Effect of Thermal Curing on the Structures and Properties of Aromatic Polyimide Films

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Received October 19, 1990; Revised Manuscript Received February 21, 1991

ABSTRACT: The effect of thermal curing on the thermal expansion coefficients (TECs) and morphologies of films of PMDA–ODA (pyromellitic dianhydride–4,4'-oxydianiline) and PMDA–PDA (p-phenylenediamine) has been examined by using the techniques of FTIR (Fourier transform infrared), X-ray diffractometry, and bending beam. The TECs varied significantly with annealing temperature before the films were fully cured. The PMDA–ODA film was nearly fully cured when annealed at 300 °C, while the same was true for PMDA–PDA at 250 °C. The morphology of the PMDA–ODA film did not vary with annealing, while that of PMDA–PDA changed from low to relatively high ordering when annealed at temperatures from 100 to 250 °C. During annealing of the PMDA–PDA film at 150 °C, a substantial amount of intermolecular links formed. Some of the links disappeared when the film was further annealed at 350 °C and above.

Introduction

Polyimides have been used in many applications for their excellent thermal, mechanical, and electrical properties. For example, they can be used as insulation layers for semiconductor devices[1,2] or substrates for flexible printed circuits.[3] In multilevel interconnection packaging, polyimides seem to be very good candidates as dielectric materials.[4-7] In these applications, one of the major concerns about the use of polyimides is dimensional stability. This is because the applied polyimide film may have a thermal expansion coefficient different from that of the substrate. Upon thermal curing or other thermal cycling, a serious thermal mismatch may cause unwanted structural bending or warpage, cracking, or delamination. To minimize the thermal mismatch, an appropriate polyimide, which has a thermal expansion coefficient matching that of the desired substrate, is recommended.[8] In addition, an appropriate coating thickness should be used. As shown in a previous study,[9] the thermal expansion coefficient of a given polyimide film cured on a substrate may vary with the coating thickness, especially for rigid-rodlike polyimides. This is because polyimide films with different coating thicknesses have different degress of film orientation.

In this study, we have investigated the effect of curing temperature on the thermal expansion coefficients and morphologies of polyimide films cured on a substrate. Two different polyimides, one semiflexible and one rigid rodlike, have been studied. The thermal expansion coefficients of the films were measured by using a bending-beam technique.[10,11] Since the films were obtained by curing their soluble precursors, the degrees of conversion from the amic acids to imides have been determined by an FTIR technique and were correlated to the corresponding thermal expansion coefficients. The effect of thermal curing on the morphologies of the resulting films was examined by X-ray diffractometry.[12]

Experimental Section

Materials. The starting materials used in this study were pyromellitic dianhydride (PMDA) and diamines, 4,4'-oxydianiline (ODA) and p-phenylenediamine (PDA). The solvent used was N-methylpyrrolidone (NMP). These materials were used as received.

Polyamic Acids. Homopolymers of PMDA–ODA and PMDA–PDA polyamic acids were prepared as follows: In a four-neck flask, diamine, ODA or PDA, was dissolved in NMP. When the diamine was completely dissolved, dianhydride PMDA of an equal molar amount was added gradually.[13] The reaction proceeded for 8 h with stirring. The entire process was done in a nitrogen atmosphere. The resulting solutions have a solid content of 14 wt %. The molecular structures of the resulting polyamic acids and their imide counterparts are shown in Figure 1.

Thermal Curing. All of the samples, unless otherwise specified, were prepared by casting the resulting polyamic acid solutions on the desired substrates and prebaking at 80 °C for 30 min. To study the effect of curing temperature on the structures of the resulting films, the samples were annealed successively at several different constant temperatures from 100 to 400 °C with a 50 °C increment. The curing time was 30 min for each curing temperature. The samples were cooled to room temperature each time after curing and before being heated to the next curing temperature. A ramp rate of 1 °C/min was used during heating.

FTIR Specimen Preparation. For a FTIR transmission study, relatively thin films were prepared. This was done by spin-casting the amic acid solutions at 3000 rpm. The resulting films were about 2 μm thick. After each annealing and before measurement, these samples were kept in a vacuum chamber at 50 °C.

FTIR Experiment. The FTIR experiment was done by using a Bomem DA 3002 spectrometer with a KRS-5 crystal under vacuum conditions. The spectra were obtained after 200 scans. The machine resolution was 0.5 cm⁻¹. The spectra with wavenumbers ranging from 550 to 2000 cm⁻¹ were recorded. The degree of imidization for each sample after annealing was determined according to the ratio of the integrated intensity of the symmetric C=O stretching at 1776 cm⁻¹ to that of the aromatic vibration at 1012 cm⁻¹.[14-16] In the calculation, it was assumed that the films after being cured at 400 °C were fully imidized.

X-ray Specimen Preparation. Each X-ray specimen was prepared by stacking many layers of the same kind of film together. The specimen should be thicker than 200 μm so that the applied X-ray would not penetrate through the films. One could therefore compare the results quantitatively. Details are given in the previous paper.[12]

X-ray Diffraction Experiment. X-ray diffraction experiments were done by using a Rigaku wide-angle X-ray diffractometer with nickel-filtered Cu Kα₁ radiation. Its power was set at 40 kV and 20 mA. The arrangements of the X-ray diffraction experiments are illustrated schematically in Figure 2. For the in-plane diffraction, the sample is so arranged that its film plane
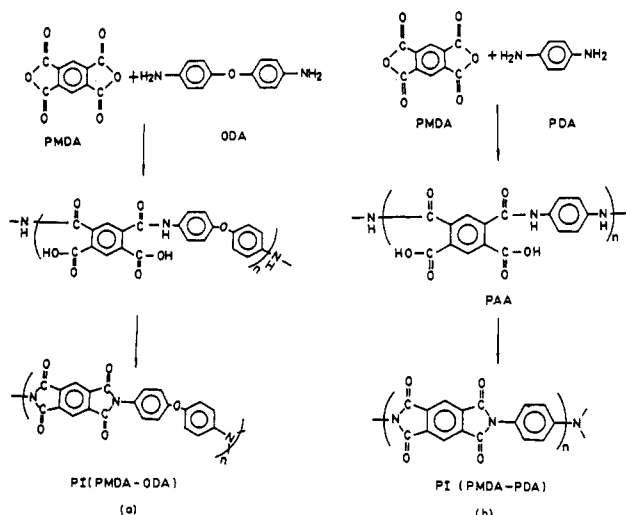
Figure 1. Molecular structures of the resulting polyamic acids and their imide counterparts after thermal curing: (a) PMDA–ODA and (b) PMDA–PDA.

is parallel to the plane formed by the incident and reflected beams. For the out-of-plane diffraction, the film plane is perpendicular to the plane formed by the incident and reflected beams. Here, the in-plane direction means the film plane direction, and the out-of-plane direction means the film thickness or transverse direction.

