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Synthesis, structure, and properties of high performance alternating copolyimides

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Summary

A new diamine monomer, N,N'-bis(4-aminophenyl)-2,5-(diisopropoxycarbony)benzene-1,4-dicarboxamide was synthesized. Using the diamine, several alternating copolyimide precursors were successfully synthesized by its condensation polymerization with dianhydrides. The structure and properties (mechanical properties and thermal expansivity) of alternating copolyimides imidized thermally were characterized, and compared with those of the corresponding random copolyimides prepared from the copoly(amic acid)s. The alternating copolyimides exhibited relatively higher chain order and in-plane orientation in films than the random copolyimides. The higher chain order and in-plane orientation led to the higher tensile modulus and lower thermal expansivity in the alternating copolyimides. Such effect of comonomer sequence was found to be highly pronounced in copolyimides consisting of comonomers which have a large difference in the chain rigidity. It was demonstrated in this study that the formation of alternating copolyimides is a suitable route to improve the performance of properties.

Introduction

Fully aromatic polyimides are widely used in the fabrification of microelectronic devices, such as semiconductor chips and multi-chip modules as dielectric materials owing to the excellent electrical properties, high thermal stability, excellent mechanical properties, high chemical resistance, and easy processability.[1,2] Advanced semiconductor chips and multi-chip modules are generally designed in multilayered structures.[3,4] In multilayered devices, a dielectric polyimide is interfaced to itself as well as several different materials, such as silicon and silicon derivatives, metals, and ceramics. Thus, the reliability of multilayered devices generally depends upon the degree of stability at all interfaces. The high degree of interfacial stability requires low (or zero) interfacial stress and high adhesion strength: that is, lower interfacial stress and stronger interfacial adhesion give higher interfacial stability, consequently leading to higher reliability on multilayered microelectronic devices. In paricular, interfacial stress is primarily generated by the mismatch of thermal expansion coefficients (TECs) between the interfaced layers through thermal cycles and further increased by the mismatch of mechanical properties of the interfaced layers.[5,6] Metals and inorganic materials (silicon, ceramics and so on) are known to have relatively lower TEC and much higher modulus than polymers.[5-8] For polymers interfaced with metals or

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inorganics, matching TECs is easier than matching moduli, because polymers generally have a larger window for TEC than for modulus. Therefore, the control of TEC in a polymer is an adequate way to minimize residual stress on its interfaces to the other polymers, metals or inorganic materials, consequently enhancing the interfacial stability.

In general, rodlike polyimides exhibit low TEC, high modulus, high glass transition temperature, and high thermal stability, but show high brittleness. In contrast, flexible polyimides show high mechanical ductility and good interfacial adhesion, but exhibit high TEC, low modulus, low glass transition temperature, and low thermal stability. Thus, the properties required to the advanced applications cannot be easily achieved by a single homopolymer. One approach to achieve the required properties is to make copolymers, in particular alternating copolymers of rodlike and flexible homopolymers. In this study, several alternating copolyimide precursors were synthesized and thermally converted to the alternating copolyimides in thin films. The structure and properties (namely, TEC and mechanical properties) of alternating copolyimide films were characterized. The film properties were interpreted together with considering of comonomer sequence, molecular order, chain order and orientation, and imidization history. In addition, the structure and properties of alternating copolyimides were compared with those of the corresponding random copolyimides prepared from the copoly(amic acid) precursors.

Experimental

A new diamine monomer, N,N'-bis(4-aminophenyl)-2,5-(diisopropoxycarbonyl)benzene-1,4-dicarboxamide (I) was synthesized by the following two-step reactions (see Fig.1), which was recently reported by Rhee *et al.*[9]: Pyromellitic dianhydride (PMDA) was added to dry isopropanol in excess and reflexed for 1 h. The reaction products were obtained as a mixture of meta- and para-isomer. When the product solution was cooled in a refrigerator overnight, the para-isomer, namely 2,5-(diisopropoxycarbonyl)terephthalic acid crystallized. The para-siomer crystals were isolated by filtration and washed with n-hexane. The isolated para-isomer was dried under a vacuum and then dissolved in dry tetrahydrofuran. Ethyl chloroformate was stoichiometrically added to the para-isomer solution at a low temperature of -10°C and stirred for 0.5 h, resulting in the carboxylic-carbonic anhydride form of 2,5-(diisopropoxycarbonyl)terephthalic acid. The carboxylic-carbonic anhydride

