SHORT COMMUNICATIONS

X-RAY EVIDENCE FOR THE PRESENCE OF SINGLE CRYSTALS OF SODIUM SALTS IN KEVLAR 49 FIBRES

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IT is well-known that the high strength, high modulus fibres of Kevlar 49, [poly (*p*-phenylene terephthalamide)], have a wide range of industrial applications. Extensive data on the behaviour and properties of this fibre are available in literature[1–3]. Recently, Morgan and Pruneda[4] have shown from chemical analysis that impurities in the form of sodium salts are present in Kevlar 49 fibres and have discussed the effect of such impurities on fibre characteristics such as microvoid formation, moisture sorption, hydrolytic stability etc. In this communication, results of X-ray diffraction experiments are reported which provide further evidence for the presence of sodium salts in Kevlar 49 fibres.

X-ray diffraction pattern recorded from Kevlar 49 fibres is shown in figure 1. The pattern is obtained from an approximately 0.3 mm thick bundle of stretched fibres, in the transmission geometry, using copper Kα radiation incident normally on the fibres. The thickness of each fibre in the bundle was 10–12 μm. It is observed that in addition to the reflections from poly (*p*-phenylene terephthalamide)[5], the diffraction pattern includes a large number of randomly distributed Laue spots. Occurrence of such distinct reflections indicates the presence of some minute, single crystals distributed outside the lattice of poly (*p*-phenylene terephthalamide).

The $\sin^2\theta$ values of the Laue spots observed in figure 1 have been found to agree with those calculated for Na_2SO_4[6], Na_2SO_3[7] and Na_2CO_3[8] (table 1), thereby indicating that the single crystals included in the fibres are those of Na_2SO_4, Na_2SO_3 and Na_2CO_3. It may be pointed out that as the diffraction pattern did not include any powder lines, the sodium salts are present exclusively as single crystals. Also, the varying size of the Laue spots suggests that crystallites of different dimensions are present in the fibres. Also, the random distribution of the Laue spots observed in figure 1 indicates that the crystallites which cause them are also randomly

