Solvent Effects in Thermal Curing of Poly(4,4′-oxybis(phenylenepyromellitamic acid))

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ABSTRACT: Thermal curing of poly(4,4′-oxybis(phenylenepyromellitamic acid)) (PAA) films prepared from PAA solutions using a novel solvent system composed of tetrahydrofuran (THF) and methanol (MeOH) has been investigated. In the drying process of casted PAA films, MeOH was entirely evaporated, while a significant amount of THF remained in the dried film. The progress of thermal imidization was observed during the process of drying at 80 °C. NMR measurements for the dried film revealed that the thermal imidization of trans-amidized PAA predominated over that of cis-amidized PAA. Dynamic mechanical thermal analyses (DMTA) pointed out that the dried PAA film containing THF showed no significant plasticization during the thermal cure. This indicates the mobility of polymer chain would be low during the thermal cure so that the resulting polyimide film has a higher in-plane orientation. The coefficient of thermal expansion (CTE) of the polyimide film was found to be low compared with a film obtained from a PAA solution using NMP.

Introduction

Polyimides have been widely used in many applications. Since aromatic polyimides have outstanding thermal, mechanical, and electrical properties as well as solvent resistance, they have been used for interlayer dielectrics for semiconductor devices, wire coating materials, or substrates for flexible printed circuits. Among the aromatic polyimides, poly(4,4′-oxybis(phenylenepyromellitimide)) (PI) which has excellent heat resistance, mechanical strength, and flexibility is one of the most important polyimides.

PI films are usually prepared by casting a poly(4,4′-oxybis(phenylenepyromellitamic acid)) (PAA) solution and thermal curing of the resulting PAA films.[1] Solvents capable of dissolving the PAA are so-called aprotic polar solvents, such as *N,N*-dimethylformamide (DMF), *N,N*-dimethylacetamide (DMAc), *N*-methyl-2-pyrrolidone (NMP), dimethyl sulfoxide (DMSO), and the like. These aprotic polar solvents can be used not only for dissolving the PAA but also as a solvent for the polymerization. The PAA can be easily produced by reaction of pyromellitic dianhydride (PMDA) with 4,4′-oxydianiline (ODA) in these solvents.[1] Since the PAA strongly associates with the solvents,[2–4] removing the solvent from the PAA films is not easy. Thermogravimetric analysis of the PAA films from DMAc solution suggested that 1 mol of solvent associates with each carboxyl group of the PAA.[2] Feger et al. found that unstable 4/1 and stable 2/1 complexes are formed between NMP and each repeating unit of the PAA.[3,4] Residual solvents in the PAA films result in plasticizing the films and increasing the mobility of the polymer chain during the thermal curing process.[5] Due to the residual solvent in the PAA films, properties of the resulting PI are greatly influenced by the curing conditions.[5–9] Feger also reported that curing conditions affect the morphology of PI.[6] Coburn et al. studied the influence of curing conditions on properties of spin-coated PI films and found that the degree of in-plane orientation of polymer molecules is decreased with an increase of the heating rate.[6] The in-plane orientation relates to the coefficient of thermal expansion (CTE). Yamamoto et al. reported that the in-plane orientation of PI films is strongly influenced by the imidization method and found that chemical imidization leads to a high in-plane orientation and a low CTE value for PI.[8]

Recently, we found that highly polymerized PAA can be dissolved in a mixture of tetrahydrofuran (THF) and methanol (MeOH) in spite of the fact that these solvents can not dissolve the PAA when used alone. The PAA solution can be prepared easily in the mixed solvent by reaction of PMDA with ODA.[10] Properties of PI films obtained from this novel solvent system are of interest to us. In this report, we studied thermal curing of the PAA films obtained from the PAA solution using the mixed solvent of THF/MeOH.

Experimental Section

Preparation of PAA Solutions. Polymerization grade PMDA and ODA were purchased from commercial sources and were used as received. THF, MeOH, and NMP were reagent grade materials and were used as received.

