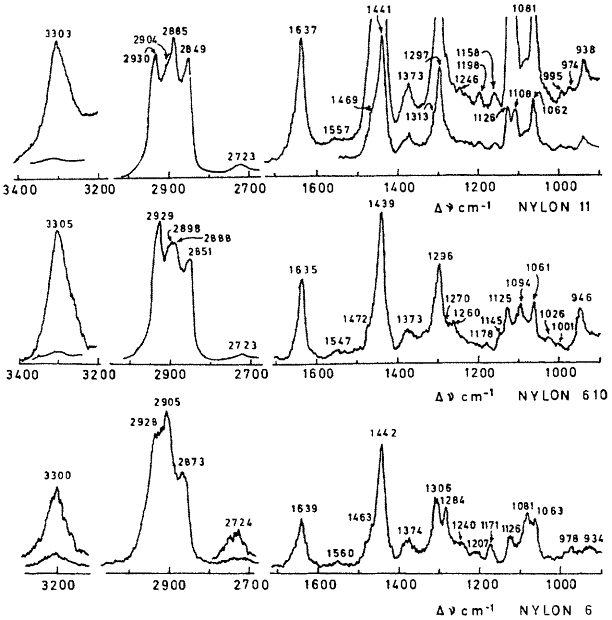
(a) The majority of the more prominent bands in the spectra are due to vibrations confined to the amide grouping, particularly 'Amide A' at *ca.* 3300 cm^{-1}, 'Amide I' at *ca.* 1650 cm^{-1}, and 'Amide II' at *ca.* 1550 cm^{-1}.

(b) Bands due to vibrations of the $[CH_2]_n$ sequence tend to be of relatively low intensity.

(c) The spectrum appears to increase in complexity with increasing $[CH_2]_n$ sequence length.

(d) The spectra change with crystalline form, and this property has particular importance in the understanding of the relation between the spectrum and polymer structure, although it has no analytical use.[6]

Although there remain serious experimental difficulties in recording adequate Raman spectra of polyamides, the use of helium–neon and argon–ion laser sources has effected something of a revolution and, with care, good spectra are now obtainable in the more favourable cases. We report spectra of nylons 6, 6·10, and 11 and demonstrate that depolarisation data can be recorded on transparent specimens and can be useful in interpreting the spectra. All the results were obtained using Spex 1401 and Cary 81L spectrometers with Spectra-Physics models 140 (argon–ion at 5145 Å) and 125 (helium–neon at 6328 Å) laser sources. Experimental details will be published elsewhere. Spectra are shown in the Figure and the depolarisation data for nylon 6 in the Table. Bands having a depolarisation ratio of 0·75 ± 0·06 were regarded as being depolarised, the remainder polarised. This rather low precision results from refractive index discontinuities in polymer specimens which tend to scramble the source radiation.



FIGURE

A number of points are evident in comparing the i.r. and Raman spectra:

(a) The 'Amide A' (ν_{NH}) and CH stretching modes appear in positions close to their i.r. counterparts, but the intensity of the ν_{NH} is very low in the Raman spectrum.

(b) Although a Raman band arising from the 'Amide I' vibration is always found at *ca.* $\Delta\nu$ 1640 cm^{-1}, it varies in intensity and is sometimes quite weak. That due to 'Amide II' is very weak and diffuse.

(c) The $[CH_2]_n$ sequence vibrations in the $\Delta\nu = 1000$—1500 cm^{-1} region give rise to Raman bands which dominate the spectrum. Comparison with polyethylene enables one to identify some of these as: $\Delta\nu$ *ca*, 1440 cm^{-1} CH_2 symmetric deformation; *ca.* $\Delta\nu$ 1295 cm^{-1} CH_2 twist; and two of the bands near $\Delta\nu$ 1100 cm^{-1} are due to carbon skeletal modes.