Bending-Beam Specimen Preparation. For the bending-beam experiment, the films studied were prepared by spin-casting their amic acid solutions on silicon strips. The dimensions of the silicon strips were 7.5 cm in length, 0.5 cm in width, and 390 μm in thickness. The resulting samples were prebaked at 80 °C for 30 min to solidify. For clamping and reflecting the laser beam, both ends of the films were cut away by 1 cm.

Bending-Beam Experiment. Figure 3 shows schematically the experimental setup of a bending-beam apparatus used for the film stress measurements. After the sample was mounted on a clamp, a thermocontrolled oven with an optical window to admit laser light was enclosed. A nitrogen purge was used to prevent moisture uptake in the film at low temperature. While ramping up, the deflection positions of the reflected laser beam from the silicon strip were recorded. At the end of each measurement, the corresponding zero deflection position was determined so that one could calculate the absolute stress in the studied film. This was done by measuring the deflection position of the reflected laser beam after removing the film. To remove the film without disturbing the clamping status, an acid solution was carefully sprayed on the specimen so that the film could be easily stripped from the silicon substrate.

According to the geometry of the experimental setup, bending curvatures of the specimen at various temperatures could be calculated from the deflection position data. Likewise, stress in the film could be readily calculated from the obtained bending curvature, $1/R$, according to the equation[17,18]

$$\sigma_{2,r} = \frac{1}{6R} \frac{E_1}{(1-\nu_1)} \frac{d_1^3}{d_2(d_1 + d_2)} \tag{1}$$

where $\sigma_{2,r}$ is the residual stress in the polymer film. "R" is the curvature radius of the specimen. E_1, ν_1, and d_1 are Young's modulus, Poission's ratio, and the thickness of the substrate, respectively. d_2 is the thickness of the polymer film.

Upon thermal cycling, the difference in the film stresses at any two given temperatures can be attributed to the mismatch in the thermal expansion coefficients of the polymer film and the silicon substrate. It can be expressed as

$$\Delta\sigma_{2,r} = \frac{E_2}{(1-\nu_2)} \int_{T_i}^{T_j} \Delta\alpha \, dT \tag{2}$$

where $\Delta\sigma_{2,r}$ is the residual stress change in the polymer film. E_2 and ν_2 are the relaxation modulus and Poisson's ratio of the
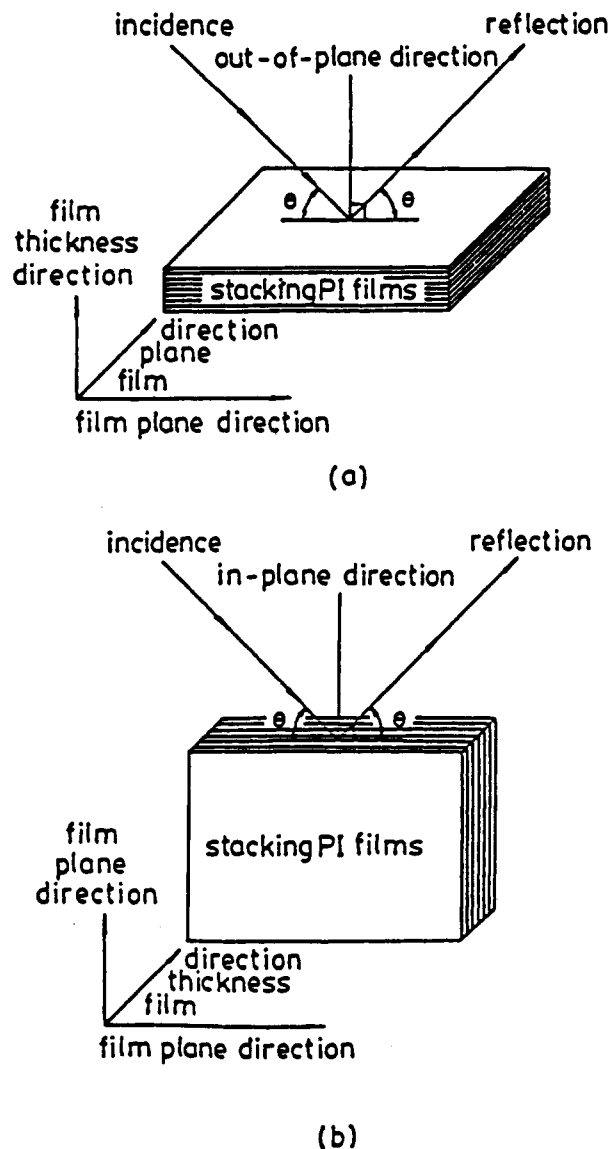

(a)

(b)

Figure 2. Schematic illustration of the arrangements of X-ray diffraction experiments: (a) the out-of-plane diffraction, in which the sample is so arranged that its film plane is perpendicular to the plane formed by the incident and reflected beams, and (b) the in-plane diffraction, in which its film plane is parallel to the plane formed by the incident and reflected beams.
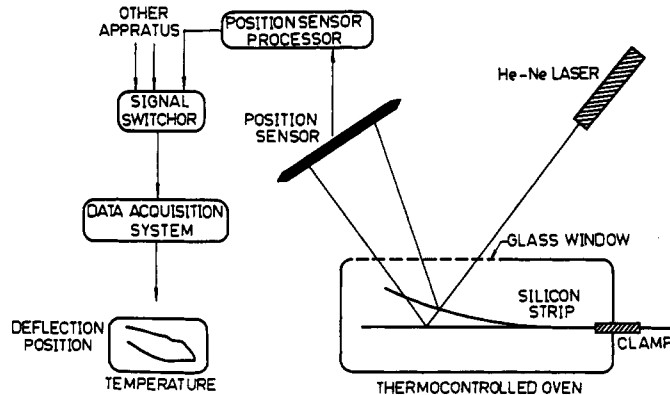

Figure 3. Schematic illustration of the experimental setup of a bending-beam apparatus used for the measurement of stress in any given polymer film coated on a silicon strip.

polymer film, respectively. $\Delta\alpha = \alpha_2 - \alpha_1$ where α_2 is the thermal expansion coefficient of the polymer film and α_1 the silicon substrate.

