^{13}C n.m.r. analysis of fluorinated polyimides and poly(amic acid)s

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The fine structure of poly(amic acid) (PAA) and the structural changes caused by thermal imidization are investigated by ^{13}C n.m.r. spectroscopy of fluorinated PAA and polyimides cured under various conditions. Split signals reflecting the isomerism of PAA are assigned by measuring model compounds, and the proportions of isomeric units are estimated. Signals assigned to the end groups of PAA are found in the spectrum of samples cured at 120°C. Depolymerization at amide groups thus occurs at low curing temperatures and the molecular weight of the polymer decreases considerably. This low-molecular-weight polymer is, however, converted into high-molecular-weight polyimide by subsequent curing at 300°C. These depolymerization and polycondensation processes are also supported by measuring the viscosity of PAA and polyimide solutions.

(Keywords: ^{13}C n.m.r.; polyimide; fluorinated polymer; poly(amic acid); isomerism)

INTRODUCTION

The introduction of fluorines or fluorinated groups into the repeat unit of polyimide produces several attractive characteristics. As reported previously[1-3], the present authors have developed novel fluorinated polyimides with a diamine of 2,2′-bis(trifluoromethyl)-4,4′-diaminobiphenyl (TFDB). These polyimides have low dielectric constants, low refractive indices, low water absorption and high optical transparency. In particular, the polyimide synthesized from 2,2′-bis(3,4-dicarboxyphenyl) hexafluoropropane dianhydride (6FDA) with TFDB is soluble in polar solvents like N,N′-dimethylacetamide (DMAc), tetrahydrofuran (THF) and acetone. This is because the hexafluoroisopropyridene groups (6F-groups) bonded to the main chain make the chain packing loose. This solubility enables analysis by methods that have not been used on conventional polyimides.

The physicochemical phenomena occurring during the cure of PAA films are of special interest and have been studied mainly by i.r. spectroscopy and thermogravimetry. Young and Chang[4] have reported that the anhydride band was observed by reflectance-*FT*i.r. during imidization at a fairly low temperature. This suggests initial depolymerization of PAA, but amino groups have not yet been spectroscopically identified in the depolymerization products of PAA. This early depolymerization is very important for the curing process of PAA films. More precise information, which can be ascribed to individual atoms, is needed.

^{13}C n.m.r. spectroscopy is a powerful tool in analytical chemistry, but ^{13}C chemical shifts and their behaviour have not yet been reported for polyimides because conventional polyimides (like Dupont's Kapton) are insoluble in organic solvents. The fluorinated polyimide 6FDA/TFDB, though, is freely soluble in polar organic

solvents. In our previous study[2], ^{1}H n.m.r. spectra of 6FDA/TFDB cured at a series of temperatures were measured and imide conversion from the signal intensities of COOH protons was calculated. These measurements revealed that the imidization reaction begins at just over 70°C and is completed at about 200°C.

Furthermore, dianhydride ring-opening during acylation with diamines gives rise to isomeric chain units in the *meta*- and *para*-positions of the aromatic ring of the dianhydride moiety. Denisov *et al.*[5] used ^{13}C n.m.r. spectroscopy to observe the isomerism of PAA and estimate the proportions of isomeric units for conventional PAAs. Comparison of these proportions between PAA and model compounds gives information about the polymeric nature of PAA. (It is usually difficult to estimate the ratio of different carbons from the proton-decoupled ^{13}C n.m.r. spectra. In this case, however, only the relative proportion of the same carbon with different isomeric connectivities is discussed. For such conditions, the degree of nOe (nuclear Overhauser effect) seems to be almost equivalent for all the isomeric units, and it is possible to roughly estimate their proportions.)

In the present study, more detailed information about the molecular structure of PAAs and polyimides during imidization has been obtained by measuring ^{13}C n.m.r. spectra of fluorinated PAAs and polyimides under a series of curing conditions. The n.m.r. spectra of model compounds for PAA and polyimides were also measured.

EXPERIMENTAL

Materials

Poly(amic acid)s. The preparation of PAAs for n.m.r. measurement has been described in detail previously[2].