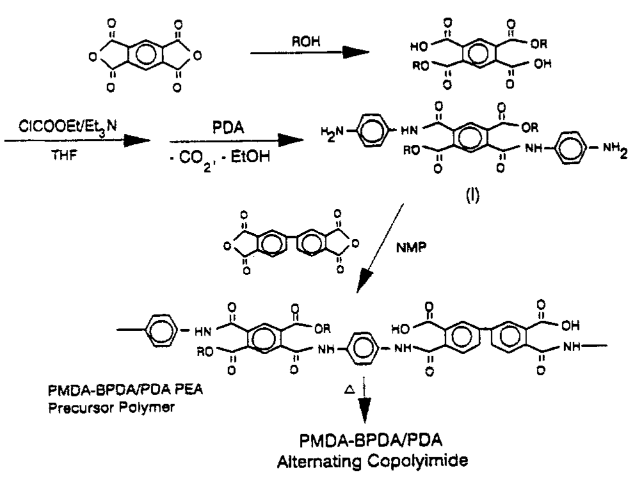

Fig.1. Synthesis scheme of a new diamine and its polyimide precursor, alternating copolyimide precursor: ROH, isopropyl alcohol; PDA, *p*-phenylene diamine.

was added dropwise to a small excess amount of *p*-phenylene diamine (PDA) in dry tetrahydrofuran and then stirred at room temperature for 1 day. The new diamine product (I), N,N'-bis(4-aminophenyl)-2,5-(diisopropoxycarbonyl)benzene-1,4-diacrboxamide in the solution was precipitated by adding diethyl ether, filtrated, and washed with hot water of 70°C. The new diamine was further purified by recrystallization from N-methyl-2-pyrrolidinone (NMP). The polymerization was carried out under a dry nitrogen flow by adding the equivalent stoichiometric amount of an dianhydride [namely, either 3,3',4,4'-biphenyltetracarboxylic dianhydride (BPDA) or 3,3',4,4'-bezophenonetetracarboxylic dianhydride (BTDA) or 4,4'-oxydiphthalic anhydride (ODPA)] to the new diamine (I) solution in dry NMP, and followed by continuous stirring for additional 2 days (see Fig.1). Poly(ester-*alt*-acid) (PEA) precursors of three different alternating copolyimides were synthesized in NMP (ca. 10 wt% solid content): poly[(*p*-phenylene pyromellitamic diisopropyl ester)-*alt*-(*p*-phenylene biphenyltetracarboxamic acid)] (PMDA-BPDA/PDA PEA), poly[(*p*-phenylene pyromellitamic diisopropyl ester)-*alt*-(*p*-phenylene benzophenonetetracarboxamic acid)] (PMDA-BTDA/PDA PEA), and poly[(*p*-phenylene pyromellitamic diisopropyl ester)-*alt*-(*p*-phenylene oxydiphthalamic acid)] (PMDA-ODPA/PDA PEA). The corresponding random copoly(amic acid) (PAA) precursors were synthesized by the polycondensation of PDA with a mixture of two dianhydrides. Equivalent moles of two dianhydries chosen were dissolved in dry NMP, and slowly added dropwise to the stoichiometric amount of PDA in dry NMP under a dry nitrogen flow. Then, the polycondensation was continued by stirring at room temperature for 2 days, giving PMDA-BPDA/PDA PAA, PMDA-BTDA/PDA PAA, and PMDA-ODPA/PDA PAA solutions (ca.10 wt% solid content). Molecular weights were controlled to be ca. 25k $\overline{M}n$ by stoichiometric imbalances between the used dianhydride and diamine. The precursor solutions were filetered, tightly sealed, and stored in a refrigerator before use.

