An ESR Study of The Film Formation Steps of Vapor Deposition Polymerization of Polyamic Acid

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SYNOPSIS

A film of polyamic acid is formed by vapor deposition polymerization of pyromellitic dianhydride (PMDA) and 4,4'-diaminodiphenyl ether (ODA). We have taken ESR spectrum during the polymerization process and compared it with the ESR spectrum of films obtained from solution polymerization. In the intermediate polymers during vapor deposition polymerization, the amide bond (—CONH—) is coplanar with the benzene ring and two protons in the PMDA molecule. This intermediate polymer has one unpaired electron that interacts with the two nitrogen nuclei equally. On the other hand, in the polymer obtained by solution polymerization, the amide bond and the benzene ring of PMDA are not coplanar. In this polymer, too, some of the molecules have an unpaired electron that seems to have almost no coupling with NH groups. These results imply that the polymer formation via vapor deposition proceeds through different intermediates and different molecular configurations from that via the solution process.

1. INTRODUCTION

When pyromellitic dianhydride (PMDA) and 4,4'-diaminodiphenyl ether (ODA) are codeposited from the vapor phase in vacuum,[1,2] they polymerize on the substrate and form a film. In previous studies, we have reported on the basis of microscopy and IR spectroscopy that the monomer molecule migrates on the substrate and the polymerization reaction starts immediately after vapor deposition. On the basis of electronic spectrum, it was found that the charge transfer complex is formed in the polymerization process and that by ESR spectrum free radical species were detected in the film.

The purpose of the present report is to elucidate the species by ESR spectra observed from the film, which was obtained with the vapor deposition polymerization, and to compare the results with the data of the intermediate obtained in the PMDA–ODA complex in solution polymerization.

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2. EXPERIMENTAL

2.1. ESR Measurement of the Film Formed by Vapor Deposition Polymerization

The details of the vapor deposition polymerization apparatus are described elsewhere.[1,2] The rough description of the deposition chamber is as follows: The substrate was held at the upper central part of the chamber. The materials that were vaporized, PMDA and ODA, had been kept in the raw material vessel located at the bottom of the chamber. These vessels were heated with halogen lamps. The timing of vaporization and the quantity of vaporized materials were controlled by the shutter placed over the vessels and by the temperature attained by the radiation of the halogen lamps. In the present experiment, 100 mg each of PMDA and ODA were stored in each vessel. The substrate had 200 cm^2 of surface area to which PMDA and ODA were deposited at the rate of 0.8 mg/min. The growing rate of the polymer film was 400 Å/min. After 50 min of vapor deposition, a 2 μm thickness of polymer film was formed, the weight of which is ca. 40 mg. ESR

spectrum of the film was measured 90 min after vapor deposition.

2.2. ESR Measurement of the Intermediate Formed by Solution Method

Since dimethylacetamide (DMAc) has a high dielectric constant due to the presence of $-C=O-$ (NMe$_2$), the ESR spectrum could not be measured in a conventional quartz tube of 5 mm diameter. Therefore, the following three methods were employed for the measurement.

2.2.1. Method Using a Thin Sample Tube

A sample consisting of PMDA (30 mg) and ODA (30 mg) was grounded well and was placed in a sample tube of 2 mm diameter. DMAc and the sample tube were connected to a vacuum line, and the DMAc was distilled, after degassing of PMDA and ODA, into the sample tube under vacuum. To assist the solubilization of PMDA and ODA, the sample tube was heated with steam. The measurement was undertaken after PMDA and ODA powders were dissolved completely.

2.2.2. Method by Which DMAc Is Removed after Dissolution and Polymerization

A sample consisting of 50 mg PMDA and 50 mg ODA was placed into a sample tube with a diameter of 5 mm. The solvent, DMAc, was added to it. To get polyamic acid, both PMDA and ODA must be dissolved with DMAc. Therefore, this sample tube was heated with steam as described in the previous section. When PMDA and ODA completely dissolved, the sample tube was sealed off from the vacuum line. Then, this sample tube contained PMDA, ODA, and DMAc at its bottom end and nothing at its top end. Then, when the top end of the sample tube was cooled with liquid nitrogen, only the solvent DMAc evaporated and condensed at the cooled end of the tube, leaving a thin film of polyamic acid at the bottom end after 3 h. By sealing off the DMAc section of the sample tube, a dry sample of polyamic acid was obtained, which was used for ESR measurement.