(d) Although there are overall similarities between the spectra of the different nylons, subtle changes in frequency occur with variations in $[CH_2]_n$ sequence length. This is particularly so for the bands primarily associated with this grouping. Further, as expected, the spectra approach that of a normal paraffin, in the region $\Delta\nu$ 1050—1600 cm^{-1}, as the value of n increases, particularly for $n > 6$.

The depolarisation results for nylon 6 are interesting when compared with those for polyethylene because there is a surprising degree of coincidence between the data for the two. The detailed interpretation of the results is very complex because polyethylene crystallises with two chains per unit cell and correlation effects are encountered. An explanation of the spectrum of this polymer will be found elsewhere,[7-9] but a summary is included in the Table.

TABLE

Polyethylene			Nylon 6		
Major lines	Depol. data	Assignment line grp.	Major lines	Depol. data	Assignment line grp.
			848 vw.	pol.	?
			934 mw.	pol.	?
			978 w.	pol.	?
1063 m.	dp.	B_{2g} skel.	1063 m.	dp.	B_{2g} Assym. skel. ν_{C-C}
			1081 s.	pol.	CN skel. ?
1130 m.	pol.	A_g skel.	1126 ms.	pol.	A_g Symm. Skel. ν_{C-C}
1170 w.	part. pol.	B_{1g} CH_2 rock.	1171 mw.	pol.	B_{1g} CH_2 rock.
			1207 w.	pol.	?
			1240 w.	pol.	?
			1284 ms.	pol.	Amide III ?
1296 s.	—	B_{3g} CH_2 twist.	1306 ms.	dp.	B_{3g} CH_2 twist.
1370 vw.	—	B_{2g} CH_2 wag.	1374 mw.	pol.	B_{2g} CH_2 wag.
1417 mw.	dp.	Overtone			
1440 m.	—	A_g CH_2 sym. def.	1442 vs.	dp.	A_g CH_2 symm. def.
1461 mw.	—	?	1463 mw.	dp.	?
			1560 vw.	pol.	Amide II
			1639 vs	pol.	Amide I.
2724 mw.	pol.	?	2724 vw.	—	
2851 vs.	pol.	A_g ν_{CH}			
2884 vvs.	dp.	?	2873	pol.	A_g CH_2 symm. stretch.
2901 s.	pol.	?	2905 s.	pol.	B_{2u} CH_2 symm. stretch.
2921 ms.	pol.	B_g ν_{CH}	2928 s.	pol.	B_g CH_2 assym. stretch.
			3300 w.	pol.	Amide A.

It is not surprising that most of the bands in the Raman spectrum of nylon 6 are polarised; this simply demonstrates that the species has a relatively low symmetry. A polarised band close to the frequency of the Amide I i.r. absorption is observed. This probably arises from a symmetrical analogue of the motion giving rise to the absorption and not to the same vibration. The strong, depolarised band at $\Delta\nu = 1442$ cm^{-1} is in excellent agreement with that found for polyethylene and confirms the suggestion made that it is associated with the CH_2 symmetric deformation.

From the depolarisation data given, and using information on polyethylene and normal-co-ordinate calculations on hydrocarbons,[10] it is reasonable to make the tentative assignments shown in the Table.

It is clear that, since it is now possible to record good Raman spectra of nylons relatively easily and also to obtain depolarisation ratios, it is worthwhile expending considerable effort on the Raman spectroscopy of Nylons. This should lead to clarification of the current somewhat tentative assignments of observed bands in the i.r. and Raman spectra to fundamental modes. This should, in turn, lead to a clearer definition of the conformation of $[CH_2]_n$ sequences. Such information has considerable importance in materials science and particularly fibre technology. From an analytical viewpoint, the new approach which this technique offers has great promise for the identification of nylon specimens and the determination of the polymorphic type.

Some of the above data on polyethylene has not been published previously. It must be regarded as preliminary and the interpretation as a little naive. Full experimental details for an assignment based on space-group vibrational characteristics will be published in the near future.

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