ODA was dissolved in a mixed solvent consisting of THF and MeOH (4:1 by weight), and the temperature of the resulting solution was kept at 30 °C. An equimolar amount of PMDA was added to the solution in one portion, and the mixture was stirred for 3 h to yield a homogeneous, yellow solution. The solids content of the resulting solution was 15.1% by weight. The intrinsic viscosity of the obtained PAA was 0.9.

In a similar manner, the PAA solutions were prepared using NMP. The intrinsic viscosity of the obtained PAA was 1.0.

Preparation of PAA Films. Each of the PAA solutions was coated on a glass plate using an automatic film applicator (Yasuda Seiki Co., Ltd.) at a speed of 40 mm/s and to a thickness of 500 μm. After 30 min of drying at 40 °C (THF/MeOH solution) and at 80 °C (NMP solution), the thus formed films were removed from the glass plate to yield transparent PAA films with a thickness of 60–80 μm.

Measurements of IR Spectra. Infrared (IR) spectra were recorded on an FTIR spectroscopic system (Perkin-Elmer system 2000) at 20 °C.

Measurements of ^{1}H-NMR Spectra. ^{1}H-NMR spectra were recorded on an NMR spectroscopic system (Varian 300 MHz) at 20 °C.

Thermogravimetric Analysis. Thermogravimetric analysis (TGA) was conducted with a thermogravimetric analyzer (Perkin-Elmer Model TGA 7) at heating rates of 2 and 9.5 °C/min in a nitrogen atmosphere. All samples for TGA were dried at 80 °C for 2 h after removal from the glass plate.

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Analysis of Volatilized Gas during Cure. The PAA film was placed in a thermogravimetric analyzer unit (Model TGA-50 Shimadzu Co., Ltd.) and was heated from room temperature to 500 °C at a heating rate of 9.5 °C/min in a He stream. Volatilized gas was introduced to a mass spectroscopic unit (Model GCMS-QP1000 Shimadzu Co., Ltd.), and the mass spectrum was recorded at a time interval of 1 min.

Dynamic Mechanical Thermal Analysis. Dynamic mechanical thermal analysis (DMTA) was performed with an automatic dynamic viscoelastometer (Rheovibron Model DDV-II-EP Toyo Baldwin Co., Ltd.) in an auto-tension control mode at a constant tension of 50 mN. The PAA films of dimensions 30 ± 5 mm long and 3 mm wide were mounted with clamps along the length direction, and curing experiments were conducted at 11 Hz in a nitrogen atmosphere. The temperature was controlled from 30 to 300 °C at heating rates of 2 and 9.5 °C/min.[11]

Birefringence Measurements. PAA solutions were spin coated onto a glass slide for 30 s at different speeds ranging from 500 to 5000 rpm. The resulting PAA films were dried for 30 min at 40 °C (THF/MeOH solution) and at 80 °C (NMP solution). Dried films were heated from room temperature to 300 °C at a heating rate of 5 °C/min, and the temperature was held at 300 °C for 3 h in a nitrogen atmosphere.

The refractive indices were measured using a prism coupling system (Metricon Model PC-2000). The measurements were made at a wavelength of 633 nm (He−Ne laser) at ambient conditions. The birefringence (Δn) was calculated from the difference between the in-plane and vertical refractive indices:

$$\Delta n = (n_{\mathrm{TE}} - n_{\mathrm{TM}})$$

where n_{TE} and n_{TM} are the in-plane and vertical refractive indices, respectively.

CTE Measurements. The sample films for CTE measurements were prepared as follows.

1. Off-substrate/rapid cure: The PAA films removed from the glass plate were placed into an oven preheated to 300 °C for 2 h in a nitrogen atmosphere.
2. Off-substrate/slow cure: The PAA films removed from the glass plate were heated from room temperature to 300 °C at a heating rate of 1 °C/min, and the temperature was held at 300 °C for 2 h in a nitrogen atmosphere.
3. On-substrate: The PI films on the slide glass (samples for the birefringence measurements) were peeled from the slide glass.

CTE measurements were conducted with a thermomechanical analyzer (Perkin-Elmer Model TMA 7). PI films of dimensions 13 mm long and 3 mm wide were mounted with clamps along the length direction, and a constant force of 20 mN was applied. Sample films were heated from 30 to 250 °C at a heating rate of 10 °C/min. CTE values were determined from 100 to 250 °C.

