A solid-state ^{13}C n.m.r. spectroscopic study of metal-containing polyimides

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Metal-containing polyimides having ionic linkages in the main chain, and their parent polyimides, were synthesized. The structures of these materials were investigated by using solid-state n.m.r. spectroscopy and some characteristic features of the ^{13}C n.m.r. spectra of the polyimides are described.

(Keywords: polyimide; ^{13}C n.m.r. spectroscopy; chemical shift)

INTRODUCTION

Polyimides were first prepared by Bogert and Renshaw[1] in 1908, and they were then widely used and rapidly developed in the early 1960s. Characterization was normally carried out by i.r. spectroscopy, on account of their insolubility. Metal-containing polyimides had also been prepared and characterized[2–4], but polyimides with metal atoms in the main chain had not been prepared as far as we were aware. We therefore prepared a series of metal-containing polyimides where the metal (e.g. Ca, Sr, Zn, Pb and Ni) is in the main chain, and characterized them by i.r. spectroscopy[5]. In this present paper, however, the structures of these polyimides were studied by solid-state ^{13}C n.m.r. spectroscopy, and some characteristic features of the spectra of these polymers are established.

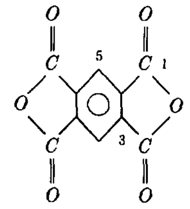
EXPERIMENTAL

The samples were prepared by using the procedures described previously[5]. The solid-state ^{13}C n.m.r. spectra were collected on a CMX-300 n.m.r. spectrometer (Chemagnetics) under the following conditions: contact time = 1.5 ms, pulse delay = 2 s and number of acquisitions = 500. For comparison purposes, the ^{13}C n.m.r. spectra of some of the samples in DMSO-d_6 were recorded with a proton noise decoupling Varian XL-200 spectrometer.

RESULTS AND DISCUSSION

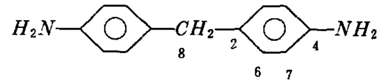
Characterization of monomers

Pyromellitic dianhydride (PMDA) (I) was characterized by ^{13}C n.m.r. spectroscopy in DMSO-d_6: the major peaks in its spectrum can be assigned as follows: C1, 161.4; C3, 137.7; C5, 121.9 ppm.



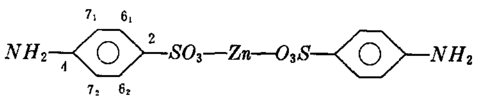
(I)

4,4′-Diaminodiphenylmethane (4,4′-methylenedianiline) (MDA) (II) was characterized by ^{13}C n.m.r. spectroscopy in DMSO-d_6: the major peaks in its spectrum can be assigned as follows: C2, 129.5; C6, 128.9; C7, 114.0; C4, 146.3; C8, 39.8 ppm.



(II)

The zinc salt of *p*-aniline sulfonic acid (ASA(Zn)) (III) was characterized by solid-state ^{13}C n.m.r. spectroscopy; the major peaks in its spectrum can be assigned as follows: C4, 145.1; C2, 137.3; C6_1, 127.3; C6_2, 129.4; C7_1, 124.7; C7_2, 121.6 ppm.



(III)

Characterization of polyimides

Parent polyimide. The parent polyimide (IV) was examined by solid-state ^{13}C n.m.r. spectroscopy in order to determine the characteristic chemical shifts. By comparison with the spectrum of the monomer, the chemical shifts of the polyimide can be assigned as follows: C1, 166.0; C2, 141 (shoulder); C3, 137.8; C4, 132 (shoulder); C5, 130.0; C6, 127 (shoulder); C7, 119.5; C8, 41.2 ppm.