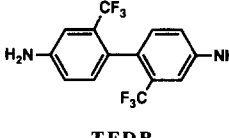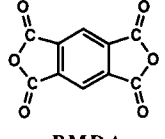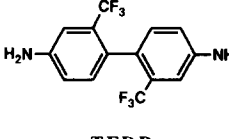**Table 1** Structures of PAAs, polyimides and model compounds
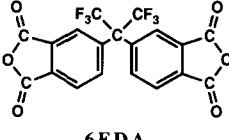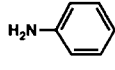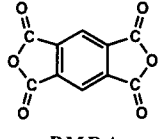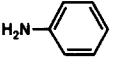
Sample	Description	Dianhydride	Diamine (amine)
6FDA/TFDB	Film	**6FDA**	**TFDB**
PMDA/TFDB	Film	**PMDA**	**TFDB**
6F-model-1 6F-model-2	Powder Powder	**6FDA**	**Aniline**
P-model	Powder	**PMDA**	**Aniline**

Table 2 Curing conditions for 6FDA/TFDB polyimide films

Abbreviation	Curing temperature and time
70°C	Same as PAA (70°C 2 h)
100°C	100°C 2 h
120°C	120°C 2 h
150°C	150°C 2 h
200°C	160°C 1 h + 200°C 1 h
250°C	160°C 1 h + 250°C 1 h
300°C	160°C 1 h + 300°C 1 h
350°C	160°C 1 h + 350°C 1 h
120 + 300°C	120°C 2 h + 300°C 1 h

Table 1 lists the structures of PAAs, polyimides and model compounds studied here. For comparison, PAA and a model compound synthesized from pyromellitic dianhydride (PMDA) were also prepared. The films of PAA for PMDA/TFDB and 6FDA/TFDB were prepared by spinning a DMAc solution onto a silicon wafer, followed by drying *in vacuo* at 70°C for 2 h. Even after vacuum drying, a small amount of solvent was retained in the films. The initial concentration of the spun solution was 15 wt% and the average thickness of PAA films was 20 μm.

Polyimides. A series of imidized samples was prepared by varying the temperature at which 6FDA/TFDB PAA films were cured. The PAA films on silicon wafers were heated under nitrogen at the temperatures listed in *Table 2* and were then slowly cooled to room temperature. The samples cured at over 200°C were first cured at 160°C for 1 h to avoid sudden evaporation of residual solvent.

Model compounds. Three kinds of model compounds were synthesized to certify the signal assignment of PAAs

and polyimides. The dianhydrides were PMDA and 6FDA, and the amine was aniline. Two diamic acid compounds, P-model and 6F-model-1, were synthesized in the same manner as PAA, but with an aniline content 20 mol% in excess of their dianhydride content. As stated below, the signals ascribed to aniline were observed in the ^{13}C n.m.r. spectra of these compounds. However, since the *m*-isomer of P-model was found to be significantly more soluble than the *p*-isomer, the proportion of isomers in these samples was maintained by not purifying them. The DMAc was removed by evacuation at 40°C for 24 h, and the absence of dianhydride and monoanhydride was verified by ^{13}C n.m.r. Another model compound of polyimide with 6FDA, 6F-model-2, was prepared by curing 6F-model-1 at 250°C for 2 h. This compound was recrystallized from acetone.

^{13}C n.m.r. measurement

^{13}C n.m.r. spectra at 100.63 MHz were measured at room temperature with a Bruker MSL-400 spectrometer. Films of PAA and polyimide were removed from the silicon wafers and dissolved to a concentration of 6 wt% in deuterated dimethylsulphoxide (DMSO-d$_6$). The powdered samples of model compounds were also dissolved in DMSO-d$_6$. The repetition time for n.m.r. measurement was 10 s and the ^{13}C chemical shift was directly read off from internal tetramethylsilane (TMS). DEPT (distortionless enhancement by polarization transfer) sequence n.m.r. measurement, which observes only the signals originating from protonated carbons, was made for all samples. This method was very helpful for assigning signals in the complicated spectra of PAAs. A value of 155 Hz was used as a C–H coupling constant for phenyl groups.

Viscosity measurement

Solution viscosity coefficients were measured at room temperature with a rotation viscometer (Tokyo Keiki, E-type). Films of PAA and polyimide were removed from the silicon wafers and dissolved in DMAc to a concentration of 15 wt%.

RESULTS AND DISCUSSION

A model compound and PAA derived from PMDA

Figures 1 and *2* show 100.63 MHz ^{13}C DEPT and proton-decoupled n.m.r. spectra of the phenyl region (from 110 to 145 ppm downfield from TMS) for P-model, PMDA/TFDB PAA, TFDB (diamine) and PMDA tetracarboxylic acid (pyromellitic acid, PMTCA). In the proton-decoupled spectra (*Figure 2*), assignments of the signals observable in the DEPT spectra (*Figure 1*) are not indicated. *Figure 3* shows the isomeric structures and numbering of the carbons at the PMDA moiety. In the spectra of the P-model and PMDA/TFDB PAA, the protonated carbons 2 and 5 split into three peaks, and the non-protonated carbons (1, 3, 4 and 6) are split into four peaks. This reflects the isomerism of the PMDA moiety, where the chemical shift differences between model compound and PAA were less than 1 ppm. In assigning these split peaks, we considered the substituent shifts produced by $-CONHC_6H_5$ and $-COOH$ groups and the empirical fact that substituent shifts at the *meta*-position of aromatic rings are relatively small for these groups. This assignment is in accordance with the peaks for Kapton-type PAA observed by Denisov *et al.*[5]. The ^{13}C chemical shift displacements caused by the polymerization of dianhydride and diamine (acylation) are listed in *Table 3*.