Results and Discussion

Weight changes of the PAA film obtained from the NMP solution (which is denoted by PAA (NMP) film) (a) and the PAA film obtained from the THF and MeOH solution (which is denoted by PAA (THF/MeOH) film) (b) during the curing process at heating rates of 2 °C/min (solid line) and 9.5 °C/min (broken line) are shown in Figure 1. The PAA films were dried at 80 °C for 2 h before the TGA measurements. The weight loss of the PAA (NMP) film of 39.0% by weight agrees with the reported value.[4] On the other hand, the weight loss of the PAA (THF/MeOH) film was 24.8% by weight. If no residual solvent exists in the PAA (THF/MeOH) film, the weight loss will be only 8.6% by weight. Therefore, the solvent remains in the PAA (THF/MeOH) film before thermal imidization despite drying at 80 °C (which is higher than the boiling point of THF or MeOH) for 2 h.

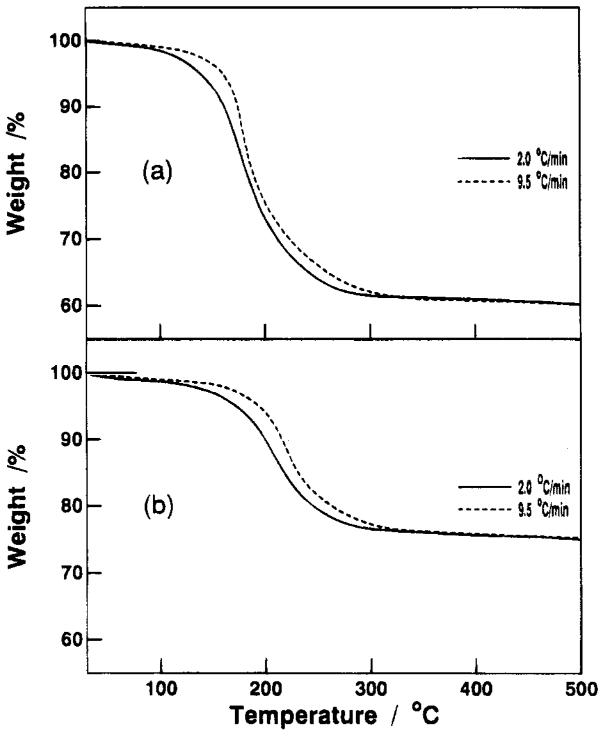

Figure 1. Weight change of the PAA (NMP) film (a) and the PAA (THF/MeOH) film (b) during the curing process at heating rates of 2 °C/min (solid line) and 9.5 °C/min (broken line).

Table 1. Residual Solvents in PAA Films

sample[a]	drying time at 80 °C (h)	THF[b] (mole ratio of THF/ PAA repeat unit)	MeOH[c] (mole ratio of MeOH/ PAA repeat unit)
b	0	1.6	0.12
c	2	0.96	not detected
d	6	0.85	not detected
e	24	0.71	not detected

[a] All sample films were predried at 40 °C for 30 min before drying at 80 °C. [b] Calculated from the peak area ratio of THF protons/aromatic protons. [c] Calculated from the peak area ratio of methyl protons/aromatic protons.