When the thermal expansion coefficient (or biaxial modulus) of the film is known, its biaxial modulus (or thermal expansion
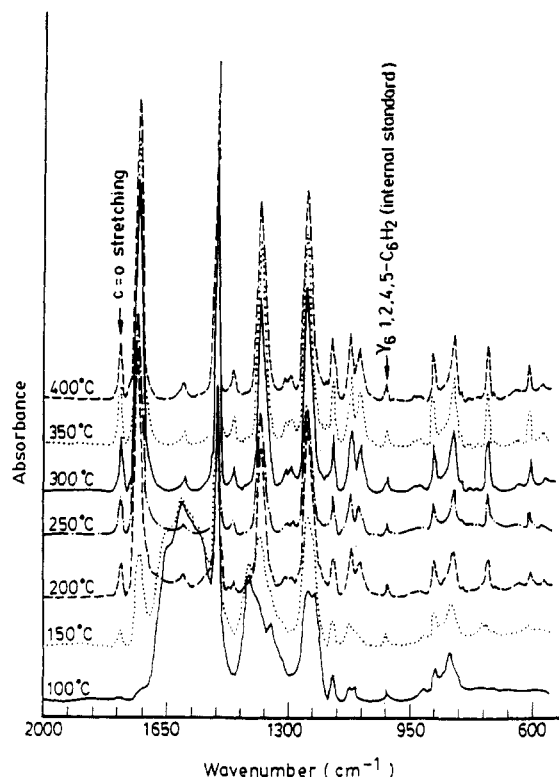
Figure 4. Effect of curing temperature on the FTIR spectra of the PMDA–ODA film.

coefficient) can be obtained from the slope of the resulting curve of stress vs temperature according to eq 3.

$$\frac{d\sigma_{2,r}}{dT} = \frac{E_2}{(1 - \nu_2)}\Delta\alpha \tag{3}$$

Results and Discussion

FTIR Results. Figure 4 shows the effect of curing temperature on the FTIR spectra of the PMDA–ODA film. As seen, the absorption peak at 1776 cm^{-1}, which corresponds to the C=O symmetrical stretching of polyimide, could hardly be observed at 100 °C. This means that the film imidized very little at this temperature. At 150 °C and above, the peak appeared and its intensity increased with an increase of curing temperature and leveled off at 300 °C. Apparently, below 300 °C, the film has only partially imidized. From the integrated intensities of the peaks, one can calculate the degrees of imidization of the film as a function of the curing temperature.

Figure 5 summarizes the percent conversions of imidization at various curing temperatures for the films of (a) PMDA–ODA and (b) PMDA–PDA. As seen, both of the films had imidized less than 5% at 100 °C. At 200 °C, the degrees of imidization were greater than 50%. The film of PMDA–ODA was nearly fully cured at 300 °C. The film of PMDA–PDA showed a similar imidization pattern, except that it was nearly fully imidized when cured to 250 °C. The results from the bending-beam experiments are also shown for comparison and will be discussed in more detail in a later section.

For the same films the FTIR spectra in the 800–1200 cm^{-1} region, as shown in Figure 6, also varied with curing temperature. As seen in part a, below 200 °C, the band (or peaks) at around 1120 cm^{-1} is relatively weak. The band corresponds to the absorption of a (CO)$_2$NC imide group.[19] At 200 °C, two well-separated peaks appeared. Their intensities apparently increased at temperatures above 200 °C. These phenomena coincide with the imi-
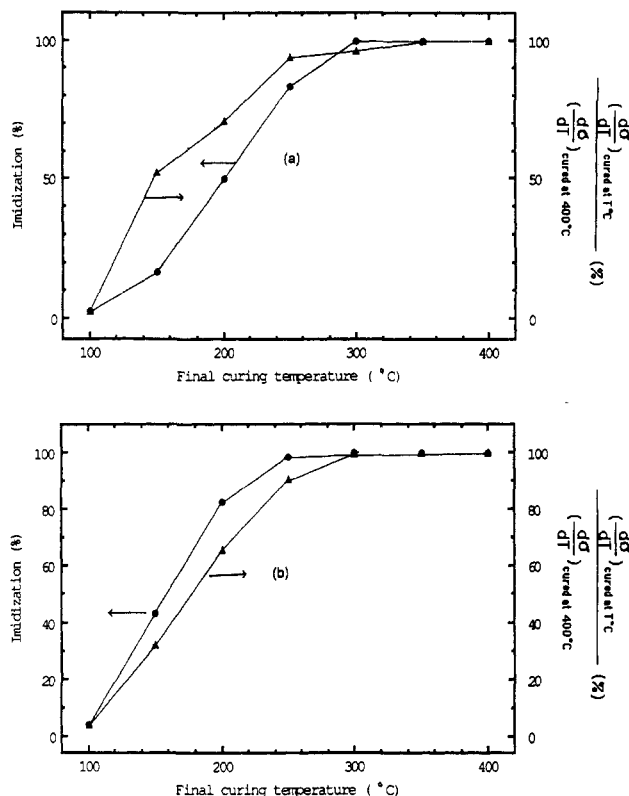

Figure 5. Percent conversions of imidization vs curing temperature for the films of (a) PMDA–ODA and (b) PMDA–PDA: (●) results from the FTIR experiment; (▲) results from the bending-beam experiment.

dization results mentioned in the last section. From the results of X-ray diffraction (Figures 7 and 8), the ordering of the PMDA–ODA film was poor, although not completely amorphous, and did not enhance with an increase of the degree of imidization. It is found that the film morphology did not vary with curing. Therefore, one may attribute the significant spectrum change when increasing the curing temperature from 150 to 200 °C to a rapid increase of the amount of the (CO)$_2$NC imide group.