Although the signals from residual aniline overlap, the signal intensity estimation for carbons 3 and 6 (*Figure 2*) shows dominance of the *m*-isomer in P-model. This indicates the inherent preference for the *m*-unit in the PMDA moiety. On the other hand, no significant difference was observed between *m*- and *p*-units in
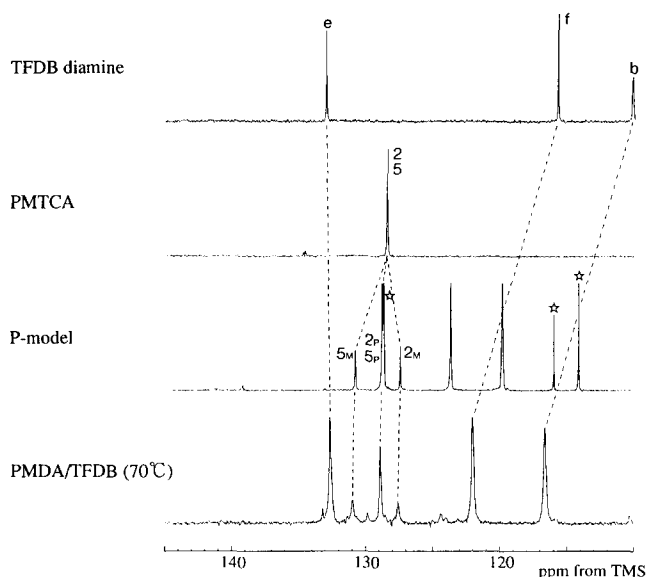

Figure 2 100.63 MHz ^{13}C proton-decoupled n.m.r. spectra of TFDB diamine, pyromellitic acid, P-model and PMDA/TFDA PAA
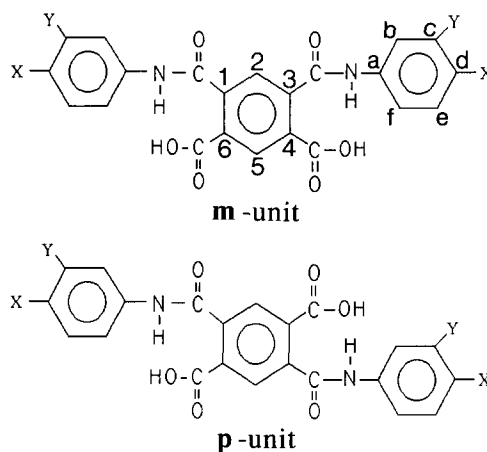
Figure 3 Isomeric structures of the PMDA moiety in PMDA/TFDB PAA and P-model

PMDA/TFDB PAA. The relative dominance of the *p*-unit in polymeric chains can be explained by the steric effect. As shown in *Figure 3*, the molecular structure around the PMDA moiety is congested and the permitted conformation for PAA is more restricted. In particular, two amide bonds connected to PMDA aromatic ring always take the *trans*-conformation, and amide and carboxylic groups of PAA form intramolecular or intermolecular hydrogen bonds with solvent. In such a condition, a *m*-unit is more likely than a *p*-unit to cause steric hindrance in a polymer chain.

Model compounds, PAA and polyimides derived from 6FDA

Figures 4 and *5* show 100.63 MHz ^{13}C n.m.r. spectra for the phenyl region of 6F-model-1, 6FDA/TFDB PAA, 6FDA/TFDB polyimide, 6F-model-2 TFDB, 6FDA tetracarboxylic acid (2,2'-bis(3,4-dicarboxyphenyl)hexafluoropropane, 6FTCA) and 6FDA. *Figure 6* shows the isomeric structures and the numbering of carbons at the 6FDA moiety. The ^{13}C chemical shift displacements