In order to clarify which of the solvents remains in the film, the solvent composition of PAA (THF/MeOH) films prepared under various drying conditions was determined by ^{1}H-NMR measurements. The sample films were dissolved in DMSO-d_6 to perform the NMR measurements. The results, which are summarized in Table 1, clearly indicate that a significant amount of THF still remains in the film dried at 80 °C for 24 h while a major part of the MeOH in the film is evaporated even by predrying at 40 °C for 30 min. Furthermore, interestingly in fact, the NMR measurements for the PAA films revealed that thermal imidization proceeds to some extent even at 80 °C, and the reaction rate of thermal imidization is different between the two PAA isomers (i.e., trans- and cis-amidized PAA). Figure 2 shows and compares the ^{1}H-NMR spectra of the PAA films dried at 80 °C for (c) 2 h, (d) 6 h, and (e) 24 h, respectively. The aromatic protons of the PMDA moiety in PAA, which are represented as H_a, H_b, and H_c in Figure 3, should exhibit three chemical shifts. Two of them can be identified at 7.97 and 8.33 ppm, while the other one is overlapped with a peak around 7.7 ppm due to the protons of the ODA moiety. Among these peaks, the peak at 7.97 ppm can be ascribed to the H_a proton.[12] Therefore, the trans/cis ratio of PAA can be determined by comparing the peak area at 7.97 ppm with that at 8.33 ppm. Furthermore, three peaks at 7.87, 8.14, and 8.24 ppm are clearly observed in the spectra of both (d) and (e). These peaks can be ascribed to the aromatic protons represented as H_d, H_e, and H_f in Figure 3.[13] The

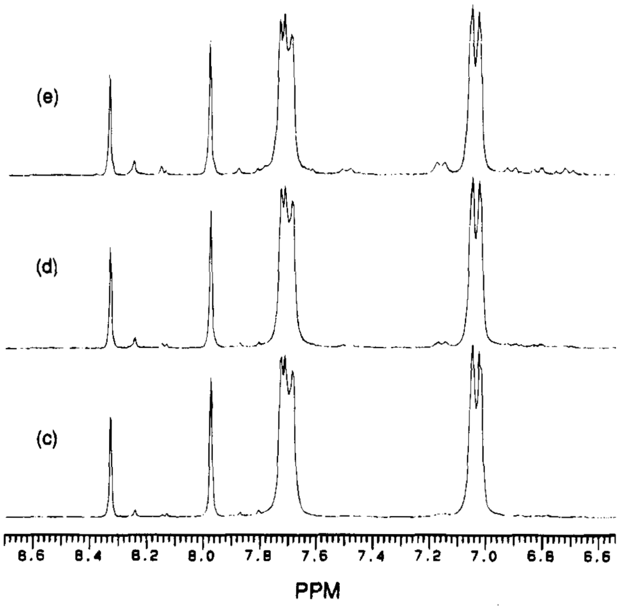

Figure 2. ^{1}H-NMR spectra of the PAA (THF/MeOH) films dried at (c) 80 °C for 2 h, (d) 80 °C for 6 h, and (e) 80 °C for 24 h. All sample films were predried at 40 °C for 30 min.

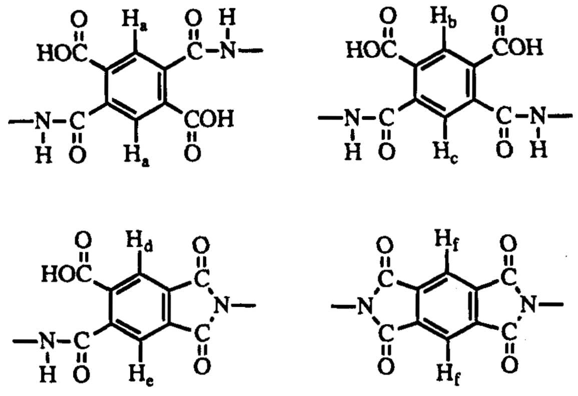

Figure 3. Aromatic protons of the PMDA moiety.

Table 2. Thermal Imidization of PAA

sample^a	drying time at 80 °C (h)	degree of imidization (%)	trans/cis ratio of PAA
c	2	<1	44.8/55.2
d	6	2	44.5/55.5
e	24	8	43.6/56.4

^{a} All sample films were predried at 40 °C for 30 min before drying at 80 °C.

area of these peaks becomes much larger with an increase of the drying time because of the progress of imidization. Furthermore, as a matter of course, the peak area ratio of amide protons[14]/aromatic protons was decreased with an increase of the drying time. Therefore, the degree of imidization in the PAA films can be determined by this peak area ratio. Results obtained from the NMR measurements are summarized in Table 2. As clearly shown in the table, the thermal imidization of trans-amidized PAA predominated over that of cis-amidized PAA during the drying process at 80 °C. This suggests that the pK_a of the carboxylic acid proton is different between the two PAA isomers.

