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The High Resolution ^{13}C NMR Spectrum of Poly(N,N'-bis(phenoxyphenyl) pyromellitimide), (Kapton)

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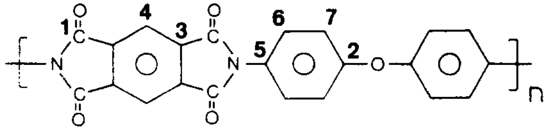
Summary

The high resolution ^{13}C NMR spectrum of Kapton in sulfuric acid solution is reported. Assignments to the spectrum were made by comparison with non-proton-decoupled spectra, and with improved solid-state spectra. The solid-state spectrum of the reprecipitate from a H_2SO_4 solution showed that no change in the chemical structure of Kapton occurred during dissolution, but that the regular morphology present in the original film had been disrupted.

Introduction

Poly(N,N'-bis(phenoxyphenyl)pyromellitimide)or Kapton (Du Pont) (I) is a polymer with a high resistance to thermal degradation(1) and to ionizing radiation(2) and maintains its high modulus and strength to high temperatures(3). The polymer is difficult to characterize due to its insolubility and infusibility; it is normally provided and used as a biaxially oriented film.



I

As part of our investigations of relationships between molecular structures of high temperature polymers and their radiation resistance we have studied changes in various properties of Kapton, e.g. volatile, small molecule products, ESR spectra and tensile stress/strain behaviour after γ-irradiation(4). ^{13}C NMR can be used to distinguish chemical changes, such as the formation of crosslinks, in irradiated polymers(4,5).

The solid-state, ^{13}C NMR spectrum of Kapton obtained by magic-angle spinning with cross-polarization has been reported by Havens et al.(6) and the five resonances which were observed have been assigned to particular carbon atoms. Unfortunately, the resonances were relatively broad and the spectrum was not well resolved.

We have obtained excellent high-resolution spectra of Kapton in concentrated sulfuric acid and have utilized the decoupled spectrum to distinguish quaternary and aromatic methine resonances, resulting in new and further assignments in the spectrum, which together with improved solid-state spectra may lead to observation of chemical changes due to irradiation.

Experimental

Kapton film (10µm thickness) was dissolved in concentrated, analytical reagent H_2SO_4 at 30°C with slow stirring for 12 hours to give an amber 1% w/v solution. A 10% solution required 40 hours for complete dissolution. The possibility of degradation of the Kapton by the H_2SO_4 was examined by measurement of the viscosity of the 1% solution in a Ubbelohde viscometer over a period of time. No significant change was observed over 48 hours and less than 10% reduction in viscosity over 200 hours.

^{13}C NMR spectra were obtained for a 10% solution of Kapton in H_2SO_4 with a JEOL FX100 spectrometer at 25 MHz and 30°C. A 90° pulse and a 5s recycle time were used, and a capillary containing DMSO-d_6 provided the lock signal. The spin-lattice relaxation times measured using the progressive saturation method were from 1-2s in duration. The Nuclear Overhauser Enhancement was approximately equal to 1.5 (max. of 3) for each carbon resonance. Resonance positions were referenced to TMS via the DMSO-d_6 signal. Spectra were recorded with proton decoupling, except for "weak-noise decoupled" spectra for which the proton irradiation frequency was shifted to 20 kHz downfield from the proton resonances. The effect of this was to broaden resonances of carbon bound to one or three protons while leaving quaternary or methylene carbon unaffected. The NMR spectrum of Kapton was unchanged after the solution in H_2SO_4 had been standing for 2 weeks.

Solid-state ^{13}C NMR spectra were obtained with a Bruker CXP300 spectrometer at 75.46 MHz by stamping out 5 mm diam. discs from film and stacking them in deuterated poly(methyl methacrylate) or boron nitride rotors. The samples were spun at the magic angle at ca. 2.5 kHz; the spinning sidebands were removed using the Dixon sequence. However, variation in the spinning frequency due to sample imbalance within the rotor gave rise to low intensity spinning sidebands which were identified by varying the spinning rate. Spectra were recorded with dipolar-decoupling and cross-polarization (contact time of 1ms), and a recycle time of 3-5s. The chemical shifts were referenced to TMS via adamantane.