Figure 1 100.63 MHz ^{13}C DEPT n.m.r. spectra of TFDB diamine, pyromellitic acid, P-model and PMDA/TFDA PAA. Signals from residual aniline are marked with stars. P and M correspond to *p*- and *m*-isomeric units
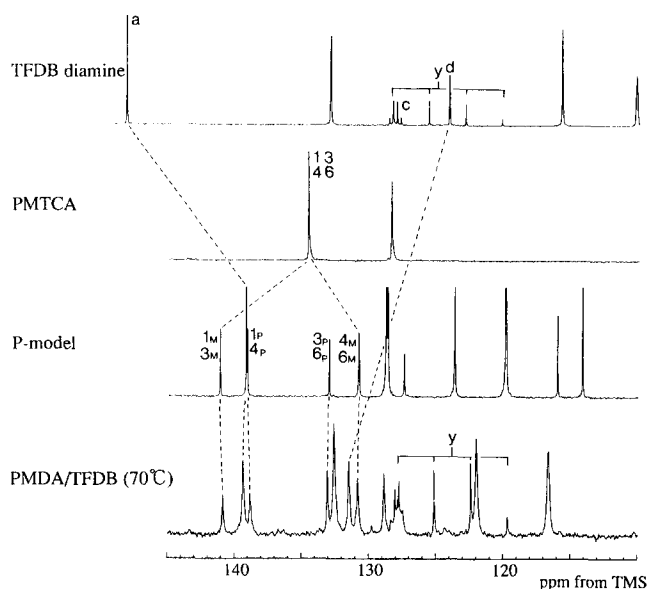
Table 3 ^{13}C chemical shift displacements[a] caused by acylation for diamic acid compounds and PAAs

Dianhydride moiety	1	2	3	4	5	6
P-model *m-*	+3.6	+5.7	+3.6	−6.7	+9.0	−6.7
PMDA/TFDB *m-*	+3.4	+5.7	+3.6	−6.7	+9.0	−6.7
P-model *p-*	+1.5	+7.0	−4.6	+1.5	+7.0	−4.6
PMDA/TFDB *p-*	+1.4	+7.0	−4.4	+1.5	+7.2	−4.4
6F-model-1 *m-*	−3.6	+2.6	+6.7	−1.7	+4.5	−6.6
6FDA/TFDB *m-*	−3.3	+3.0	+6.4	−2.3	+4.9	−6.8
6F-model-1 *p-*	−5.9	+4.9	−2.2	+7.3	+2.6	−3.9
6FDA/TFDB *p-*	−5.5	+5.0	−2.3	+6.9	+2.8	−3.6

Diamine moiety	a	b	c	d	e	f
P-model	−9.4	+5.8	0.0	+7.5	0.0	+5.8
PMDA/TFDB	−8.9	+6.3	−0.4	+7.2	−0.5	+6.1
6F-model-1	−9.2	+5.6	−0.1	+7.7	−0.1	+5.6
6FDA/TFDB	−8.8	+6.2	−0.3	+7.2	−0.4	+6.0

[a]Chemical shift displacement is the difference between the chemical shift of PAA or diamic acid and those of dianhydride or diamine. Plus and minus values correspond to deshielding and shielding shifts, respectively
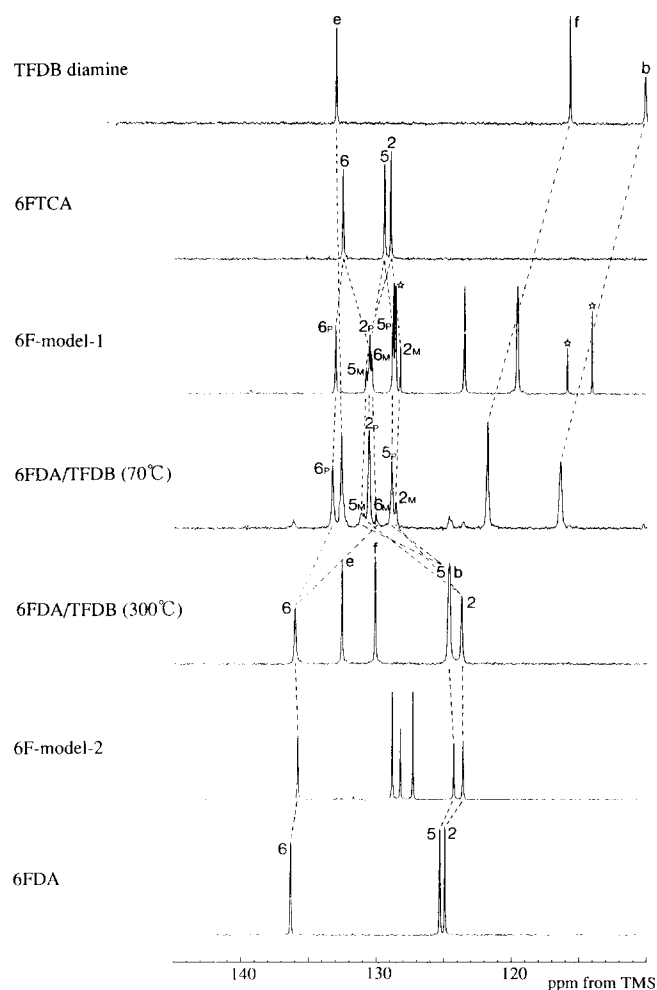