Furthermore, FTIR measurements for the PAA or PI films prepared under various drying/curing conditions were performed. (The drying/curing conditions are (b) 80 °C × 0 h, (d) 80 °C × 6 h, (e) 80 °C × 24 h, (f) 80 °C × 2 h and 150 °C × 2 h, and (g) 80 °C × 2 h and 300 °C × 2 h.) Figure 4 shows and compares the FTIR spectra of the PAA/PI films. In the spectra of (b), (d), and (e), the absorption band at 1070 cm^{-1}, which corresponds to C–O–C antisymmetrical stretching of neat THF, does not appear in spite of the fact that THF exists in the films. On the other hand, the absorption band at 1051 cm^{-1} appears. This band at 1051 cm^{-1} is diminished in the cured films of (f) and (g). Furthermore, it was confirmed that any absorption bands between 1020 and 1100 cm^{-1} do not appear in the case of the PAA (NMP) film. Consequently, the absorption band at 1051 cm^{-1} should be attributed to the antisymmetrical stretching of THF existing in the PAA film.

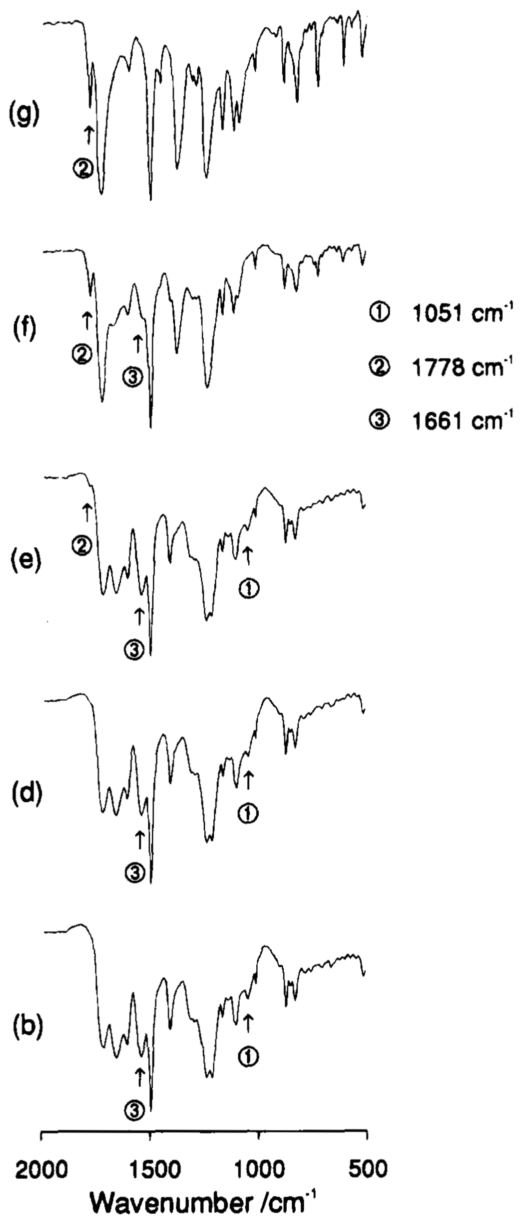

Figure 4. FTIR spectra of the PAA (THF/MeOH) films treated at (b) 80 °C for 0 h, (d) 80 °C for 6 h, (e) 80 °C for 24 h, (f) 80 °C for 2 h and 150 °C for 2 h, and (g) 80 °C for 2 h and 300 °C for 2 h. All sample films were predried at 40 °C for 30 min. In the sample film of (g), the heating rate from 80 to 300 °C was 10 °C/min.