2.2.3. Method by Which the Paramagnetic Intermediates Are Collected on Silica Gel

PMDA (2.9 mg) was dissolved completely in 10 mL of DMAc at 80°C, and 2.3 mg of ODA was dissolved in 10 mL of DMAc. Both solutions were mixed and heated at 100°C for 1 h. A pale brown color appeared

in the solution, and an absorption spectrum was observed. Then, 1.0 g of silica gel was added to the solution to trap the colored substance formed. This silica gel was dried under reduced pressure (0.01 Pa) for 5 h, then dried under vacuum (0.013 Pa) for 1 h and used for the ESR measurement.

2.2.4. NMR and IR Experiments to Detect the Radical Type Intermediates

It would be desirable to observe the radical-type intermediate polymers, which have been detected and recorded by the ESR method, by some other methods. As such candidates, NMR and IR techniques might be nominated. The present authors have tried to detect and establish structural parameters of the radical-type intermediate polymers by IR and NMR methods. The difficulties encountered in this trial have been the sensitivity and selectivity of these methods. The number of radical polymer is some 10^{15}/g and is mixed with non-radical-type polymers. The ESR method detects only the paramagnetic polymer, but IR and NMR methods detect all the polymers alike. In other words, the spectrum of 10^{15} radicals mixed with that of 3×10^{21} nonradicals must be separately detected. For this reason, detecting the radical-type intermediate polymers by IR and NMR methods has not been successful.

3. RESULTS AND DISCUSSION

3.1. Analysis of ESR Spectrum Observed in the Vapor Deposition Polymerization Process

The ESR spectrum due to free radical (paramagnetic ions) species formed upon vapor deposition polymerization is shown in Figure 1. The spectrum con-
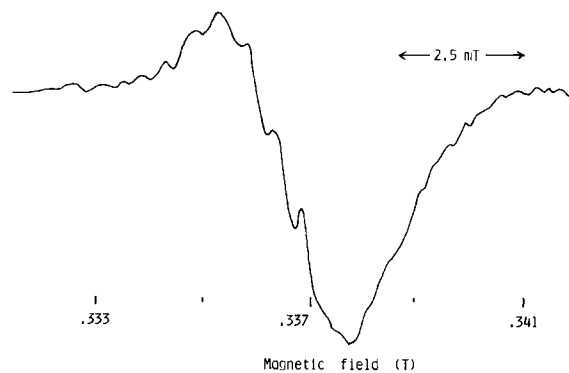

Figure 1 ESR spectrum of the film during the formation step of polyamic acid by the vapor deposition polymerization method. The center is at g = 2.004.
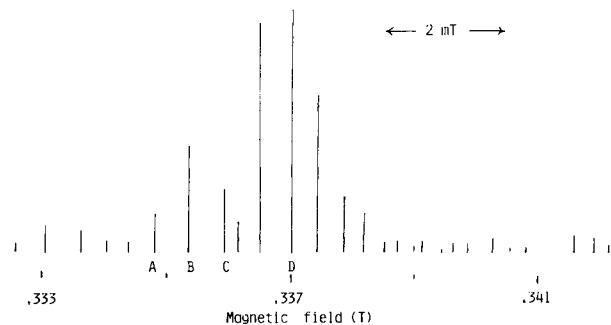
Figure 2 Approximate stick spectrum of the component having an hfs in Figure 1.

sists of two components, one having hyperfine structure and another having no structure. The resonance positions of the spectrum component for hyperfine structure is shown in Figure 2.