Similar to the results of PMDA–ODA, two well-separated peaks can be observed when annealing the film of PMDA–PDA at 200 °C and their intensities also increased at elevated temperatures. However, these two different polyimides exhibit different absorption spectra when annealed at 100 or 150 °C; i.e., there is an observable peak splitting phenomenon in the spectrum of PMDA–ODA, while none in that of PMDA–PDA. This may be attributed to the fact that, at 100 or 150 °C, most of the amic acid chains of PMDA–PDA that cured have actually converted to intermolecular links instead of imide chains.[20] This can also be evidenced by the extraordinary peak exhibited in the X-ray out-of-plane diffraction patterns shown in Figure 9, which will be further discussed later. Besides, in the paper,[20] it has been mentioned that the absorption band of the C=O imide group would overlap with that of the C=O group in the link. This indicates that the film of PMDA–PDA that partially "imidized" at these low temperatures as presented above may, actually, have been mostly converted to intermolecular links. If this is true, in the absence of enough imide chains, the concentration of the (CO)$_2$NC imide group in the film would be very low. Consequently, the resulting (CO)$_2$NC imide groups, if any, would be very unlikely to be intimately neighboring to one another and interact. As a result, no peak splitting in the absorption band of the C=O imide group could be observed.
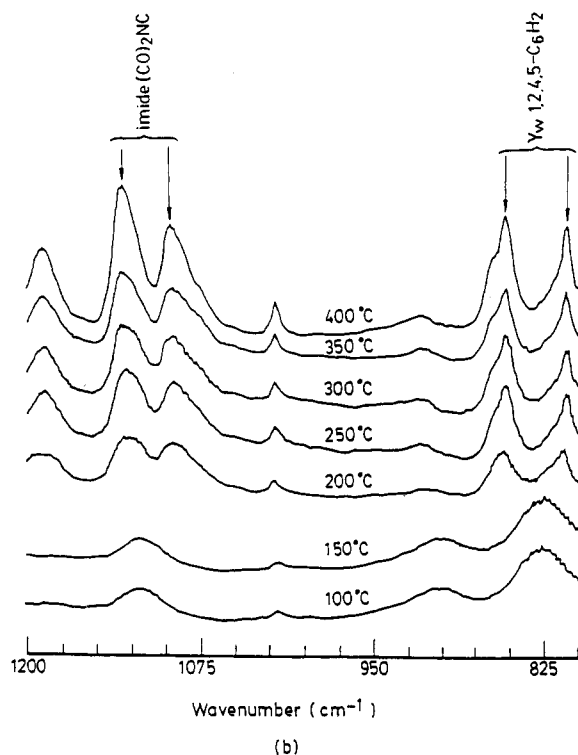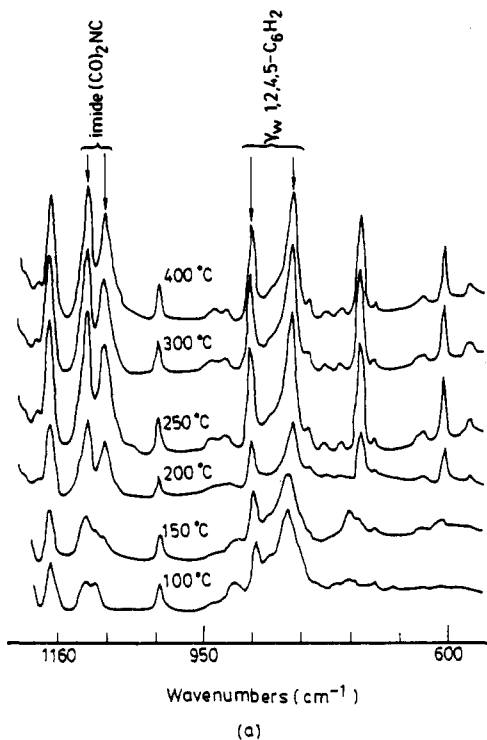
(a)

Figure 7. Effect of curing temperature on the out-of-plane X-ray diffraction pattern of the film of PMDA–ODA.

(b)

Figure 6. Effect of curing temperature on the FTIR spectra of the films of (a) PMDA–ODA and (b) PMDA–PDA in the 800–1200-cm^{-1} region.

Furthermore, unlike the imidization result shown previously, the intensities of the two separated peaks of PMDA–PDA kept increasing even above 350 °C. Such a phenomenon was not observed in the film of PMDA–ODA. According to the integrated intensity of the absorption peak of the C=O symmetrical stretching of polyimide, both of these two different films were nearly completely imidized at 300 °C or even below. The above phenomenon could, presumably, be related to the conversion of the intermolecular links that formed at temperatures below 350 °C to imides at elevated temperatures. At least, some
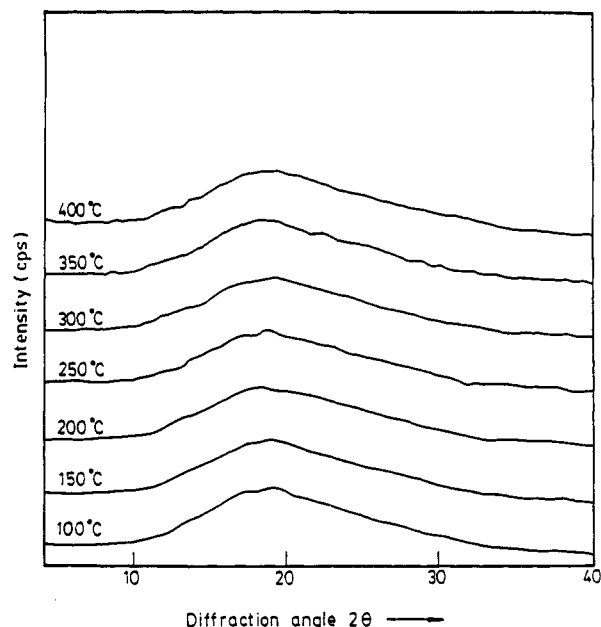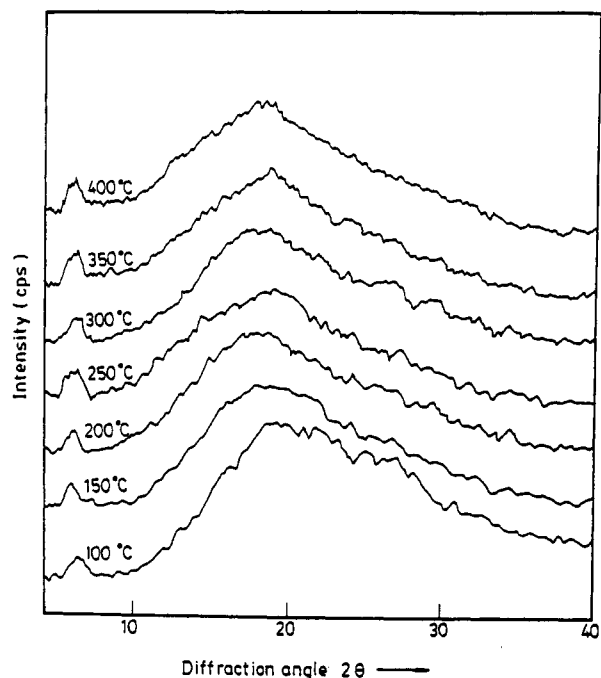