In the spectrum of (e), the shoulder at 1778 cm^{-1},[1,3,9] which corresponds to C=O symmetrical stretching of PI, appears because of the progress of imidization. (The degree of imidization is 8% according to the NMR measurements.) In the spectrum of (g), the absorption band at 1661 cm^{-1},[1,3,9] which corresponds to the amide stretching of PAA, is entirely diminished. Furthermore, it was indicated from the FTIR measurements that

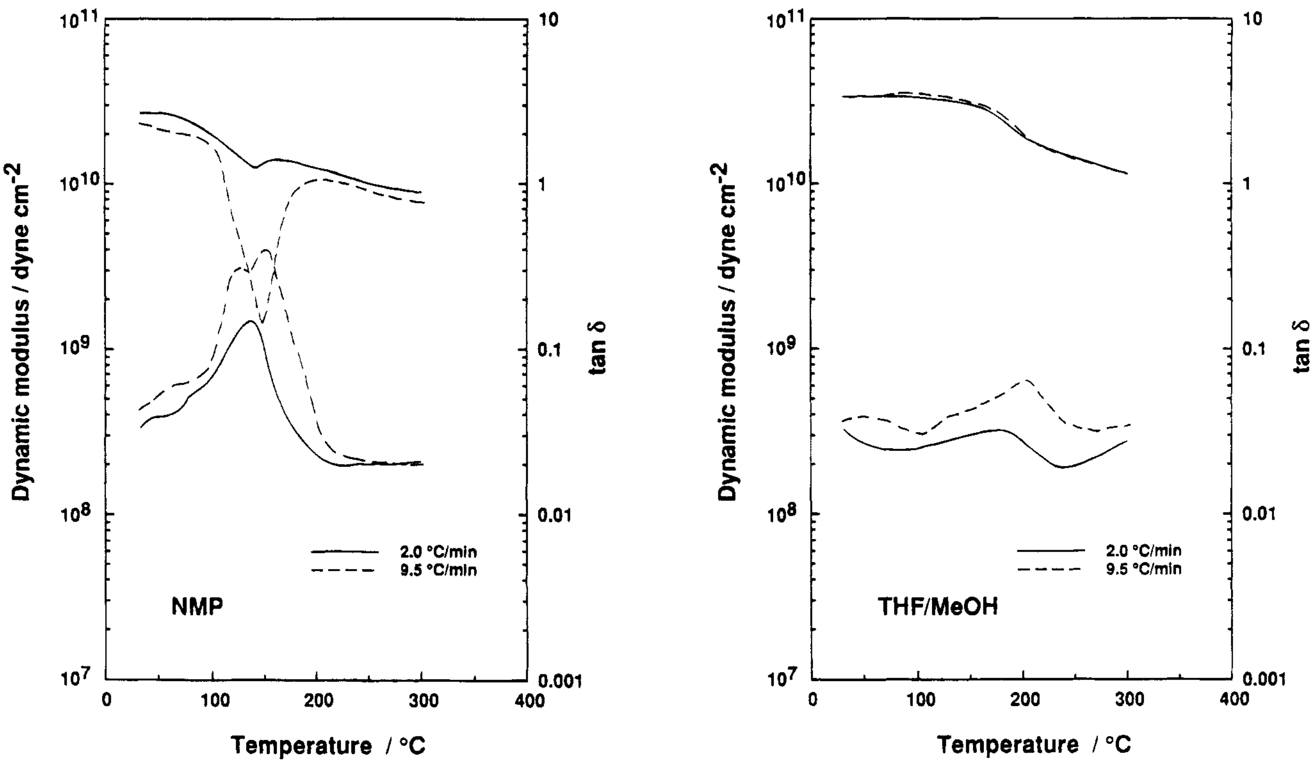

Figure 5. Dynamic storage modulus and tan δ changes of the PAA (NMP) and PAA (THF/MeOH) films at heating rates of 2 °C/min (solid line) and 9.5 °C/min (broken line).

there are no differences in the degree of imidization between the PI film cured at 300 °C for 2 h and that cured at 300 °C for 2 h and at 400 °C for 30 min. (The heating rate from 300 to 400 °C was 10 °C/min.) Accordingly, the thermal imidization of PAA (THF/MeOH) films is considered to be completed at 300 °C for 2 h. This agrees with results reported in the literature,[5,9,15] in which PI films were prepared from the conventional PAA solution using aprotic solvents such as NMP.

