Characterization of Alicyclic Polyimides Based on Cyclobutane Ring Dianhydride and Aromatic Diamine

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SYNOPSIS

Films of alicyclic polyamic acid and polyimide containing cyclobutane ring in dianhydride moiety and aromatic ring with p- or m-linkages in diamine moiety were characterized by infrared (IR) spectroscopy, dynamic viscoelasticity, differential-scanning calorimetry (DSC), density, and wide-angle X-ray diffraction analyses. Partially and fully imidized polyimides were obtained by varying the imidization temperature, e.g., 150°C, 250°C, and 350°C. It was found from the results of IR spectra, dynamic viscoelasticity, and DSC measurements that the imidization of alicyclic polyamic acid was reduced at about 150°C and needed a higher imidization temperature than aromatic polyamic acid. Alicyclic polyimide with m-linkage in the diamine moiety had a higher density and a much more ordered structure than with p-linkage. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Polyimide films are characterized by their heat-stability, solvent resistance, and excellent mechanical properties.[1] They are especially used in electronic devices which require heat-stability, low dielectric constant, thin film formation, etc. Polyimides have structures composed of various dianhydride and diamine moieties, namely, various primary structures. This gives rise to various possible functionalities in addition to the properties mentioned above. Usually, dianhydride and diamine moieties contain aromatic rings, which results in heat-stability and excellent mechanical properties with a high glass transition temperature. This is mainly attributed to the rigid conformation of the aromatic ring as well as that of the imide group.

Recently, the synthesis of dianhydrides having cyclobutane rings has become feasible.[2] Polyimides consisting of alicyclic cyclobutane rings instead of aromatic benzene rings are of interest from the standpoint of various functions. Such an alicyclic polyimide is used as an orientation membrane which can tilt liquid crystalline molecules from a substrate surface.[3] This novel alicyclic polyimide has not been well studied. An understanding of the structure–properties relations of alicyclic polyimide is required to further develop a general understanding of polyimides and to apply them to industrial uses.

In this article, alicyclic polyimides, with cyclobutane rings in the dianhydride moiety and p- or m-linkages in the diamine moiety, were obtained by thermal imidization of the polyamic acids. The alicyclic polyimides obtained at various temperatures were characterized by infrared spectroscopy, dynamic viscoelasticity, differential-scanning calorimetry, density, and wide-angle X-ray diffraction, and compared with aromatic polyimides with benzene rings in the dianhydride moiety and p-linkages in the diamine.

EXPERIMENTAL

Preparation of Polyamic Acid and Polyimide

Polyamic acid, the precursor of polyimide, is generally obtained by the polycondensation of tetracarboxylic acid dianhydride and aromatic diamine.

Cyclobutane-1,2 : 3,4-tetracarboxylic acid dianhydride (CBDA) was used as the dianhydride, while 1,4-bis(4-aminophenoxy)benzene (p-BAPB) and 1,3-bis(4-aminophenoxy)benzene (m-BAPB) were used as the aromatic diamines to obtain the alicyclic polyamic acid (Scheme 1). Pyromellitic acid dianhydride (PMDA) and p-BAPB were used to obtain the aromatic polyamic acid. An equimolar amount of the dianhydride was added to a N-methyl pyrrolidone (NMP) solution of the diamine under a N_2 gas atmosphere. The polyamic acid solution, approximately 15%, was obtained after stirring for about 2–3 h.

Polyamic acids obtained were cast on a glass plate and prebaked at 80°C for 1 h. Imidization of the polyamic acid was carried out by a stepwise increase in temperature. Specimen was heated from 80°C up to 150°C at the heating rate of 0.39°C/min, kept for 20 min; succeedingly heated up to 175°C at 1.25°C/min, kept for 20 min; heated up to 200°C at 1.25°C/min, kept for 20 min; heated up to 250°C at 2.5°C/min, kept for 1 h; heated up to 350°C at 0.83°C/min, and kept for 30 min. Three final and maximum imidization temperatures of 150°C, 250°C, or 350°C were adopted below. The polyimide film was detached from the glass plate by placing the sample into water after slow cooling, and then dried thoroughly for 24 h. The alicyclic and aromatic

polyamic acids and polyimides obtained are abbreviated as follows: $X.Y$-Z, where X is either C or P, corresponding to CBDA or PMDA, respectively, in dianhydride moiety; Y- is either p- or m-, meaning the linkage in diamine moiety; and Z means either polyamic acid unimidized: PAA, or maximum imidization temperature: 150°C, 250°C, or 350°C.

Procedure

### Infrared (IR) Spectroscopy

IR transmission spectra were measured on films, about 10 μm thick, at ambient temperature using a JASCO IR-700 infrared spectrometer manufactured by Japan Spectroscopic Co., Ltd. Spectra were obtained by co-adding five scans in the wave number range from 3,000 to 1,000 cm^{-1}.