Figure 4 ^{13}C DEPT n.m.r. spectra of TFDB diamine and the samples derived from 6FDA

Figure 5 ^{13}C proton-decoupled n.m.r. spectra of TFDB diamine and the samples derived from 6FDA

m-unit m-unit

m-unit p-unit

p-unit p-unit
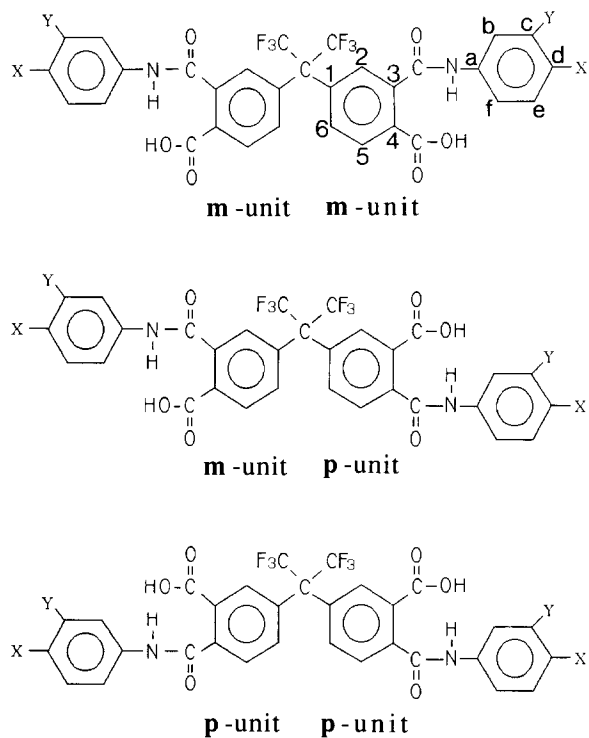
Figure 6 Isomeric structures of 6FDA moiety in 6FDA/TFDB PAA and 6F-model-1

caused by acylation and imidization of these samples are also listed in *Tables 3* and *4*. The differences of ^{13}C chemical shift between model compounds and polymers are very small.

Although there are three kinds of isomeric structure for the 6FDA moiety, each of the carbon 1–6 signals is split into two peaks (*Figure 4*). This indicates that [13]C
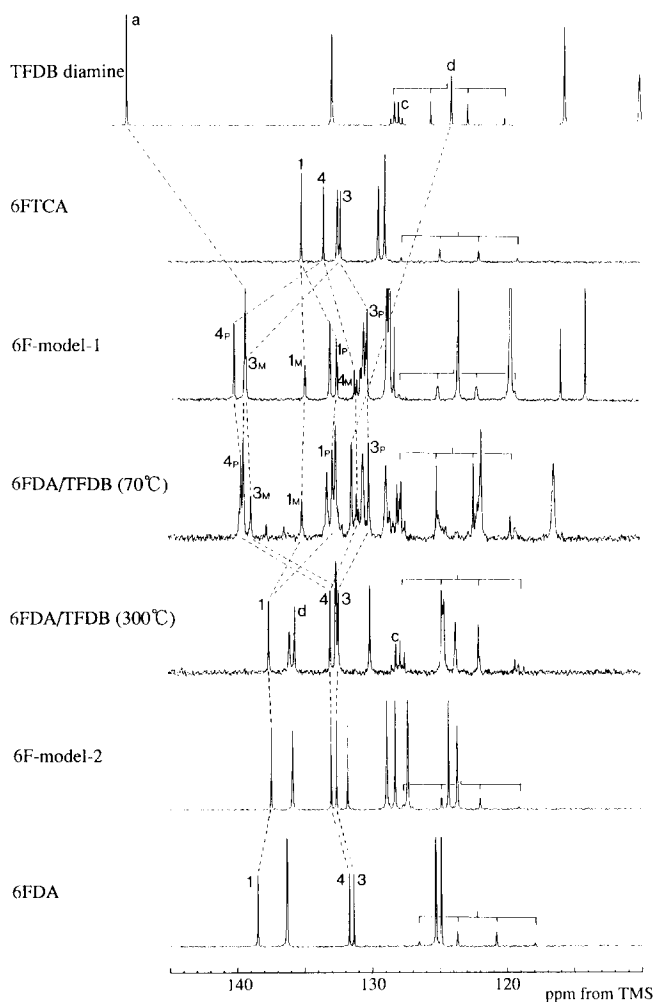
Table 4 ^{13}C chemical shift displacements caused by imidization for imide compound and polyimide