Precursor solutions were cast on glass slides using a spin-coater or a doctor blade and followed by drying on a hotplate at 80°C for 3 h. Dried precursor films were thermally imidized under a nitrogen flow through a step-cure process: 200°C/1 h and 400°C/1.5 h with a ramping rate of 2.0 K/min. The thickness of copolyimides was 12 -19 μm.

Wide-angle x-ray diffraction (WAXD) measurements were conducted at room temperature in both reflection and transmission geometry using a horizontal x-ray diffractometer (Model M18XHF, MAC Science Co.) with an 18 kW rotating anode x-ray generator. The CuK_α radiation source was operated at 50 kV and 100 mA. One-degree divergence slit was employed together with two receiving slits of 0.15° and 0.3°. All measurements were carried out in θ/2θ mode. The 2θ scan data were collected at 0.02° intervals over the range of 3° - 60° and the scan speed was 0.4°(2θ)/min. The measured WAXD data were corrected for background. Mechanical properties were measured using an Instron mechanical tester (Model 4502). The gauge length was 50 mm and the crosshead speed was 2.0 mm/min. The width of film strips was 6.35 mm. In addition, thermal expansion coefficients were measured at a heating rate of 10.0 K/min under a nitrogen flow using a Perkin-Elmer thermomechanical analyzer (Model TMS-2). The gauge length was 7.5 mm and the width of film strips was 2.0 mm.

Results and Discussion

In general, amic acid type of polyimide precursors are in the equilibration of monomer-precursor polymer so that they are very sensitive to water as well as temperature variation.[1] For the nature of monomer-precursor polymer equilibration, a simple cocondensation polymerization of a diamine with an equivalent mixture of two dianhydrides may result in random copolyimide precursor rather than regularly sequenced alternating copolyimide precursor. This random copolymer formation can be avoided by utilization of a monomer synthesized newly in this study, N,N'-bis(4-aminophenyl)-2,5-(diisopropoxycarbonyl)-benzene-1,4-dicarboxamide (I) which owns two amic ester linkages. Using this stable diamine monomer, three alternating copolyimide precursors were nicely synthesized through its polycondensation reaction with one of three common dianhydrides (i.e., BPDA, BTDA, and ODPA): PMDA-BPDA/PDA PEA, PMDA-BTDA/PDA PEA, and PMDA-ODPA/PDA PEA. These alternating copolyimide precursor products consist of two different types of linkages, amic isopropyl ester and amic acid which were originated from the new diamine monomer and the conventional amine-anhydride condensation reaction, respectively. Therefore, these precursor polymers are still sensitive to water and temperature, owing to the amic acid linkages in the equilibration of monomer-precursor. However, in comparison with conventional poly(amic acid)s alternating copolyimide precursors are hydrolytically more stable and more soluble in solvents, due to the contribution of amic isopropyl ester linkages on the backbone.

The structure of copolyimides in thin films, which were thermally imidized at 400°C, was investiagted by wide-angle x-ray diffraction in both transmission and reflection geometry: Transmission run in which the diffraction vector is in the film plane can provide structural information in the film plane, whereas reflection run in which the diffraction vector is in the direction normal to the film plane can give structural information in the out-of-film plane. The WAXD patterns measured are shown in Figs.2-4. The alternating PMDA-BPDA/PDA copolyimide revealed a crystalline-like x-ray diffraction peaks in the transmission run. The peaks, which are at 9.58° (9.22 Å in *d*-spacing), 13.10° (6.75 Å), 16.28° (5.44 Å), 28.26° (3.16 Å), 38.26° (2.35 Å), and 44.96° (2.01 Å) in 2θ, could be assigned by (006), (008), (0010), (0018), (0024), and (0028), respectively (see the peaks marked by arrows in Fig.2). The reason is in the following. The projected length of one