Results and Discussion

The ^{13}C NMR spectrum at 25 MHz of a 10% solution of Kapton in conc. H_2SO_4 is shown in Fig. 1A. The resonances can be divided into four regions, labelled A-D from low to high field. The spectrum obtained with weak-noise decoupling of the protons is shown in Fig. 1B. The polymer contains only quaternary and aromatic methine carbons; the methine carbon resonances will be broadened and effectively disappear without full decoupling, whereas the quaternary carbons will be relatively unaffected.

It is apparent that peaks A,B,C and the two central peaks in the broad region D are due to quaternary carbon atoms. We can assign A and B to <u>1</u> carbonyl C=O and <u>2</u> C-O carbon atoms respectively, in agreement with Havens et al.(6). The relative intensities of these peaks are approximately 2:1 in agreement with the relative numbers of carbon atoms in the structure I.

It is interesting that both of these resonances are split into doublets of equal intensity with chemical shift differences of ca. 1 ppm. Similar resonance splittings observed by Close et al.(7) in ^{13}C NMR spectra of Kevlar in fuming H_2SO_4 were attributed to cis-trans conformations. Ishida et al.(8) saw broadening of IR resonances of highly amorphous Kapton films, arising from various conformations. A reasonable explanation for the twin resonances in Kapton solutions would be rotational conformations of equal energy.

The sharp resonance at 137 ppm must be due to a quaternary carbon atom from the evidence of the weakly decoupled spectrum, and therefore cannot result from <u>4</u>, the aromatic methine carbon atom of the phenyl ring situated between the two imide rings. We assign it to 3, the quaternary carbon atom adjacent to the carbonyl groups in the imide rings. There are four of these atoms, which is consistent with the intensity of the resonance.

The multiple resonance region D can be divided into two quaternary and three methine resonances. The two quaternary resonances are assigned to 5, the aromatic carbon bound directly to the imide nitrogen. Again, the quaternary resonance shows equal, doublet splittings which could be due to rotational conformers. On the basis of chemical shifts predicted from model compounds(9,10) the three protonated aromatic resonances are assigned to carbon atoms 6, 4 and 7 from low field to high field. The broadening at the extreme high field end of the spectrum is unassigned, but may be due to incipient splitting of a methine peak. The area of region D corresponds closely to 12 carbon atoms of types 4, 5, 6 and 7. The assignments of all the carbon atoms in structure I are shown in Table 1.

Table 1 Assignments of resonances in ^{13}C solution and solid-state NMR spectra to carbon atoms in Kapton (structure I).

PEAK REGION	PEAK NUMBER	NUMBER OF CARBONS	QUATERNARY OR METHINE	CHEMICAL SHIFT,PPM		INTENSITY[a]
				Soln.	Solid	
A	1	4	Q	168	165	3.9
B	2	2	Q	155	155	2
C	3	4	Q	137	137	4.4
D	4	2	M	125	128	ΣD=11.2
D	5	2	Q	125	126	
D	6	4	M	129	131	
D	7	4	M	122	119	

a, solution spectrum, relative to peak B taken as 2 carbon atoms

Fig. 2A shows the solid-state ^{13}C NMR spectrum of the Kapton film observed at 75.46 MHz. The resolution is considerably better than that reported by Havens et al.(6) but the resolution of peaks A and B into doublets is not evident and region D is only resolved into 3 peaks.

The resonance positions do not coincide exactly with the chemical shifts of the peaks in the solution spectra (Table 1). Shifts in peak positions of the order of 2-3 ppm in the solid-state spectra of semi-crystalline polymers compared with their solution spectra have been reported(11,12).

The solid-state ^{13}C NMR spectrum of the brownish-yellow powder obtained by precipitation of a 10% solution of Kapton in H_2SO_4 solution after standing for 48 hours at 30°C (the time taken to prepare and run an NMR sample), is shown in Fig. 2B. The chemical shifts of the carbon resonances are almost identical to those obtained for the original film (Table 1), indicating that the chemical structure has been unaltered by