Focusing on the absorption lines, A, B, C, and D in Figure 2, and neglecting the lines at the higher magnetic field side (the right-hand side of the spectrum might have larger line widths than does the left-hand side of the spectrum[3]), the spectrum in Figure 2 may be regarded as consisting of several groups of triplet lines such as (A-B-C). The number of triplet groups seem to be five, each group having a group intensity ratio of $1 : 2 : 3 : 2 : 1$. This understanding gives a typified spectrum as shown in Figure 3. A simulation spectrum may be drawn as shown in Figure 4, assuming that the spectrum has a Lorenzian shape with a half-width of 0.2 mT. A local averaging procedure (smoothing) made with Figure 1 gave Figure 5. The composite spectra (named spectrum C) were computed from two spectra, Figure 4(f) and Figure 5(b) as component spectra, according to the equation, $c = f + x \cdot b$,
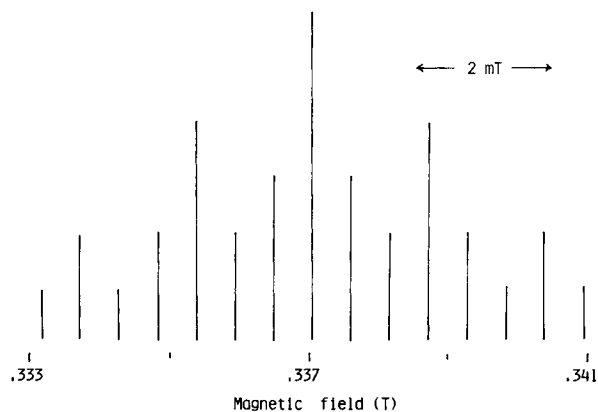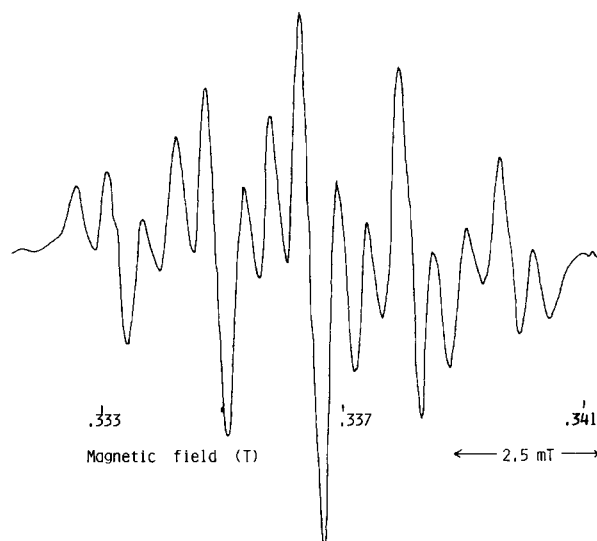
Figure 4 The first derivative ESR spectrum obtained by a simulation using the resonance positions of Figure 3 and a half-width of 0.2 mT; Lorenzian function was used.

varying x values from 1 to 10. The solid line in Figure 6 is a spectrum with $x = 6.0$. The dotted line is identical to Figure 1. On the left-hand side of the spectrum, the peak positions of both solid and dotted lines are found to coincide fairly well. On the right-hand side, the maximum and minimum positions of the curves appear at identical positions, but the dotted curve has a smaller amplitude of variation. This may be caused, though not yet verified, by the spectrum of Figure 1 having a broader line width at the higher magnetic field side. From the above results, it appears that the unpaired electron spin has an interaction with two protons and two nitrogen nuclei.

We propose that the structure of the intermediate formed during the polymerization is that of Figure
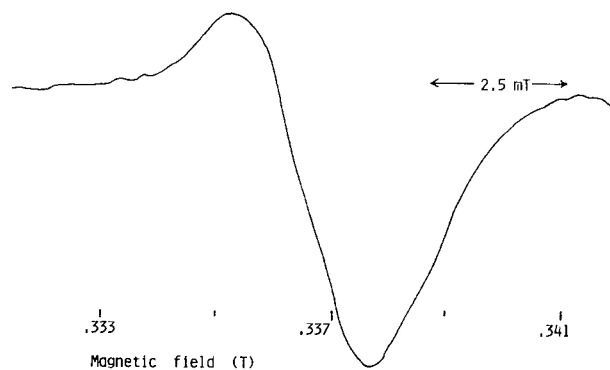
Figure 3 Calculated spectrum focusing on A, B, C, and D in Figure 2 (stick spectrum).

Figure 5 Structureless component obtained by the smoothing of Figure 1.
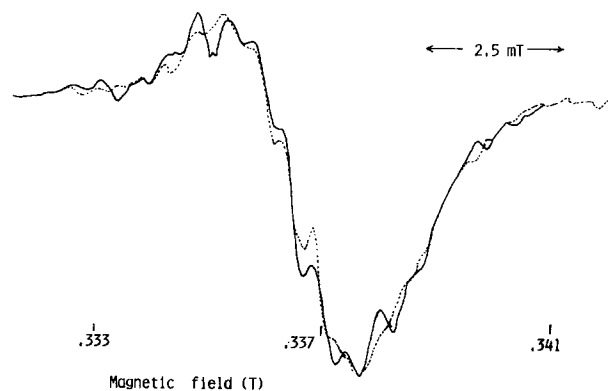
Figure 6 Synthetic spectrum (solid line), which composes 1.0-fold of the spectrum in Figure 4 and 6.0-fold of the spectrum in Figure 5. The spectrum identical to the one in Figure 1 (dotted line) is also shown for comparison.