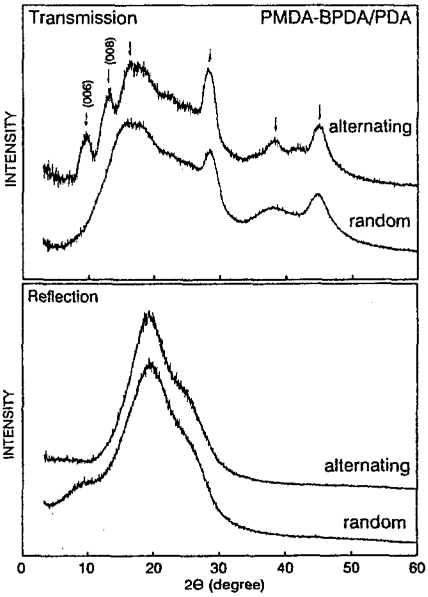

Fig.2. WAXD transmission and reflection patterns of alternating and random PMDA-BPDA/PDA copolyimides thermally imidized at 400°C. CuK_{α} radiation was used.

chemical repeat unit is 12.17 Å for poly(*p*-phenylene pyromellitimide) (PMDA-PDA) and 15.80 Å for poly(*p*-phenylene biphenyltetracarboximide) (BPDA-PDA).[10] With these values, the projected length of one repeat unit on their alternating copolyimide is easily estimated to be 27.97 Å. The copolyimide chain has one kink per chemical repeat unit, due to the biphenyl linkage of BPDA unit: that is, the copolyimide chain is not rod-like. Thus, the *d*-spacing for (001) diffraction is 55.94 Å rather than 27.97 Å. With the *d*-spacing 55.94 Å, *d*-spacing is estimated to be 9.33 Å for (006) diffraction, 6.99 Å for (008), 5.59 Å for (0010), 3.11 Å for (0018), 2.33 Å for (0024), and 2.00 Å for (0028). These *d*-spacings are very close to the *d*-spacing values obtained from the peaks in the transmission pattern. From the multiple (00*l*) peaks, it is concluded that the alternating copolyimide molecules are highly ordered along the chain axis. In addition, it is noted that higher ordered (00*l*) peaks, such as (0018), (0024), and (0028), are abnormally high in intensity and broad in shape. This may result from the overlapping of the (00*l*) peaks with other diffraction peaks in some degrees.

The multiple (00*l*) peaks, which were observed in the transmission pattern, did not reveal in the reflection pattern, indicating that the highly ordered alternating copolyimide chains were preferentially aligned in the film plane. The reflection pattern showed only a big amorphous halo with a weakly broad shoulder. This suggests that the alternating copolyimide molecules are poorly packed each other. The mean intermolecular distance, which was estimated from the big amorphous halo at 19.34° (2θ), is 4.59 Å, which is an intermediate value between the intermolecular distances of PMDA-PDA and BPDA-PDA homopolymers: 4.27 Å for PMDA-PDA and 4.84 Å for BPDA-PDA.

In a comparison with the x-ray diffraction patterns of PMDA-PDA and BPDA-PDA,

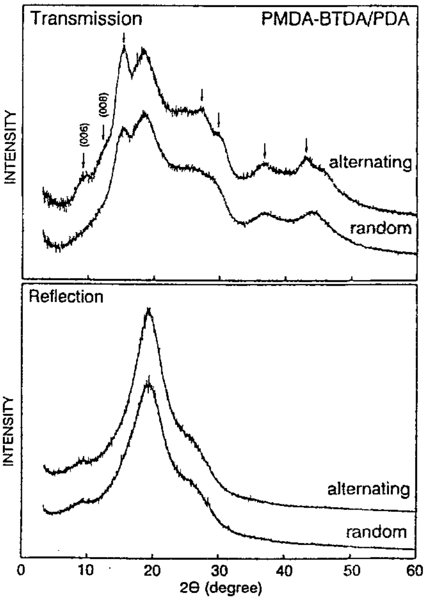

Fig.3. WAXD transmission and reflection patterns of alternating and random PMDA-BTDA/PDA copolyimides thermally imidized at 400°C. CuK_α radiation was used.

their alternating copolyimide shows the BPDA-PDA like transmission pattern, due to the biphenyl kink conformation on the backbone, and the PMDA-PDA like reflection pattern, mainly due to the high glass transition temperature (T_g) which is much higher than imidization temperatures. BPDA-PDA, which has a T_g of ca. 320°C (that is, the onset temperature of galss transition), is known to form a frozen smectic-E like crystalline structure with its extended chain conformation in the solid state, revealing a high degree of molecular chain order as well as intermolecular packing order.[10] However, PMDA-PDA is known to form a frozen smectic-A like crystalline structure with the fully rodlike chain conformation in the solid state, exhibiting a very poor intermolecular packing order.[10] Therefore, from the WAXD results it is suggested that the alternating PMDA-BPDA/PDA copolyimide molecules are in a frozen smectic-A like crystalline state.