Figure 8. Effect of curing temperature on the in-plane X-ray diffraction pattern of the film of PMDA–ODA.

of the links have disappeared at the elevated temperatures, as indicated by the decrease of the intensity of the X-ray difraction peak corresponding to the intermolecular link, as shown in Figure 9. At low temperatures, the formation of the intermolecular links is thought to be sterically favorable.[20,21] At elevated temperatures, these thermodynamically less stable intermolecular links would more or less convert to imides, whose structure is supposed to be more stable thermodynamically. Therefore, it seems reasonable to attribute the increase of the intensity of the (CO)$_2$NC imide group absorption band to the formation of some imides converted from the links.

Both of the films, PMDA–ODA and PMDA–PDA, exhibited a very clear peak splitting phenomenon when annealed at 200 °C or above, indicating they were in an "ordered" state. However, this has been observed in the film of PMDA–DOA during the entire curing process. This
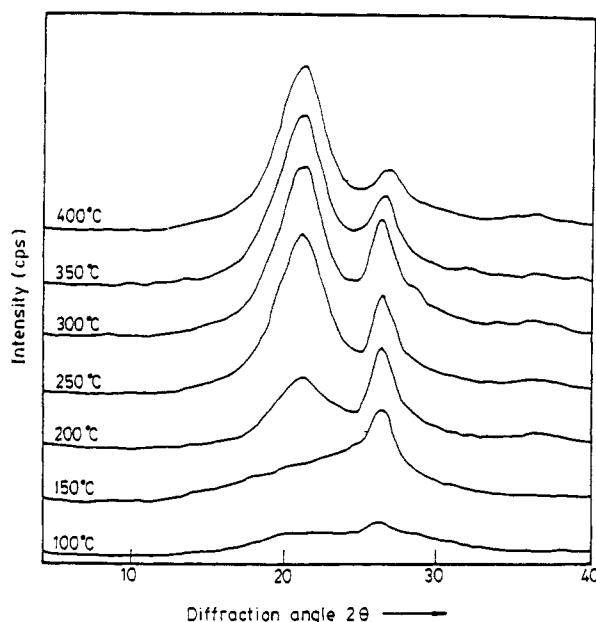
Figure 9. Effect of curing temperature on the out-of-plane X-ray diffraction pattern of the film of PMDA–PDA.

implies that PMDA–ODA has formed an ordered structure from the beginning, though its ordering is not very prominent. The trend in the increase of the intensity of the $(CO)_2NC$ imide group absorption band coincides with that in the imidization result mentioned above. This indicates that no intermolecular link formation or disappearance has been involved during the curing process of PMDA–ODA. According to the intermolecular link structure proposed by Snyder et al.,[21] it seems that intermolecular links are more likely to form if any given two amic acid chains are coplanar. Since the structure of the amic acid chain of PMDA–ODA is very flexible, relatively speaking, they could hardly be coplanar to one another. This may be why no indication of the presence of intermolecular links in the film of PMDA–ODA could be found in the above experiments.

Similarly, all the above phenomena can also be observed from the absorption bands in the 827-cm^{-1} region shown in Figure 6. The absorption bands correspond to the vibration modes of the $1,2,4,5$-C_6H_2 imide group.[19] However, for brevity, the discussion of these phenomena is omitted.

X-ray Diffraction Results. Figure 7 shows the effect of curing temperature on the out-of-plane X-ray diffraction pattern of the film of PMDA–ODA. It should be kept in mind that the film has been cured on a substrate. The structure of a given polyimide film cured on a substrate would be different from that cured freely; i.e., curing polyimide films on a substrate can result in an in-plane orientation.[22] As mentioned in other papers,[12,22–24] out-of-plane X-ray diffraction patterns can effectively provide information about the intermolecular ordering of a polyimide film with an in-plane orientation. As seen, the film of PMDA–ODA exhibited some degrees of intermolecular ordering according to the diffraction peak at $2\theta = 19.7°$. However, the peak is relatively diffuse and broad. It is indicated that the degree of crystallinity of the film should be relatively low, if it can be calculated. However, the calculation would not be easy and may be impossible. It is our thought that it would not be correct using the traditional wide-angle X-ray diffraction method to determine the degree of crystallinity of a given film cured on a substrate by simply using its out-of-plane diffraction pattern alone. It is because of this that a film cured on a

substrate is usually anisotropic in the resulting structure. This is also evidenced by the X-ray results shown in Figure 8. Upon viewing from two different directions, i.e., in-plane and out-of-plane, the film of PMDA–ODA showed two different diffraction patterns. There is an observable peak in the small-angle region in the in-plane diffraction pattern, while none in the out-of-plane pattern when comparing Figures 7 and 8. For rigid-rodlike polyimides, the difference between the in-plane and out-of-plane diffraction patterns will be more pronounced.[12] Therefore, it would not be adequate using only the out-of-plane diffraction pattern to calculate the degree of crystallinity in such a case.

Using both the out-of-plane and in-plane diffraction patterns, one may be able to obtain correct quantitative results concerning the film crystallinity. However, this is beyond the scope of this study. Since these polyimides do not exhibit glass transitions below 400 °C, their melting points should be so much higher that they would decompose prior to melting. It is therefore also impossible using typical calorimetric methods to quantify the degrees of crystallinity of these films. There may be some other way for determining the degrees of crystallinity of these anisotropic films. This determination, however, is not our major concern. Since the resulting qualitative information regarding film morphology suffices to explain the bending-beam-stress behavior of the two different polyimide films, the X-ray results of the two different films will be compared and discussed on a qualitative basis.