Dianhydride moiety	1	2	3	4	5	6
6F-model-2	−1.0	−1.9	+0.1	+0.2	−1.9	−1.0
6FDA/TFDB	−0.9	−1.9	+0.1	+0.2	−1.6	−0.9

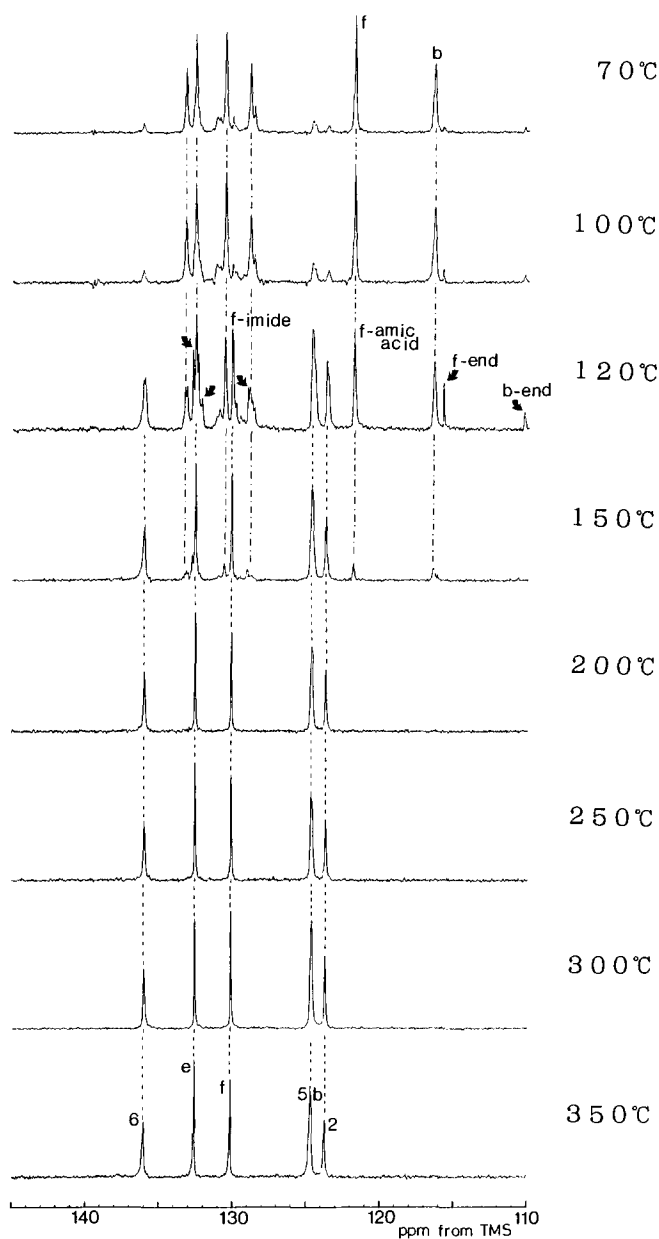| Diamine moiety	a	b	c	d	e	f
6F-model-2	−16.7	+13.4	+0.2	+13.0	+0.2	+13.4
6FDA/TFDB	−15.9	+14.3	−0.3	+11.3	−0.6	+14.2

Figure 7 ^{13}C DEPT n.m.r. spectra of 6FDA/TFDB samples cured at various temperatures. The -amic acid, -imide, and -end signals correspond to those of PAA, polyimide and end groups, respectively

n.m.r. signals reflect only the isomerism of half the 6FDA moiety. In the spectrum of 6F-model-1, the proportions of isomeric units were estimated by signal intensities of carbon 1, to which the *p*-unit contributes twice as much as the *m*-unit. For other signals as well, *p*-unit signals are always more intense than *m*-unit signals. Furthermore, the *p*-unit also dominates in the spectrum of 6FDA/TFDB

PAA. Hence 6FDA inherently prefers the *p*-isomeric unit and the acylation does not influence the proportion of *p*- and *m*-units. This can be ascribed to the bi-aromatic ring structure of 6FDA, in which steric hindrance between two amide bonds is unlikely.