The volatilized gas during the thermal cure was analyzed by mass spectroscopy. The PAA (THF/MeOH) film dried at 80 °C for 2 h was placed in a TGA chamber and heated in a He flow. The volatilized gas was introduced to a mass spectroscopic unit to analyze the gas as a function of time at a constant heating rate of 9.5 °C/min. As expected, a mass number of 71, which corresponds to THF, was clearly observed at a temperature range around 200 °C while a mass number of 31, which corresponds to MeOH, was hardly detected during the thermal cure.

In order to examine the effect of the residual solvent in the PAA films, DMTA measurements were performed during the curing process. Figure 5 shows the dynamic storage modulus and tan δ changes of the PAA (NMP) film (a) and the PAA (THF/MeOH) film (b) at heating rates of 2 °C/min (solid line) and 9.5 °C/min (broken line). Sample films were not dried after removing from the glass plate.[16] tan δ and dynamic modulus peaks observed in the PAA (NMP) film indicate that a significant plasticization occurs during the thermal cure even at a slow heating rate (2 °C/min). This phenomenon agrees with the results obtained by other researchers.[6] On the contrary, the PAA (THF/MeOH) film showed no significant tan δ peak even at a high heating rate of 9.5 °C/min. In addition, no obvious difference was observed in dynamic modulus traces between two heating rates. Such a different behavior between PAA (NMP) and PAA (THF/MeOH) films may be due to the following reasons.

1. The concentration of free THF would be maintained low in PAA (THF/MeOH) films during the thermal cure compared with PAA (NMP) films so that it would not reach the level with which the film plasticizes, because the diffusion and evaporation rate of THF (boiling point: 66 °C) must be higher than that of NMP (boiling point: 202 °C).
2. The nature of solvents may be another factor in the plasticization. The solvation capability of THF might be lower than that of NMP because THF alone does not dissolve PAA. Accordingly, the ability of THF to cause an increase of the mobility of polymer chain might be less than that of NMP.

The DMTA measurements indicate the mobility of the polymer chain during the thermal cure in PAA (THF/MeOH) films is lower than that in PAA (NMP) films, so that an in-plane orientation of the PI films obtained from PAA (THF/MeOH) films is considered to be higher than that from PAA (NMP) films. To evaluate the degree of in-plane orientation, the birefringence of PI films was measured. The sample films for the measurements were prepared on a glass slide and the measurements were carried out without removing the films from the glass slide. Figure 6 shows the dependence of birefringence of the PI films obtained from PAA (NMP) films (which is denoted by PI (NMP) films) and the PI films obtained from PAA (THF/MeOH) films (which is denoted by PI (THF/MeOH) films) on film thickness. The PI (THF/MeOH) films exhibited a high birefringence compared with the PI (NMP) films. This indicates that the degree of in-plane orientation of the PI (THF/MeOH) film is higher than that of the PI (NMP) film at identical film thicknesses.

The CTE value of PI films is also correlated to the degree of in-plane orientation of the polymer chain. The dependence of CTE values of both PI (NMP) and PI (THF/MeOH) films (which are on-substrate samples) on film thickness is shown in Figure 7. As expected from the birefringence measurements, the CTE values were increased with the increase of film thickness, and PI

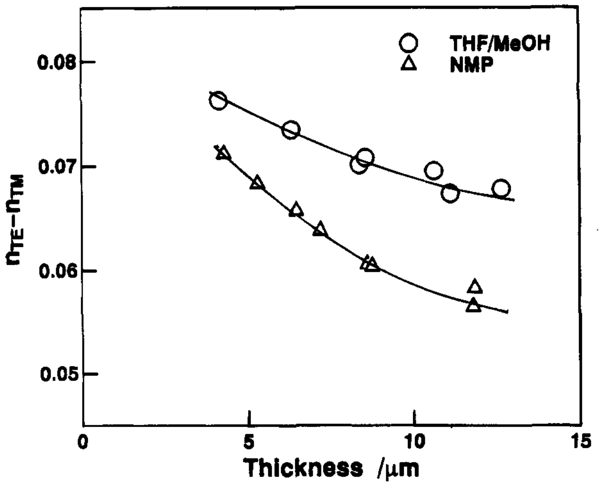

Figure 6. Dependence of birefringence of the PI (NMP) and PI (THF/MeOH) films on film thickness.