As shown in Figures 7 and 8, the diffraction patterns of the film of PMDA–ODA were very weak throughout the entire curing process. No significant increase in the intensity of any of the characteristic diffraction peaks could be observed when the annealing temperature or the degree of imidization increased. In the in-plane diffraction pattern shown in Figure 8, the peak at $2\theta = 5.94°$ corresponds to the diffraction from the intramolecular ordering of the monomeric units of the amic acid and/or imide chains of the PMDA–ODA film.[22] This result indicates that the film of PMDA–ODA had some degree of intramolecular ordering. The ordering, however, did not improve upon curing. This may be mainly attributed to the fact that both the imide and amic acid chains of PMDA–ODA contain an ether linkage in each repeating unit. Due to the bending conformation and easy rotating nature of the ether linkage, neither the imide nor the amic acid chains could form a highly ordered structure.

Figure 9 shows the effect of curing temperature on the out-of-plane X-ray diffraction pattern of the film of PMDA–PDA. Contrary to PMDA–ODA, the diffraction pattern of PMDA–PDA significantly varied upon curing. The ordering of the film structure of PMDA–PDA dramatically increased when the degree of imidization increased. This, of course, can be attributed to the fact that the imide chain structure of PMDA–PDA is planar and symmetric and very different from that of its amic acid counterpart, which is much more flexible.

There are two distinguishable peaks in the out-of-plane diffraction pattern of the film of PMDA–PDA. In addition to the typical characteristic peak from the intermolecular ordering of the resulting imide chains, which appears at $2\theta = 20.8°$, there is another peak at $2\theta = 26.4°$. The former peak corresponds to a spacing of 0.43 nm, while the latter one corresponds to a spacing of 0.34 nm. Similar to all other polyimide films cured on a substrate, this film also exhibited an in-plane orientation, as clearly indicated by the marked difference between its out-of-plane and in-plane diffraction patterns shown in Figures 9 and 10,
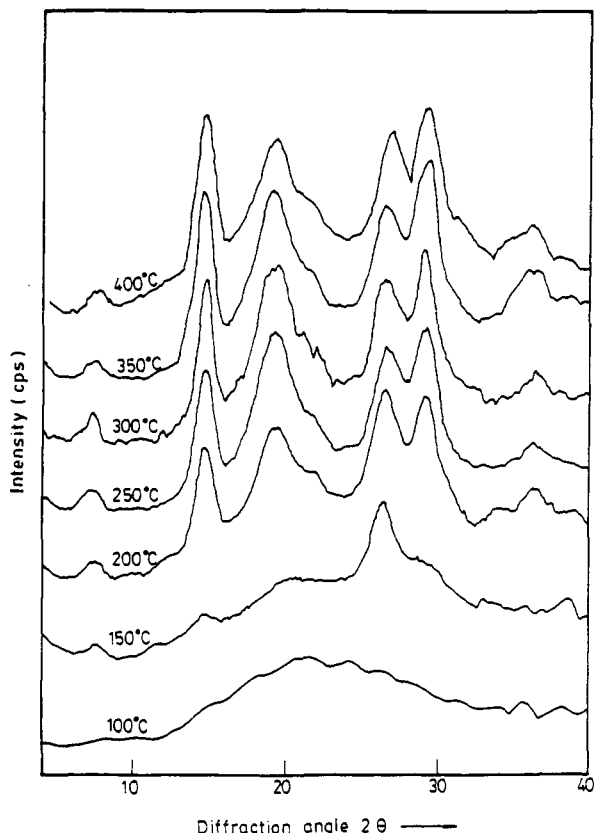
Figure 10. Effect of curing temperature on the in-plane X-ray diffraction pattern of the film of PMDA–PDA.

Figure 11. Stress–temperature behaviors of the films of (a) PMDA–ODA and (b) PMDA–PDA on silicon substrates during thermal cycling from room temperature to 350 °C. The films had been prebaked at 80 °C for 30 min before the measurements.

respectively. This also means that the molecular chains of PMDA–PDA are predominantly aligned in a direction parallel to the film. Since the diffraction pattern was taken from the out-of-plane direction, the peak that appears at $2\theta = 26.4°$ should also, presumably, result from intermolecular ordering. However, the ordering must originate from some cured chains with a structure other than imide. It is very plausible that, at least, some of the chains cured were indeed intermolecular links (also called trans imides) instead of "ring-closed" imides.[19,20]

The peak corresponding to the "intermolecular links" began to form at 100 °C and became sharper when the curing temperature increased. Compared with the diffraction peak corresponding to the formation of typical imides, the formation of intermolecular links seems to be much preferred at temperatures below 200 °C. This indicates that the steric barrier for forming the intermolecular link was much lower than that for forming the imide counterpart. At elevated temperature 350 or 400 °C the peak apparently decreased. These intermolecular links should have been converted, to some extent, to imides, as evidenced by the increase of the intensity of the $(CO)_2NC$ imide group absorption band in Figure 6b.

Figure 10 shows the effect of curing temperature on the in-plane X-ray diffraction pattern of the film of PMDA–PDA. The film exhibited highly ordered characteristics when fully cured. The peak at $2\theta = 7.98°$ corresponds to the intramolecular ordering of the monomeric unit of PMDA–PDA, which is 1.23 nm as calculated. At 100 °C, the peak could barely be observed, which indicates that the film of PMDA–PDA was in a disordered state, relatively speaking. At 150 °C, the peak apparently appeared, though it was comparatively weak. This is understandable since the film was imidized less than 50% at this stage. At 200 °C, the peak intensity became stronger. The intensity did not further increase within
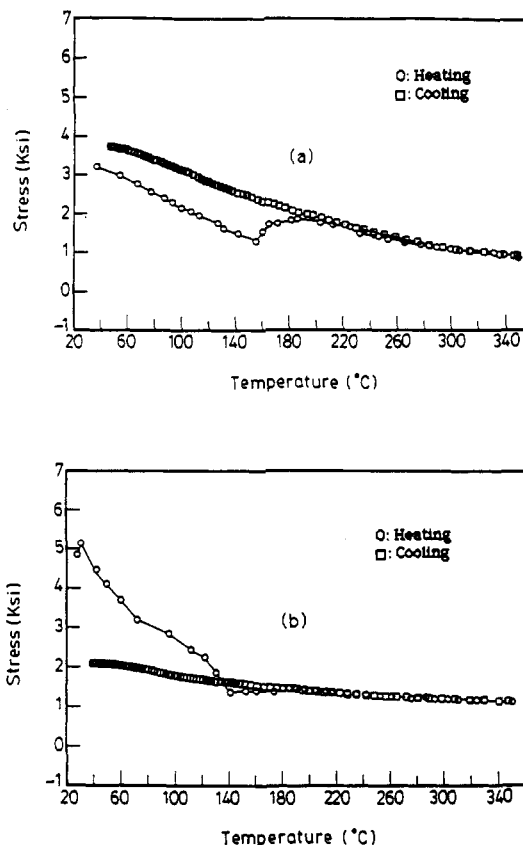
machine resolution when the curing temperature increased from 250 to 400 °C.