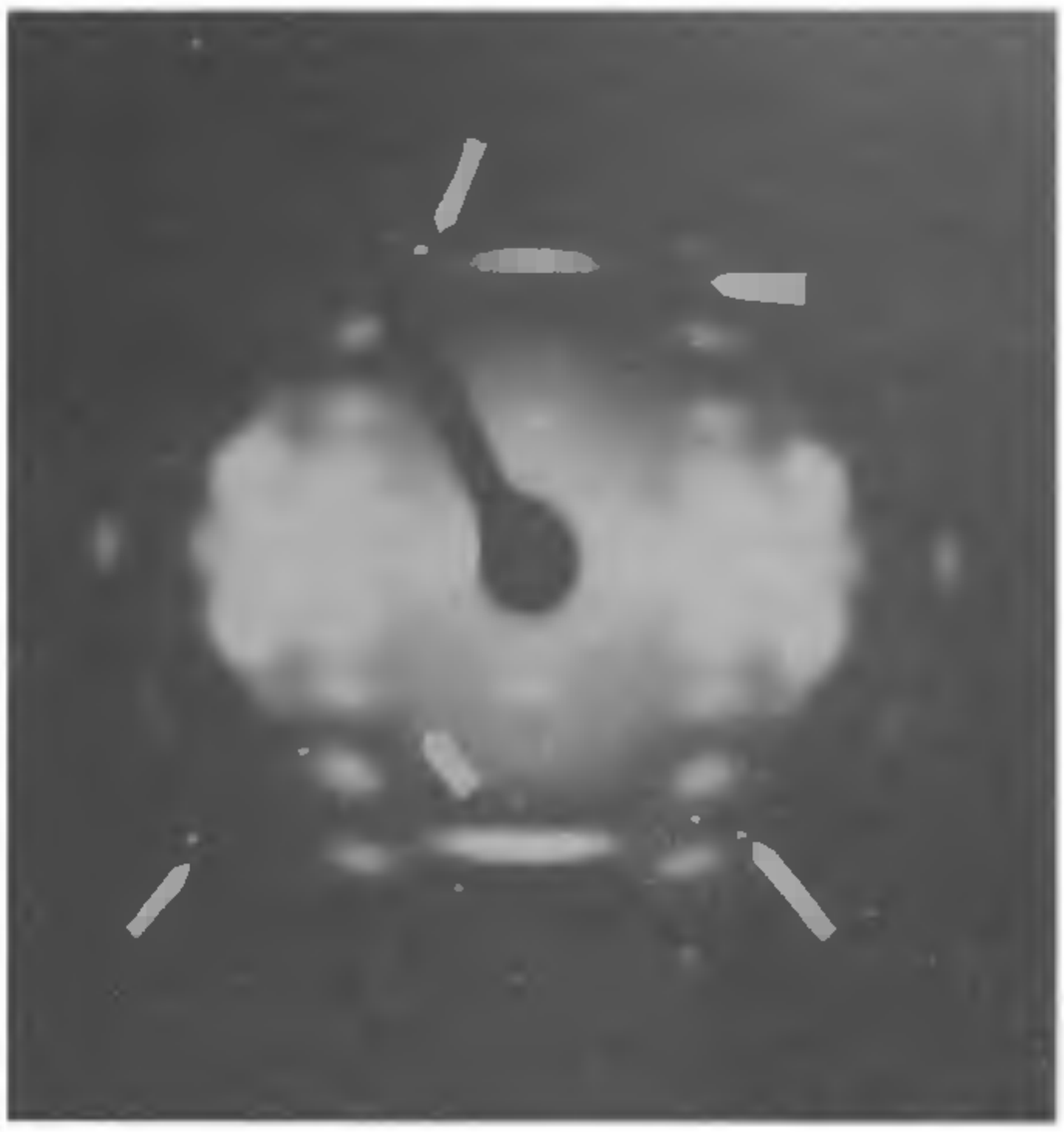

Figure 1. X-ray diffraction pattern from Kevlar 49 fibres. Some of the Laue spots from the sodium salts have been indicated by arrows.

distributed. Scanning electron microscopic examination of the fibres revealed that the outer surface of the fibres did not contain any crystallites. It is therefore likely that, the sodium salts are distributed in between the fibrils[4]. There is, however, no evidence for any periodic arrangement of the type proposed by Morgan and Pruneda[4] for the salts.

It must be emphasized that the occurrence of extra spots due to the sodium salts was not a common feature of the diffraction patterns recorded from various samples of Kevlar 49 fibres. Examination of fibres from different batches showed that in most of the fibres there was no indication of the presence of sodium salts at levels detectable by X-ray diffraction. Even among fibres which included the salts, the number of extra, Laue spots was found to exhibit a batch-to-batch variation (3–20), thereby suggesting that the amount of sodium salts included in the fibres varied from batch to batch. It is therefore suggested that for end uses which depend critically on fibre characteristics, routine X-ray examination of Kevlar 49 fibres should be carried out to check the presence and extent of possible impurities like the sodium salts.

Table 1 *Comparison of observed and calculated $Sin^2\theta$ values of the Laue spots*

$Sin^2\theta$ observed	$Sin^2\theta$ calculated	*hkl*	I/I_1 from powder data file	Salt
0 0276	0 0265	110	60	Na_2SO_4
0 0311	0.0297	020	30	Na_2SO_4
0 0417	0.0389	111	90	Na_2SO_4
	0 0420	021	90	Na_2SO_4
	0 0423	101	60	Na_2SO_3
0.0523	0.0491	002	80	Na_2SO_4
0.0639	0.0627	002	55	Na_2SO_3
0.0672	0.0677	002	90	Na_2CO_3
0.0759	0.0758	112	100	Na_2SO_4
0.0803	0.0799	110	78	Na_2SO_3
0 0859	0.0866	020	60	Na_2CO_3
	0 0859	130	90	Na_2SO_4
0.0892	0.0893	102	100	Na_2SO_3
	0.0882	$11\bar{2}$	45	Na_2CO_3
0.0914	0.0918	310	100	Na_2CO_3
0.1033	0.1058	220	80	Na_2SO_4
	0.1063	112	95	Na_2CO_3
0.1179	0.1195	040	30	Na_2SO_4
	0.1170	202	50	Na_2CO_3
0.1244	0.1251	202	20	Na_2SO_4
	0.1236	$40\bar{1}$	40	Na_2CO_3
	0.1257	$22\bar{1}$	65	Na_2CO_3
0.1329	0.1322	041	40	Na_2SO_4
	0.1348	132	30	Na_2SO_4
0.1392	0.1374	113	40	Na_2SO_4
	0.1401	023	30	Na_2SO_4
0.1555	0.1563	$40\bar{2}$ + $20\bar{3}$	35	Na_2CO_3
	0.1550	222	80	Na_2SO_4
0.1692	0.1687	042	60	Na_2SO_4
	0.1689	202	34	Na_2SO_3

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ON THE LIFETIME OF THE EXCITED STATE OF 4-METHYL-6, 7-DIMETHOXY COUMARIN

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THE fluorescence of a substance is generally more affected by its environment than the absorption[1]. The lifetime of the excited state of a fluorescent molecule in a solution shows a large dependence on the solvent environment[2], largely due to external energy loss to the solvent. The theoretical radiative lifetime τ_0 may be calculated from the integrated extinction coefficient for the same transition in absorption. Assuming a Gaussian distribution, τ_0 is given by the relation[3];

$$1/\tau_0 = 5.11 \times 10^{-9}\, n^2\, \bar{\nu}_a^2\, \sigma \epsilon_m, \qquad (1)$$

where n is the refractive index of the medium surrounding the molecule, ϵ_m the extinction coefficient at the absorption maximum, σ the half bandwidth and $\bar{\nu}_a$ the absorption maxima in cm^{-1}. The effective lifetime τ_e, the one observed experimentally, may be obtained by multiplying τ_0 by the quantum yield (q):

$$\tau_e = \tau_0 q. \qquad (2)$$

The present study was undertaken to obtain τ_0 and τ_e for 4-methyl-6, 7-dimethoxy coumarin in different polar as well as non-polar solvents.

The required coumarin was synthesized by condensation of 1, 2, 4-triacetoxy benzene with acetoacetic ester adopting a standard method[4] followed by methylation. The product was purified and checked for purity by its m. p. and TLC. All the solvents used were of analytical grade. The fluorescence emission and absorption spectra in different solvents were recorded using a spectrophotofluorometer