Dynamic Viscoelasticity

Dynamic viscoelasticity experiments on about 10-μm thick polyimide films were carried out in shear mode using a DMS100 Dynamic Mechanical Spectrometer and Rheol Station SDM5500 manufactured by Seiko Instruments, Inc. The conditions of measurements were as follows: temperature range from 50°C to 450°C, heating rate of 4°C/min, and frequency of 1 Hz.
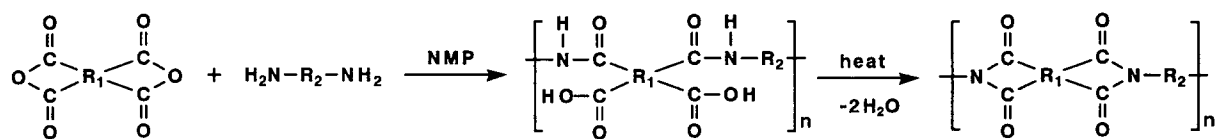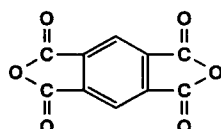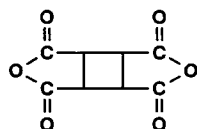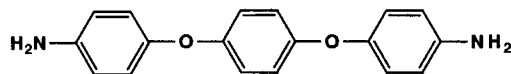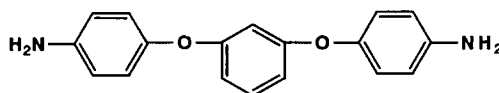

Scheme 1 Scheme of polycondensation of polyamic acid and imidization and molecular structure of dianhydride and diamine moieties.

Differential-Scanning Calorimetry (DSC)

DSC thermograms on samples about 10 mg in weight were obtained under N_2 gas flow in the 50–300°C temperature range and at the heating rate of 10°C/min using a SSC-560 type DSC with SSC-560-S type cell (Seiko Instruments, Inc.).

Density Measurement

The density of each sample was obtained by a floatation method at 25°C using a mixture of carbon tetrachloride and cyclohexane. Small air-bubbles at the specimen surface were carefully removed.

Wide-Angle X-ray Scattering

X-ray diffraction profiles of film samples stacked to a total thickness of about 500 μm were obtained in the out-of-plane (film thickness) direction at the scattering angle from 3 degrees to 30 degrees by accumulation of 10 scans. An X-ray diffractometer (RAD-RC manufactured by Rigaku Co.) with a Ni filter was operated at ambient temperature with a power of 40 kV and 80 mA.

RESULTS AND DISCUSSION

To follow the imidization process, IR spectroscopy was used. The degree of imidization was evaluated from the peak intensity at 1,375 cm^{-1} which was assigned to C–N stretching[4-6] mode of imide group, using a benzene ring stretching vibration at 1,490 cm^{-1} as an internal standard. The degrees of imidization determined are summarized in Table I. The

Table I   Degree of Imidization and α Dispersion Temperature at the Frequency of 1 Hz of Aromatic and Alicyclic Polyimides

Sample	Degree of Imidization (%)	α Dispersion Temperature (°C)
P.p-.PAA	0	148
P.p-.150	63	—
P.p-.250	96	—
P.p-.350	100	320
C.p-.PAA	0	147
C.p-.150	8	—
C.p-.250	90	—
C.p-.350	100	391
C.m-.PAA	0	128
C.m-.150	14	—
C.m-.250	98	—
C.m-.350	100	378–413

degree of imidization increased with the imidization temperature, as usually observed.[7] To compare the imidization process for the polyimide containing benzene rings with those containing cyclobutane rings, the degree of imidization of aromatic polyimides is also cited in Table I. The aromatic polyimide imidized at 150°C gave higher degree of imidization, e.g., 63% for P.p-.150, than the alicyclic polyimides, which had degrees of imidization under 15%. This suggests that imidization of alicyclic polyimide needs higher imidization temperature than that of aromatic polyimide, irrespective of glass transition temperature of each polyamic acid. The relation of imidization of polyamic acid and its glass transition temperature is described later. Full imidization was attained for imidization of both polyamic acids at 350°C.

Dynamic viscoelastic measurements were carried out for several polyimides. The temperature-dependence of storage shear modulus (G′) and loss tangent (tan δ) at the frequency of 1 Hz of P.p-.PAA and P.p-.350, C.p-.PAA and C.p-.350, and C.m-.PAA and C.m-.350 are shown in Figure 1(a), (b), and (c), respectively. The shear modulus of all the polyamic acids starts to decrease around their glass transition temperature and then increases. This means a decrease in modulus because of glass transition of polyamic acid,[8] and the subsequent increase in modulus up to the value of glassy state of polyimide because of imidization. As a result, the shear modulus above the glass transition temperature was considered to reach the modulus of polyimides imidized in the process of heating. These abrupt changes in the modulus were not observed for all the fully imidized alicyclic polyimide. The behavior of modulus above glass transition of C.m-.PAA is not understood fully. A remarkable shrinkage of C.m-.PAA is observed on imidization. There might be some crazes or cracks in the film of alicyclic polyimide with m-linkage, which could explain the low shear modulus above about 200°C.