Bending-Beam Results. Figure 11 shows typical stress–temperature behavior of the films of (a) PMDA–ODA and (b) PMDA–PDA on silicon substrates during thermal cycling from room temperature to 350 °C. Before measurement, the films were prebaked at 80 °C to remove most of the solvent. For PMDA–ODA, the film started to shrink at a temperature slightly less than 160 °C, as indicated by the sudden change in the heating curve. For PMDA–PDA, the film started to shrink at around 140 °C. Above 200 °C, the heating curve and the cooling curve fell on each other for both films. This indicated that the films seem to be nearly fully imidized when cured above 200 °C. However, it should be noted that the annealing conditions for these two experiments were different from those for all others.

Figure 12 shows the effect of curing temperature on the slope of the stress–temperature curve of the film of PMDA–ODA on a silicon substrate. For clarity, only the cooling curves are shown. As seen, when the film was cured at 100 °C for 30 min, the slope of its stress–temperature curve was relatively high. This reveals that the PMDA–ODA amic acid chain indeed has a relatively high thermal expansion coefficient since about 98% of the film was still composed of the amic acids at this stage. As illustrated in Figure 1, the amic acid chain of PMDA–ODA has eight single bonds per repeating unit along its backbone. Such a highly flexible chain structure should give a high thermal expansion coefficient. The thermal expansion coefficients of the film at the different curing stages have been calculated and are shown in a later section.

From 100 to 150 °C, the slope of the stress–temperature curve dropped more than 40% while its corresponding
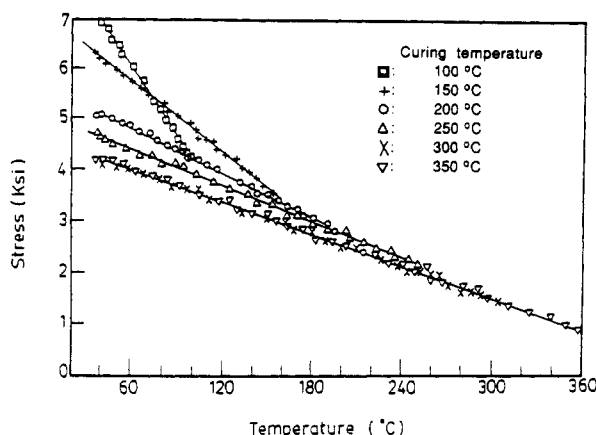
Figure 12. Effect of curing temperature on the slope of the stress–temperature curve for the film of PMDA–ODA on a silicon substrate.
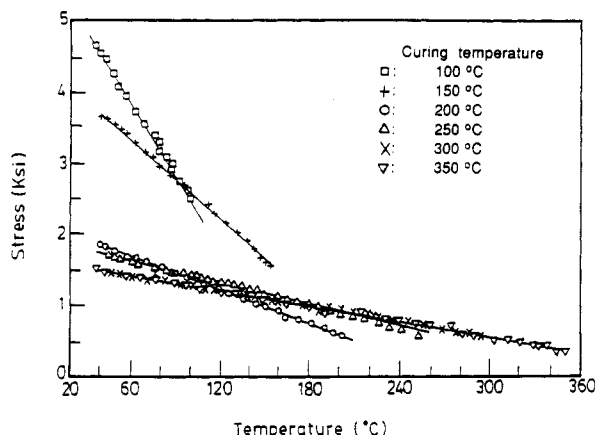

Figure 13. Effect of curing temperature on the slope of the stress–temperature curve for the film of PMDA–PDA on a silicon substrate.

degree of imidization changed from 2 to 15% according to the FTIR results. As demonstrated earlier, the film morphology did not vary throughout the entire curing process. Therefore, the change in slope must mainly result from the change in the molecular structure of the chain of PMDA–ODA upon curing, wherein amic acid chains have been converted to imide chains. Compared with its amic acid chain, the molecular structure of the imide chain of PMDA–ODA has four less single bonds per repeating unit along its backbone and should be much less flexible and have a much smaller thermal expansion coefficient. Consequently, when the average thermal expansion coefficient of the film decreased with the increase of the degree of imidization, the thermal mismatch between the film and the silicon substrate decreased, and the resulting thermal stress–temperature variation became smaller. Here, the thermal expansion coefficient of the silicon substrate, 2.5 ppm/°C at room temperature, is smaller than that of the PMDA–ODA film before or after curing. If the thermal expansion coefficient of the substrate were greater than that of the film, the above phenomena would have been reversed.

From 150 to 250 °C, the slope change was also very drastic, coinciding with the trend of the FTIR imidization result. Above 250 °C, the slope varied insignificantly. All of the resulting slope ratios, obtained by dividing the slopes at various temperatures by that at 400 °C, are summarized and shown in Figure 5a.

Figure 13 shows the effect of curing temperature on the slope of the stress–temperature curve of the film PMDA–

PDA on a silicon substrate. The change in slope was also very prominent before the film was fully cured. However, before being fully cured, the slope ratio of the film of PMDA–PDA was somewhat smaller compared with that of PMDA–ODA at any of the curing temperatures between 100 and 300 °C. The various slope ratios of PMDA–PDA are shown in Figure 5b. The above difference may be due to the difference in the curing mechanisms of the two polyimides. Or, more precisely speaking, it may be attributed to the formation of the intermolecular links in the film of PMDA–PDA. As discussed earlier, the formation of the links is considered to be sterically more favorable. This means that less deformation or distortion in the chain structure would result from link formation. This would result in a film stretched much less. As a result, the above-mentioned slope ratios of PMDA–PDA are smaller than those of PMDA–ODA. Likewise, the above hypothesis may also partly explain why there exists a reversal phenomenon in the trends of FTIR vs bending-beam data for the two different polyimide systems shown in parts a and b of Figures 5.