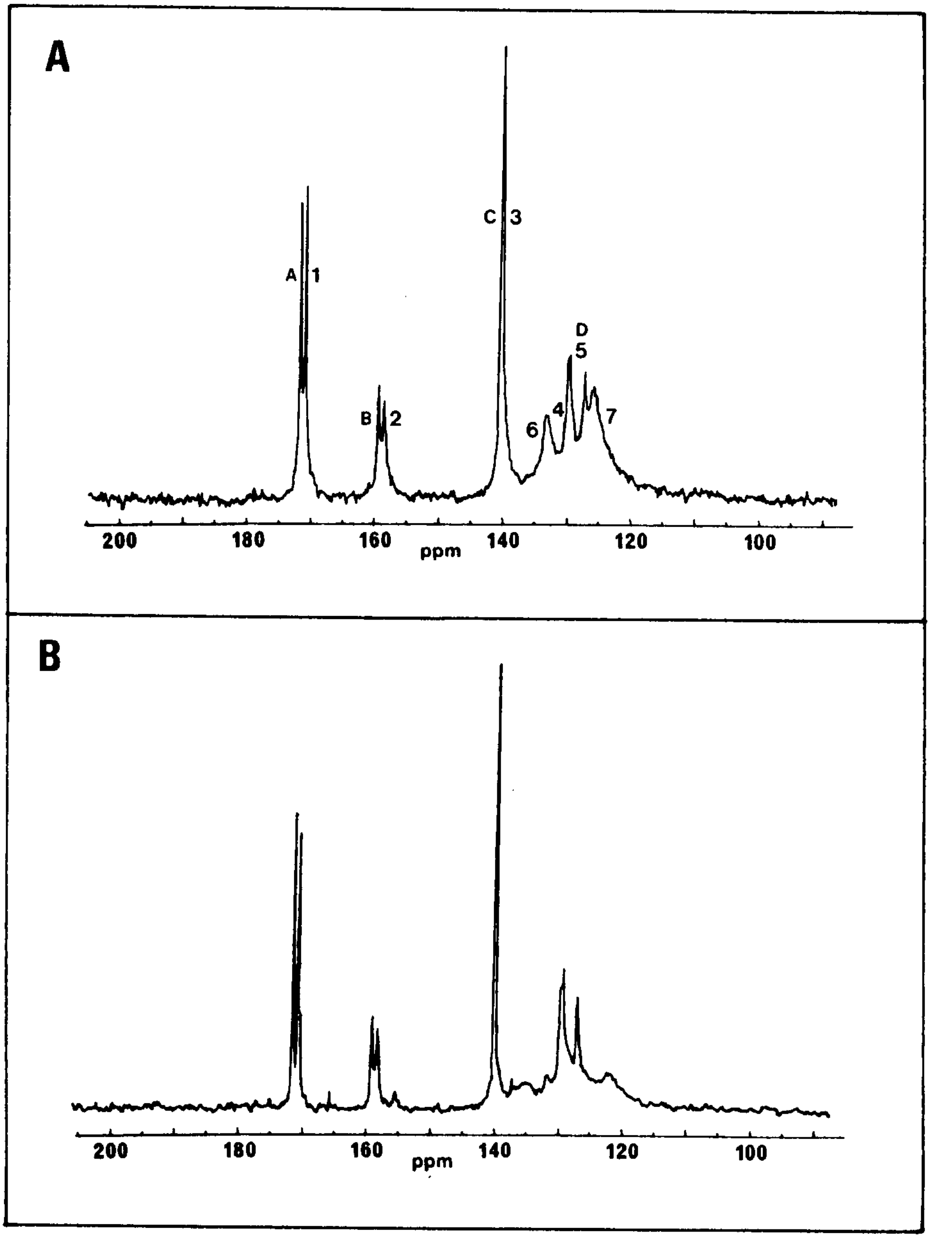


Fig.1 ^{13}C NMR spectra of a 10% Kapton solution in H_2SO_4,
(A) with complete decoupling, and (B) with weak-noise decoupling.