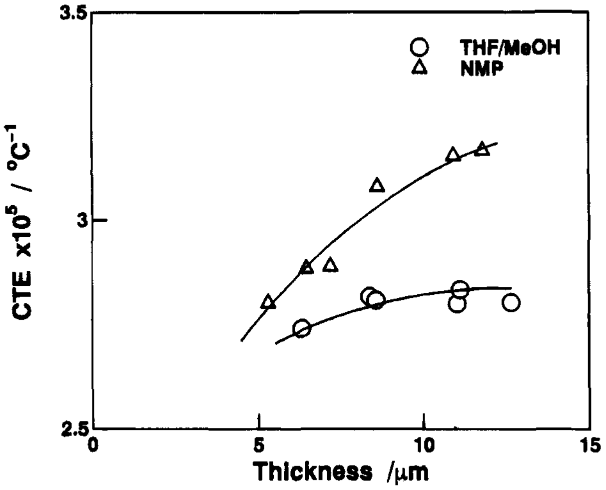

Figure 7. Dependence of CTE values of the PI (NMP) and PI (THF/MeOH) films on film thickness.

Table 3. CTE Values of PI Films (Off-Substrate)

	CTE/°C^{-1}	
solvent	rapid cure	slow cure
NMP	5.7×10^{-5}	5.0×10^{-5}
THF/MeOH	5.0×10^{-5}	4.3×10^{-5}

(THF/MeOH) films showed low CTE values compared with PI (NMP) films at identical film thicknesses. Furthermore, the CTE values of off-substrate PI (THF/MeOH) films are lower than that of PI (NMP) films, as shown in Table 3. The CTE values of off-substrate samples were higher than those of on-substrate samples. This is because shrinkage of the films along the in-plane direction occurred in thermal curing of the PAA (THF/MeOH) films as well as the PAA (NMP) films.

From the above results, it is indicated that the amount and nature of the residual solvents in the PAA films are important factors for increasing the orientation of PAA molecules and lowering the CTE of the PI films. The mismatch of the CTE between PI and substrates, such as a copper foil, which causes residual stress leading to cracking and delamination, has become a great problem in many applications. Our novel solvent system would have potential for solving these problems.

Conclusion

The PAA (THF/MeOH) film contained less residual solvents than the PAA (NMP) film. The residual solvent in the dried PAA (THF/MeOH) film was revealed to be THF alone. FTIR measurements for the dried film revealed that the absorbing band due to C−O−C antisymmetrical stretching of THF existing in the film is shifted significantly from that of neat THF. The progress of thermal imidization was observed during the process of drying at 80 °C. Furthermore, the thermal imidization of trans-amidized PAA predominated over that of cis-amidized PAA. These were confirmed by NMR measurements for the dried PAA film.

The PAA film containing THF showed no significant plasticization during the thermal cure. This indicates that the mobility of the polymer chain would be low during the thermal cure. The resulting PI (THF/MeOH) film has a higher in-plane orientation than the PI (NMP) film. CTE of the PI (THF/MeOH) films was found to be low compared with that of the PI (NMP) films at an identical film thickness.

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(11) During the thermal curing, any precipitation in the film was not observed.
(12) A peak due to the H_a proton should appear between peaks due to the H_b and H_c protons. Assignments of the H_b and H_c protons will be presented elsewhere.
(13) The peak at 8.24 ppm can be ascribed to the H_f proton because the area of this peak is different from that of the other two peaks. Assignments of the H_d and H_e protons will be presented elsewhere.
(14) Two peaks appeared at 10.52 and 10.55 ppm, which are ascribed to the amide protons due to cis- and trans-amidized PAA, respectively.
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(16) The dimension of films changed due to the solvent volatilization and imidization. To obtain actual modulus values, dimensional changes must be considered. However, since the dimension of films depends on the extent of thermal cure and it is difficult to evaluate the dimension of films during the DMTA measurements, the modulus values shown in Figure 5 are not corrected. The actual modulus values at the end of thermal cure are, therefore, higher than those in Figure 5.

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