The absence of isomerism in 6F-model-2 and 6FDA/TFDB polyimide, on the other hand, made it easy to assign their n.m.r. signals. The displacements of the ^{13}C chemical shift of the 6FDA moiety between imide compounds and their respective dianhydrides are less than 2 ppm, which indicates similarity of the electronic structure of the anhydride and imide groups. But acylation and imidization induce large displacements of the ^{13}C chemical shift for diamine carbons, except for the *meta*-position of nitrogen-bonded carbon (denoted by c and e). For diamine carbons, the displacements caused by imidization were twice as large as those caused by acylation.

Analysis of PAA curing process

Figures 7 and *8* show [13]C n.m.r. spectra of 6FDA/TFDB cured under different conditions. In these figures, it is possible to follow the chemical structural change caused by imidization. As reported previously[2], a certain fraction of PAA is imidized during the drying process. Small peaks originating from polyimide are thus
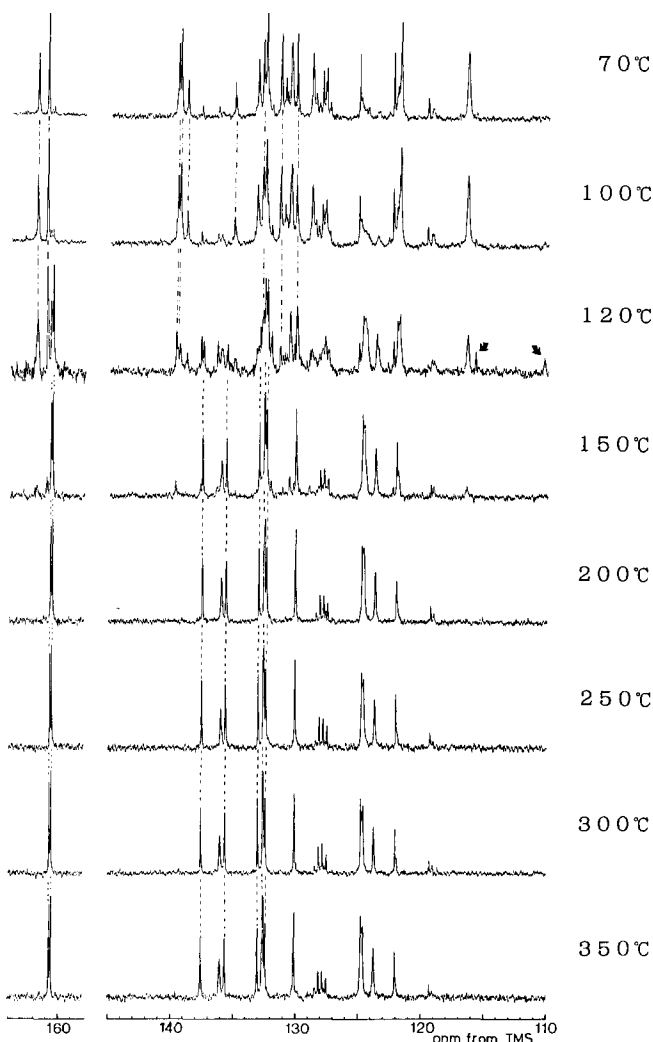
Figure 8 [13]C n.m.r. proton-decoupled spectra of 6FDA/TFDB samples cured at various temperatures
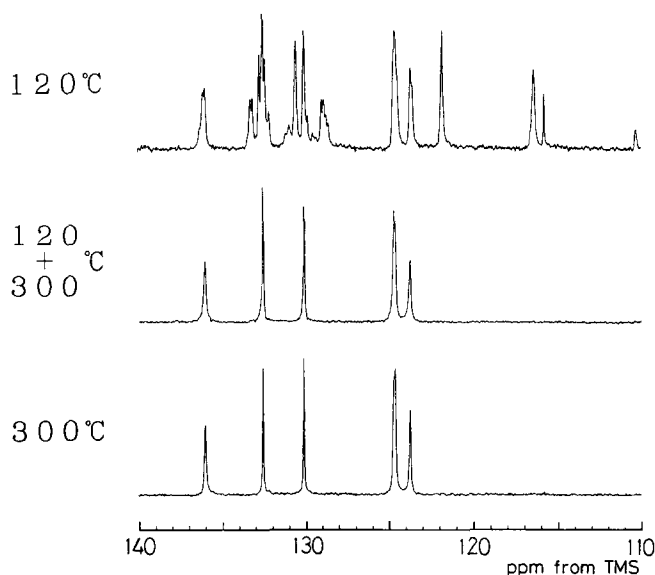
Figure 9 ^{13}C DEPT n.m.r. spectra of 6FDA/TFDB samples of 120°C, 120 + 300°C and 300°C