The random PMDA-BPDA/PDA copolyimide showed transmission and reflection x-ray diffraction patterns comparable to those of the corresponding alternating copolyimide (see Fig.2). However, in the transmission pattern the diffraction peaks at > 14.0° (2θ) are relatively weak in intensity and broad in shape in comparison with those of the alternating copolyimide. Furthermore, the two diffraction peaks, (006) and (008) reflections, did not appear for the random copolyimide, indicating that the random copolyimide molecules are relatively less ordered along the chain axis compared with the alternating copolyimide molecules. The relatively poor molecular order along the chain axis might result from a high degree of sequential disorder of comonomers on the backbone, consequently disturbing tendency that the copolyimide chains are aligned together to form a smectic-A like structure which is possible in the alternating copolyimide. The (006) diffraction, which was not observed on the transmission pattern, surprisingly appeared on the reflection, but was very weak in intensity and very broad in shape. This is evidence that the molecular in-plane orientation in the random copolyimide is relatively lower than in the corresponding alternating copolyimide.

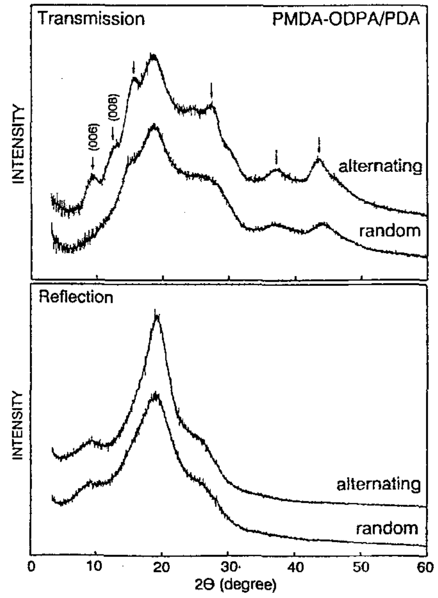

Fig.4. WAXD transmission and reflection patterns of alternating and random PMDA-ODPA/PDA copolyimides thermally imidized at 400°C. CuK_α radiation was used.

Similar WAXD results were observed for the other copolyimides, PMDA-BTDA/PDA and PMDA-ODPA/PDA as shown in Figs.3 and 4. However, for these alternating copolyimides the (00*l*) peaks in the transmission pattern are relatively weaker in intensity and broader in shape than those of alternating PMDA-BPDA/PDA copolyimide. Unlike alternating PMDA-BPDA/PDA copolyimide, these alternating copolyimides exhibited the (006) diffraction on the reflection pattern even though the diffraction peak was weak and broad. These indicate that their molecular chain order and in-plane orientation are relatively poor compared with alternating PMDA-BPDA/PDA copolyimide. For alternating PMDA-BTDA/PDA copolyimide, the projected length of chemical repeat unit and mean intermolecular distance are 29.45 Å and 4.65 Å, respectively. The alternating PMDA-ODPA/PDA copolyimide exhibited 29.09 Å projected length of repeat unit and 4.64 Å mean intermolecular distance.

Mechanical properties of copolyimide films were investigated at room temperature. For PMDA-BPDA/PDA, Young's modulus was 9.6 GPa for the alternating copolyimide and 9.1 GPa for the random copolyimide. As presented in Table I, for a chosen copolyimide system the alternating copolyimide exhibited a relatively higher modulus than the corresponding random copolyimide. The modulus difference between alternating and corresponding random copolyimide is 0.5 GPa for PMDA-BPDA/PDA, 1.0 GPa for PMDA-BTDA/PDA, and 2.8 GPa for PMDA-ODPA/PDA. In contrast to the modulus, strain at break was relatively smaller in the alternating copolyimide than the corresponding random copolyimide. However, such brittleness, which is observed for PMDA-PDA homopolyimide film, was not observed for all the copolyimides. The relatively lower strain at break observed for the copolyimides may be improved by minimizing defects in the films.