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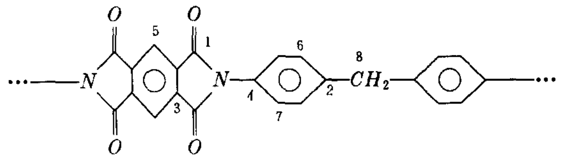
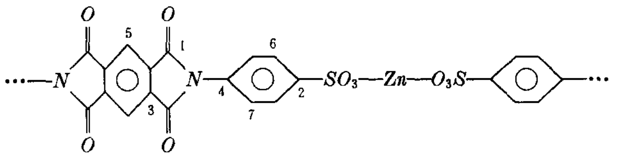


(IV)

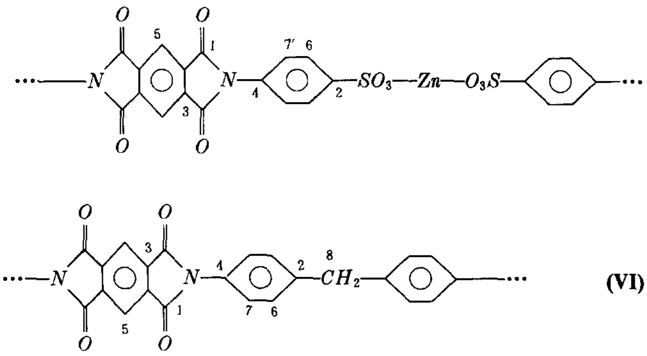
Metal-containing polyimides. By comparison with the spectrum of the parent polyimide, the solid-state ^{13}C n.m.r. spectra of the metal-containing polyimides can be determined, and their chemical shifts may be assigned respectively as follows:

(1) PI/Zn(100) (zinc-containing polyimide in which ASA (Zn) is 100 mol% in the diamine feed) (V): C1, 166.0; C2, 145.1; C3, 137.8; C4, 133.1; C5, 130.0; C6, 127.3; C7, 116.9 ppm.



(V)

(2) PI/Zn(50) (zinc-containing polyimide in which ASA (Zn) is 50 mol% in the diamine feed) (VI) (its spectrum is shown in *Figure 1*): C1, 165.4; C2, 143.0; C3, 137.8; C4, 132 (shoulder); C5, 129.4; C6, 127 (shoulder); C7, 119.0; C7′, 116.9; C8, 41.7 ppm.

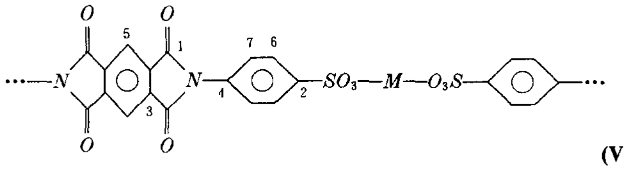


(VI)

Other metal-containing polyimides similar to PI/Zn were characterized by similar spectroscopic techniques. For polyimides where ASA(M) is 100 mol% in the diamine feed (VII), their chemical shifts, for example, can be assigned as follows:

(1) PI/Sr(100): C1, 164.9; C2, 145.3; C3, 138.3; C4, 133.0; C5 and C6, 127.9; C7, 116.4 ppm.

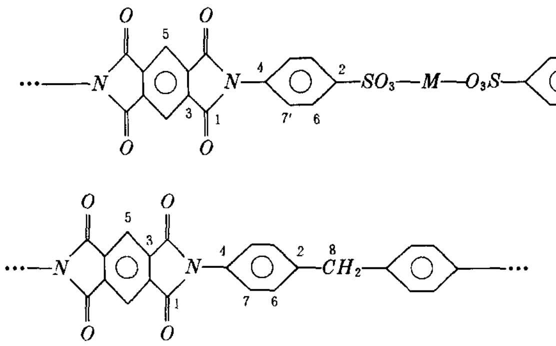
(2) PI/Pb(100): C1, 165.4; C2, 145.1; C3, 138.3; C4, 133.0; C5 and C6, 127.9; C7 116.4 ppm.