7. The spin densities at C_1 and C_2 are 0.25, and the remaining spin densities are mostly on N_1 and N_2 atoms (1.68 mT). At N_1 and N_2 nitrogen atoms, the unpaired spin does not polarize NH bond orbitals, and, therefore, the couplings between the unpaired electron and the NH protons are small. The structure of $-C_6H_4NH_2^+$, part of the charge transfer complex, proposed in Figure 7, resembles the methoxyaniline cation radical, the nitrogen splitting value of which may be somewhere in the range of 1.1–1.4 mT depending on the solvent in which it is formed.[4] Then, the obtained nitrogen splitting value of 1.68 mT deviates too much from the value expected from the proposed structural formula. This may indicate also that the orbital of unpaired electron on the N

atom has a large s-character. Therefore, the most probable electron deficient parts are at nitrogen atoms.

3.2. Analysis of the ESR Spectra Observed from the Polymer Obtained by Solution Polymerization

PMDA and ODA react in a DMAc solution to give polyamic acid. Some intermediates are supposed to be formed during the reaction. Figure 8(B) is the ESR spectrum measured by using a 2 mm diameter sample tube to observe this intermediate. Figure 8(A) is a signal obtained with an empty sample tube. Figure 9 is the ESR spectrum measured when DMAc was removed from the polymer solution after reaction of the solutes. Figures 8 and 9 are clearly different from the ESR of the radical in the vapor deposition film. Although the relative intensity ratios are slightly different between Figures 8 and 9, each is composed of two lines whose splitting constant is 0.1 mT or whose g-difference is 0.003. Figure 10, top, is the absorption spectrum of the charge transfer complex of PMDA and ODA in DMAc. Figure 10, bottom, is the ESR spectrum of the same solution adsorbed on the silica gel surface, which was then dried in vacuum. The spectrum indicates a triplet hyperfine structure due to the coupling with a nitrogen nuclei, whose coupling constant is considerably large: 5.48 mT.

The simplest interpretation may be shown as Figure 11 for the cases of Figures 8 and 9, where only the effect of H should be noticeable provided that the unpaired electron density is larger at C_2 (ca. 0.5) and small at C_1. For the case of Figure 10,
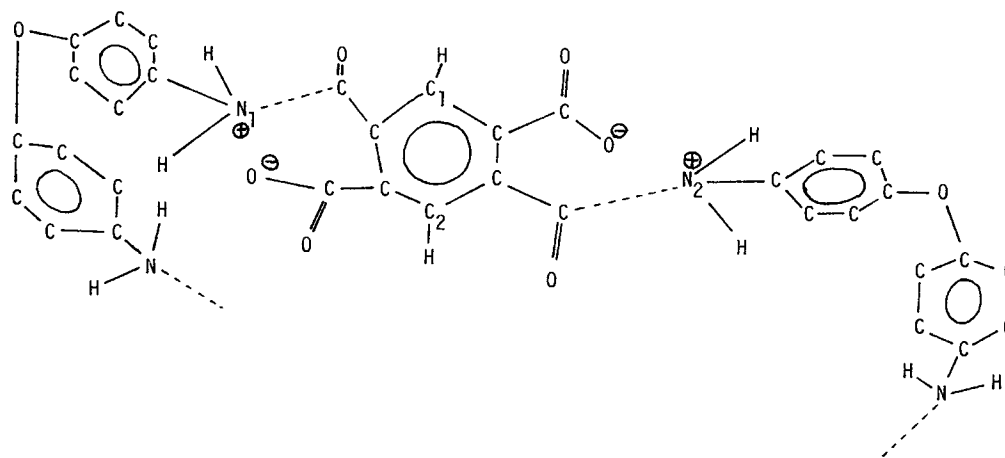