In addition, thermal expansion coefficients in the copolyimide films were measured by thermomechanical analysis. The results are summarized in Table I. For a chosen copolyimide system, thermal expansion coefficient (TEC) was lower in the alternating copolyimide than the random copolyimide. The TEC difference between alternating and corresponding random copolyimide is 3.6 ppm/°C for PMDA-BPDA/PDA, 5.9 ppm/°C for PMDA-BTDA/PDA, and 14.0 ppm/°C for PMDA-ODPA/PDA.

Table I. Mechanical properties and thermal expansion coefficients of alternating and random copolyimides in films*

Copolyimide	Modulus (GPa)	Stress at break (MPa)	Strain at break (%)	TEC# (ppm/°C)
PMDA-BPDA/PDA				
alternating	9.6	254	7	2.3
random	9.1	248	10	5.9
PMDA-BTDA/PDA				
alternating	8.4	189	4	9.3
random	7.4	216	9	15.2
PMDA-ODPA/PDA				
alternating	8.1	223	10	6.8
random	5.3	185	17	20.8

* All copolyimides were imidized at 400°C. The thickness of films was 12 - 19 μm.

\# TEC is the thermal expansion coefficient averaged over 70 - 200°C.

The modulus and TEC results indicate that for copolyimides the sequence of comonomers on the backbone plays an important role on the film properties. In general, for a polymer both modulus and TEC in the film plane are sensitive to the molecular chain rigidity, chain order, and in-plane orientation: The higher chain rigidity, chain order, and in-plane orientation give the higher modulus and the lower TEC in the film plane. Besides these factors, in this study it is evident for copolyimides that the sequence of comonomers also is a critical factor to influence those in-plane properties. In comparison, the effect of comonomer sequence on modulus and TEC was lowest for PMDA-BPDA/PDA, intermediate for PMDA-BTDA/PDA, and highest for PMDA-ODPA/PDA. This seems to be mainly related to the conformation and rigidity of comonomer components. The carbonyl linkage of BTDA unit is more flexible than the biphenyl linkage of BPDA, but less flexible than the ether linkage of ODPA. On the other hand, BPDA unit has a rotational disorder along the biphenyl bond. Thus, the BPDA may be less rigid than PMDA unit. In comparison, the rigidity is in the order PMDA > BPDA > BTDA > ODPA. Therefore, the effect of comonomer sequence seems to be highly pronounced on a copolymer system which consists of a highly rigid monomer and a highly flexible comonomer. In addition, the highest modulus and lowest TEC in PMDA-BPDA/PDA copolyimides might result from the relatively higher chain rigidity, chain order and in-plane orientation compared with those of the other copolyimides.

Conclusions

Three alternating copolyimide precursors were successfully synthesized by the condensation polymerization of a newly synthesized diamine monomer, N,N'-bis(4-aminophenyl)-2,5-(diisopropoxycarbony)benzene-1,4-dicarbox-amide with BPDA, BTDA or ODPA. The alternating copolyimides imidized thermally exhibited higher chain order and in-plane orientation in thin films than the corresponding random copolyimides prepared from the copoly(amic acid)s, due to the well sequenced comonomer units on the backbone. The higher chain order and in-plane orientation were directly reflected on the film properties: that is, the higher chain order and in-plane orientation give the higher modulus and lower TEC in the film plane. Conclusively, it is evident in this study that the sequence of comonomers plays a critical role on the performance of properties in copolyimides. The effect of comonomer sequence on the properties seems to be very high in a copolymer consisting of comonomers which have a large difference in their chain rigidity. [*This study was financially supported by the Ministry of Science and Technology (MOST) of South Korea with grant KRICT BS JG 94-2020*].

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