(VII)

M = Sr, Ca, Zn, Pb, Ni

For polyimides in which ASA(M) is not 100 mol% in the diamine feed (VIII) the chemical shifts are assigned as shown in *Table 1*.



(VIII)

From the analytical data presented above, some useful characteristic features of the solid-state ^{13}C n.m.r. spectra of polyimides can be established. The n.m.r. spectra of the polyimides (PIs) which are derived from pyromellitic

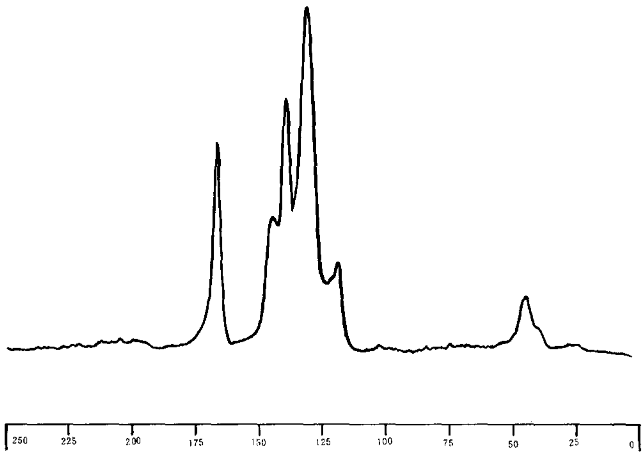


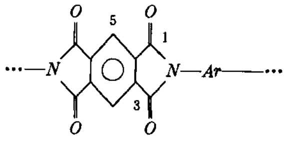
Figure 1 The solid-state ^{13}C n.m.r. spectrum of PI/Zn(5) (VI) (zinc-containing polyimide in which ASA(M) is 50 mol% in the diamine feed)

Table 1 Solid-state ^{13}C n.m.r. chemical shifts of metal-containing polyimides

Polyimide system	Chemical shift (ppm)								
	C1	C2	C3	C4	C5	C6	C7	C7′	C8
PI/Sr(50)	165.4	143.5	137.8	132.5[a]	129.4	127[a]	119.0	116.4	41.4
PI/Pb(50)	165.4	144.1[a]	137.8	132.5[a]	129.4	127[a]	119.0	116.4	41.8
PI/Ca(5)	165.4	141.4	137.3	132.5[a]	130.0	127[a]	119.0	119.0	42.3
PI/Ca(15)	166.0	142.0	137.8	132.5[a]	130.0	127[a]	118.5	118.5	42.3
PI/Ni(5)	165.4	142.5[a]	137.8	132.5[a]	130.0	127[a]	117.4	117.4	42.3
PI/Ni(15)	166.0	143.0[a]	137.8	132.5[a]	130.0	127[a]	119.0	119.0	42.3

[a] Signal appears as a shoulder

dianhydride display three characteristic chemical shifts, as follows: C1, 164–166 ppm; C3, 137–138 ppm; C5, 129–130 ppm.



(IX)

When compared with PMDA, it is found that for the polyimides the signals for C1 and C5 and shifted to low field, while that of C3 essentially remains unchanged. It is also found that the four peaks which appear at ~ 160 ppm in the spectra of the polyamide acids (because of their solubility, they are characterized by ^{13}C n.m.r. in solution) now appear as only one peak. From the spectra obtained for the various metal-containing polyimides we find that the chemical shifts of C1, C3 and C5 remain essentially constant. C7 appears in the parent polyimide and C7′ appears in PI/M(100). However, they both appear in the metal-containing polyimides in which the ASA(M) content is < 100% although these chemical shifts are then hard to resolve. This therefore shows that copolymers are formed which can be identified from the chemical shift of C2. This chemical shift shows up at ~ 141 ppm in the parent polyimide and at ~ 145 ppm in the metal-containing polyimides, but over the range 141–145 ppm in those metal-containing polyimides in which ASA(M) is not 100 mol%.

ACKNOWLEDGEMENTS

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