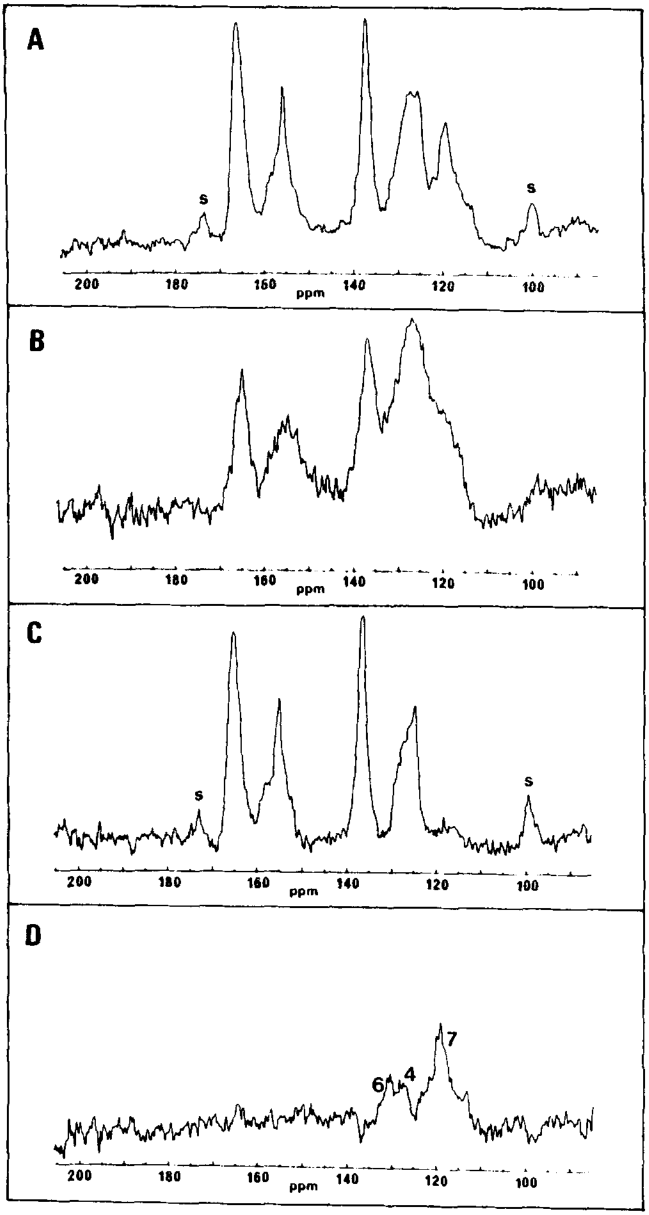


Fig.2 ^{13}C solid-state NMR spectra of (A) Kapton film, with cross-polarization; (B) Kapton reprecipitated from H_2SO_4, with cross-polarization; (C) Kapton film, quaternary enhancement; (D) Kapton film, protonated carbons only. Residual spinning sidebands are denoted by the letter S.

dissolution in conc. H_2SO_4 . Furthermore, there are no new narrow peaks in the spectrum from low molecular weight degradation products. However, increased dipole-dipole broadening would result from higher mobility, due to a lower degree of crystallinity in the reprecipitated sample. Also, the less rigid structure appears to favor cross-polarization to protonated carbon atoms relative to transfer to the quaternary carbon atoms. This is because the $1/r(CH)^6$ term ($r(CH)$ = carbon-proton distance), which affects the rate of polarization transfer(13), will show greater dependence on sample morphology (i.e. rigidity) the larger the distance of carbon-hydrogen separation.

The decreased crystallinity after reprecipitation from H_2SO_4 was confirmed by X-ray diffraction. Powder patterns of the film showed a regular repeat unit of ca. 150 nm, which corresponds to one monomer unit in an extended conformation, whereas the reprecipitated powder showed no structure, and was apparently completely amorphous. Approximately 15 wt% H_2SO_4 and 15 wt% H_2O were incorporated into the polymer after reprecipitation (determined by elemental analysis), and this would help disrupt the crystalline order.

Fig. 2C shows the solid-state NMR spectrum of the film using a "dipolar-relaxation" pulse sequence, which selectively enhances quaternary carbon resonances,and Fig. 2D is the spectrum of the protonated carbon atoms obtained by subtraction of Fig. 2C from Fig. 2A. Fig. 2C can be compared with the weak-noise decoupled spectrum (Fig. 1B) since both spectra show full intensities for quaternary carbon atoms only. They show quaternary enhancement for the same resonances. The assignments in Table 1 of resonances 4, 5, 6 and 7 in the solution spectra to quaternary and methine aromatic carbon atoms are therefore supported in the solid-state spectra (Figs. 2A, C and D).

It may be now possible to observe chemical, thermal or radiation degradation of Kapton by examination of the ^{13}C NMR spectra of the polymer in concentrated sulfuric acid, or even in the solid state.

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