Figure 7 A proposed structure of the paramagnetic species that was elucidated by the ESR spectrum in Figure 4.
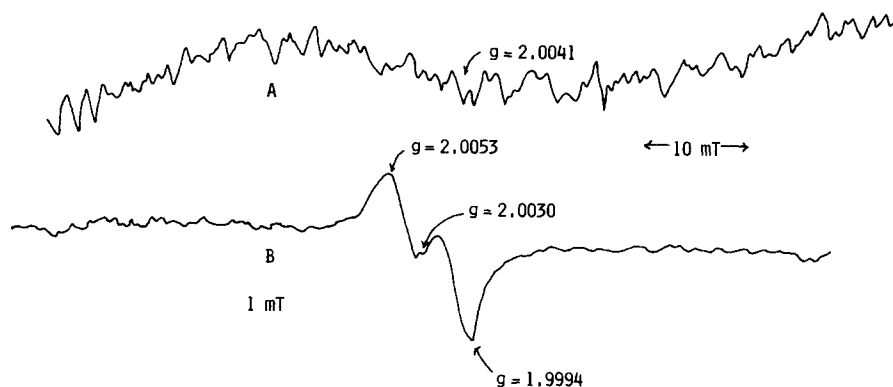
Figure 8 (A) ESR spectrum that was measured with empty sample tube (2 mm diameter tube). (B) ESR spectrum that was measured by the method that used a 2 mm diameter sample tube.

on the other hand, the unpaired spin will be localized at N_1 mostly because of large splitting constant observed: 5.48 mT. The presence of the silica gel surface in the solution of the charge transfer complex causes such a difference in the unpaired spin density distribution. The difference for the case of the vapor deposition polymerization method may be explained by the idea that C=O and H—N—H bonds (Fig. 11) are not coplanar with the benzene rings of PMDA and ODA in the polymer formed by solution polymerization and the unpaired electrons strongly localized either on C_2 or N_1 (Fig. 11).

Kreutz et al. studied a thermogravimetric analysis of polyamic acid and found that when polyamic acid was dissolved in DMAc, DMAc molecules were bonded to polyamic acid at the rate of one DMAc to one carboxylic acid group of PMDA. These bonds

were still kept after drying polyamic acid polymer at 20°C in air.[5] Therefore, one of the major differences between the polyamic acid prepared by the vapor deposition method and that prepared by the DMAc solvent method is this solvation phenomenon. The DMAc molecules, which are bonded to the =C=O group, may work as a plasticizer, and, therefore, the =C=O and =NH bonds will rotate relatively easily; as a result, the structure of the intermediate free radical changes to the one in which the unpaired spin density is concentrated on either the C_2 or N_1 atom.

4. CONCLUSION

The radical species, observed by ESR, which exists in the film formed by vapor deposition polymeriza-
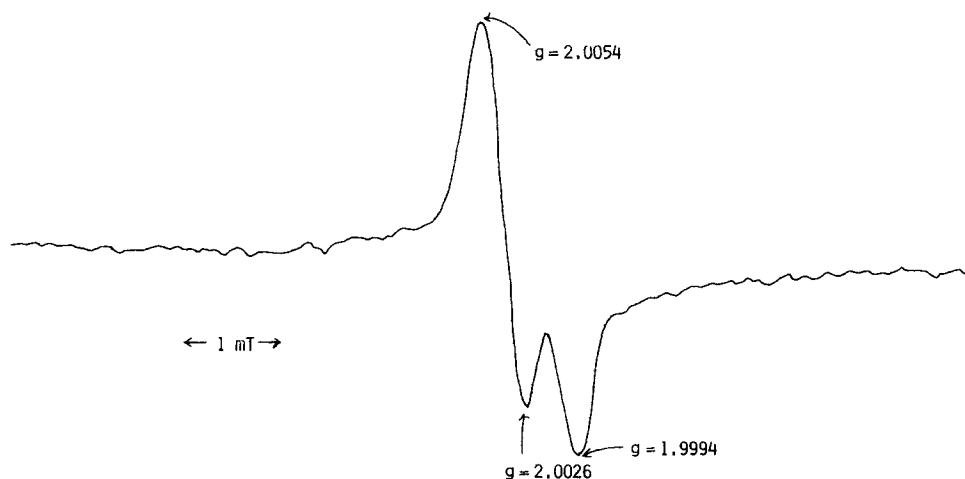