Similar to PMDA–ODA, when the film of PMDA–PDA was predominantly composed of amic acid chains, its thermal stress varied markedly with temperature. This indicates that the PMDA–PDA amic acid chain also has a relatively high thermal expansion coefficient. This should be true since the amic acid chain of PMDA–PDA is also very flexible, when compared with its rigid imide counterpart. The chain flexibility of the amic acid of PMDA–PDA can be realized from its relatively disordered structure revealed by the X-ray experiment or simply from its molecular structure, illustrated in Figure 1.

Generally speaking, the imidization results from the FTIR experiment match those from the bending-beam experiment for the two different polyimide films. However, it may be that, in Figure 5a, the curve of the imidization results leads the curve of the slope ratios at various temperatures below 300 °C for the film of PMDA–ODA. The phenomenon is reversed for the film of PMDA–PDA. As also noted, at the same curing temperature, 150, 200, or 250 °C, the degree of imidzation of the film of PMDA–PDA was always higher than that of PMDA–ODA. These differences seem, very likely, but maybe not exclusively, to result from the absence and presence of the formation of the links in the films of PMDA–ODA and PMDA–PDA, respectively, upon curing. It is because, at these low temperatures, it would be much easier to form a link due to the fact that its formation is more sterically favorable and requires a lower energy to overcome its steric barrier. As mentioned above, the absorption band of the C=O imide group would overlap that of the C=O group in the link. As a result, in the curing of the film of PMDA–PDA, not only the ring-closed imides but also the intermolecular links have a contribution to the increase in the intensities of the FTIR bands of the C=O imide group. This may be why the film of PMDA–PDA is imidized more rapidly at those low temperatures, when compared with PMDA–ODA. Coupling with the above-mentioned hypothesis, this may also reveal why the trends of FTIR vs bending-beam data for the two different polyimide systems are different.

Figure 14 shows the effect of curing temperature on the thermal expansion coefficients of the films of (a) PMDA–ODA and (b) PMDA–PDA. As seen, these thermal expansion coefficients dropped markedly when the annealing temperature increased. For PMDA–ODA, its thermal expansion coefficient dropped from 69.2 to 17.5 ppm/°C when annealed from 100 to 350 °C. For PMDA–
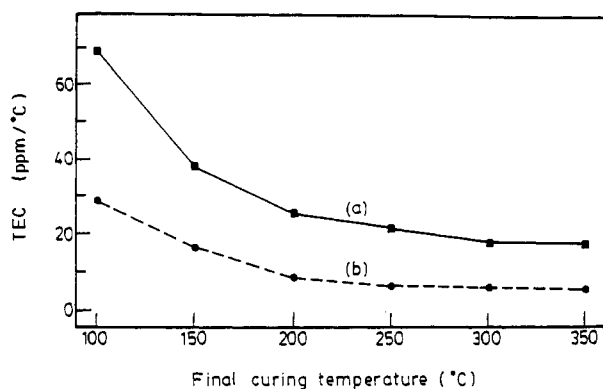
Figure 14. Effect of curing temperature on the thermal expansion coefficients of the films of (a) PMDA–ODA and (b) PMDA–PDA.

PDA, it dropped from 28.8 to 4.4 ppm/°C. In the calculations, the biaxial modulus of the film of PMDA–ODA, 641 kpsi after being cured at 400 °C, has been used, and for PMDA–PDA it is 2642 kpsi. It has been assumed that the biaxial moduli of the films did not vary upon annealing. Though this might not be a good assumption, some deviation would not affect the above results very much. If the moduli were to increase with an increase of the degree of imidization, the above trends would be more pronounced, and so would it be true reversely, according to eq 3. Ideally, the moduli of the films should increase upon annealing since more "flexible" amic acid chains have been converted to "rigid" imide chains. It is our belief that the former case is more likely to occur. However, in either case, the above thermal expansion–curing temperature relationships should hold, since the variations in the thermal expansion coefficients with respect to the curing temperature were so pronounced.

Conclusion

From this study it may be concluded that the effect of curing temperature on the thermal expansion coefficients of the imide films of PMDA–ODA and PMDA–PDA was very prominent before they were fully cured. When the films were fully cured, their thermal expansion coefficients were no longer affected by annealing at elevated temperatures. For the film of PMDA–ODA, it was nearly fully imidized when annealed at 300 °C, while for PMDA–PDA it was nearly fully imidized at 250 °C. According to X-ray diffraction experiments, the morphology of the PMDA–ODA film did not vary with annealing. In other words, its film ordering remained low and unchanged, while its degree of imidization significantly increased with an increase of the curing temperature. This can be attributed to the presence of the flexible ether linkage in both of the chains of imide and amic acid.

On the other hand, the morphology of the PMDA–PDA film apparently varied with annealing. The film structure obviously changed from low to high ordering when annealed at temperatures from 100 to 250 °C. For the PMDA–PDA film, at 150 °C, a substantial amount of intermolecular links had formed according to its X-ray out-of-plane diffraction pattern. Some of the links disppeared

when the film was further annealed at 350 °C and above. This may be attributed to the fact that the links were initially in a steric favorable but thermodynamically unstable state. At the elevated temperatures, the links have gained enough energy to overcome their steric barriers and have undergone "link-scission" reactions and converted to more stable imides, as indicated by the increase in the intensities of the FTIR absorption bands characteristic of the $(CO)_2NC$ imide group.

The imidization results from the FTIR experiment fairly match those from the bending-beam experiment for the two different polyimide systems. For PMDA–ODA, its thermal expansion coefficient dropped from 69.2 to 17.5 ppm/°C when annealed from 100 to 350 °C, and PMDA–PDA dropped from 28.8 to 4.4 ppm/°C.

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Registry No. (PMDA)(ODA) (copolymer), 25038-81-7; (PMDA)(PDA) (copolymer), 25038-82-8; (PMDA)(ODA) amic acid (SRU), 9043-05-4; (PMDA)(ODA) imide (SRU), 25036-53-7; (PMDA)(PDA) amic acid (SRU), 39311-16-5; (PMDA)(PDA) imide (SRU), 26099-65-0.