Figure 10 Viscosity coefficients of 15 wt% DMAc solutions of 6FDA/TFDB (cured as for n.m.r. measurements)

seen in the 70°C sample. Significant changes are caused by imidization at 120°C, and the spectra for those samples are more complicated, with imide and PAA signals overlapping. It is worth noting that new signals, which do not originate from PAA or polyimides, appear in the spectra of the 120°C sample. Compared with *Figure 4*, the chemical shifts of the two signals resonated at right (f-end and b-end) and those of the three signals in the centre (arrows) were exactly the same as those of TFDB and 6FTCA, respectively. These signals are therefore assigned to the end groups of PAA. This means that depolymerization of the PAA main chain had occurred at this temperature and the molecular weight of PAA was considerably decreased. Comparison of the signal intensities of carbon-f, which for PAA, polyimide and the newly observed signal are about 45, 45, and 10%, respectively, suggests that polymer chains were scissored roughly every 10 repeat units. This result coincides fairly well with the reflectance *FT*i.r. for conventional polyimides, in which there is at most one anhydride group for each four to five polymer repeat units[4]. The reason that carboxylic acid carbons rather than dianhydrides are observed in the n.m.r. spectra could be that small amounts of water in the solvent hydrolysed terminal anhydride groups. It is also possible that the water molecules formed by the imidization reaction caused hydrolysis. Depolymerization is also indicated by the fact that the 6FDA/TFDB films cured at 70°C (PAA) and at over 200°C were tough and flexible, whereas the film cured at 120°C was brittle and had many cracks.

The ^{13}C n.m.r. spectrum of the 120 + 300°C sample, on the other hand, was identical to that of the 300°C sample (*Figure 9*). This indicates that the low-molecular-weight polymer generated by low-temperature curing was converted into a high-molecular-weight polyimide by subsequent high-temperature curing.

As seen in *Figures 7* and *8*, the imidization reaction was completed at 200°C and no significant differences are seen between the spectra of samples cured over 200°C.
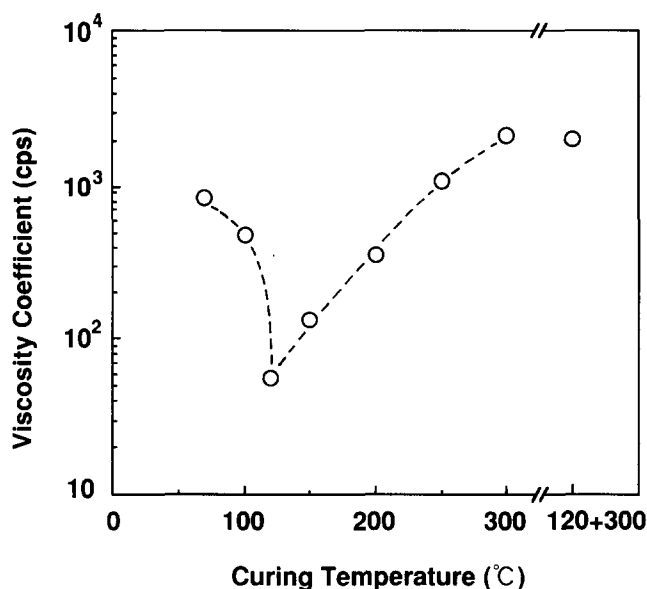
Side reactions, such as cross-linking or degradation, therefore did not occur at temperatures below 350°C. The solubility of the sample cured at 350°C, however, was different from that of samples cured at lower temperatures. All samples cured below 300°C were dissolved in DMSO-d$_6$ at ambient temperature, but the 350°C sample could only be dissolved at 100°C. Since the glass transition temperature (T_g) of 6FDA/TFDB polyimide is about 320°C[2], the aggregation form of the polyimide molecules may change above T_g.

Figure 10 shows the viscosity coefficients of 15 wt% DMAc solutions of 6FDA/TFDB cured under the same conditions as the samples for n.m.r. measurements. Owing to the low solubility of the 350°C sample, its viscosity coefficient was not measured. The low viscosity of the 120°C sample is consistent with the depolymerization at the PAA amide group and decrease of molecular weight that were identified in the n.m.r. analysis. Viscosity increases monotonically with curing temperatures from 120°C to 300°C. This shows that the polycondensation reaction proceeds and the molecular weight of polyimide increases even after imidization is completed (at 200°C). Furthermore, the similarity of viscosity coefficients for 300 + 120°C and 300°C samples also supports the effect of subsequent high-temperature curing that was observed by n.m.r.

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