Figure 9 ESR spectrum that was measured by the method that removed DMAc after dissolution and polymerization.
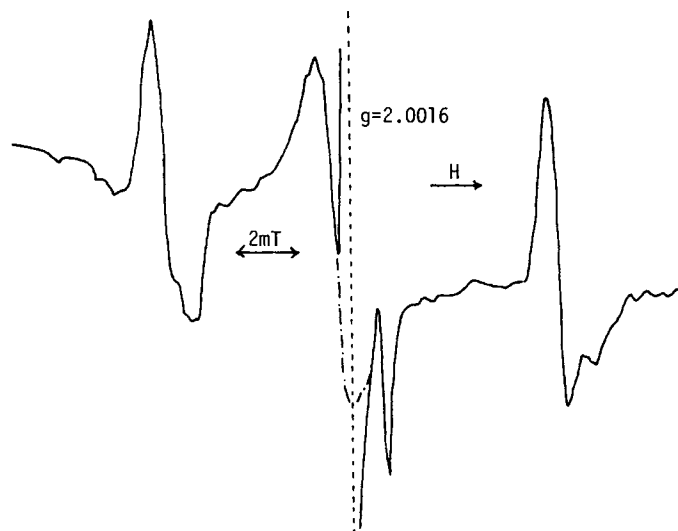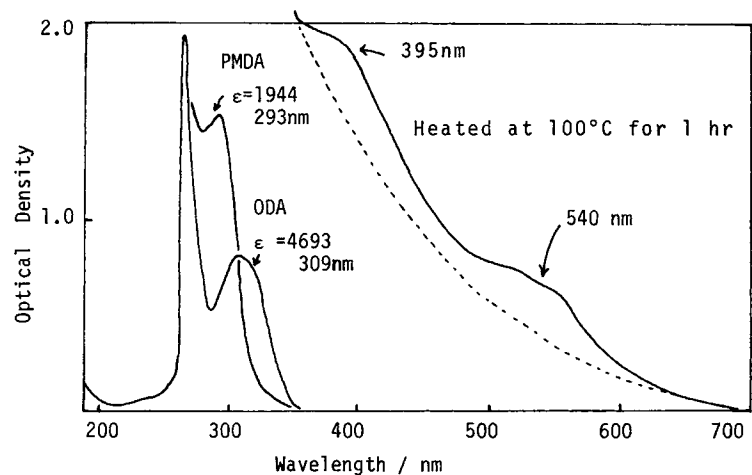
Figure 10   The absorption spectrum and ESR spectrum of the charge transfer complex obtained by PMDA and ODA. The ESR spectrum was observed after trapping the complex on the silica gel surface.
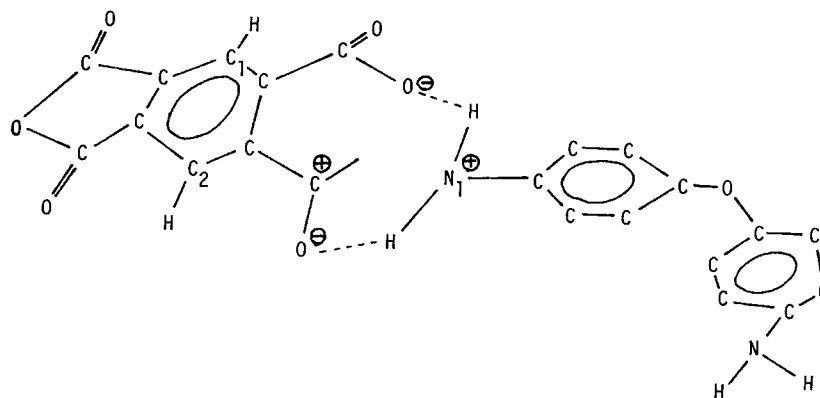

Figure 11   A proposed structure of the paramagnetic species elucidated by the ESR spectra (Figs. 8(B), 9, and 10).

tion, is clearly different from that formed by solution polymerization. This fact means that reaction intermediate radicals formed in these two of polymerization reactions are different. The present analysis of the data may indicate that the benzene ring in PMDA and the amide bond do not have a coplanar structure in the polymer obtained from solution as expected by the report of Silverman et al.[6] In the vapor deposition polymerization method, on the contrary, the polymerization proceeds by taking a positional relation where the benzene ring of PMDA and the amide bond are coplanar to each other.

Polyimide is formed by thermal dehydration of polyamic acid. The five-membered imide bond produced forms a coplanarity with the benzene ring of PMDA. Therefore, the polymer by the vapor deposition polymerization, which has a coplanar structure during the formation of polyamic acid, may be expected to form the imide bond more easily than that obtained by solution polymerization.

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