Tan δ of alicyclic polyamic acids of C.p-.PAA and C.m-.PAA showed a peak at 147°C and 128°C around their glass transition temperature, and another peak at 171°C and 169°C, respectively. The latter peak probably corresponds to a relatively slow rate of the imidization reaction. Such a peak was not observed for the aromatic polyamic acid, P.p-.PAA. This is considered to imidize comparatively faster, and the glass transition of the aromatic polyamic acid probably accompanies imidization. These tan δ results coincide with the degree of imidization as described in Table I. Namely, alicyclic polyamic acid starts to imidize quickly around 170°C, while

(a)

(b)

(c)
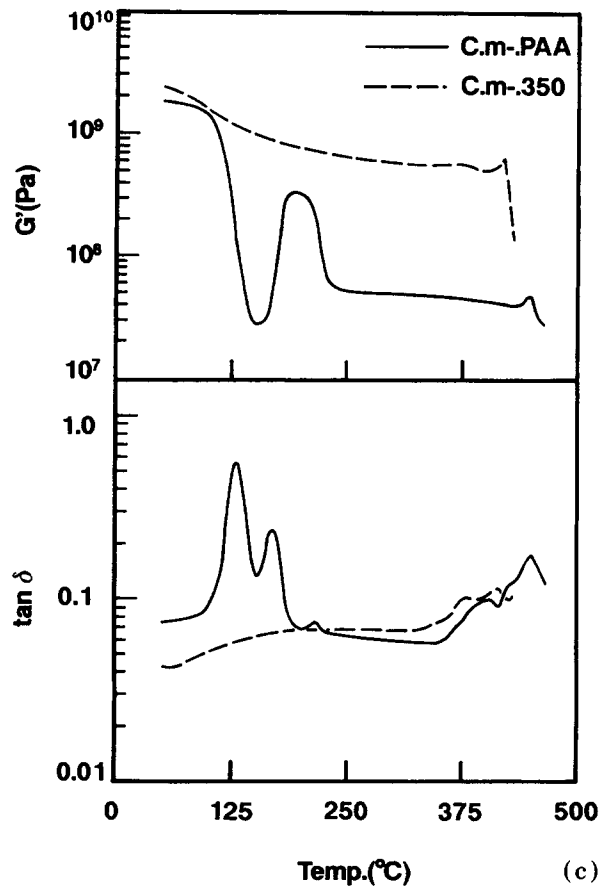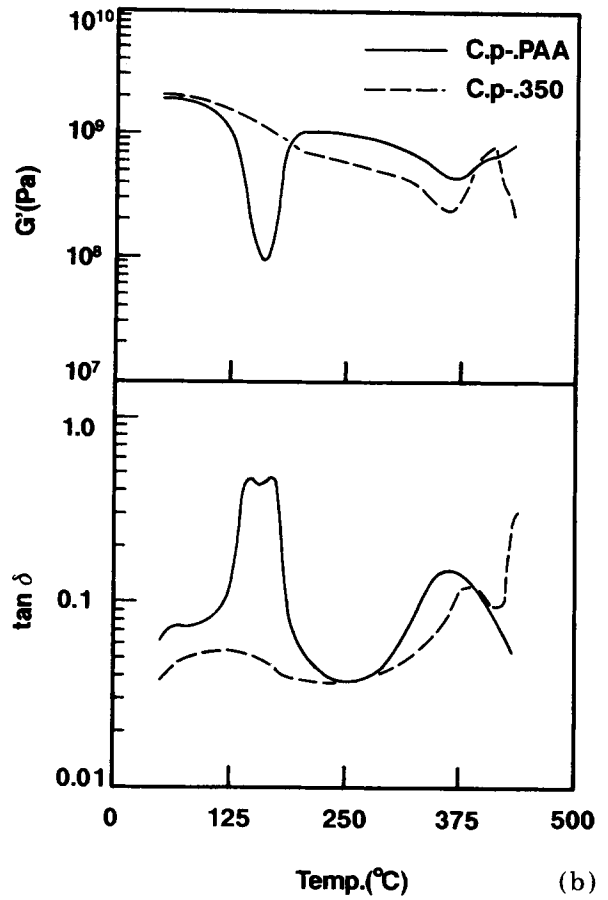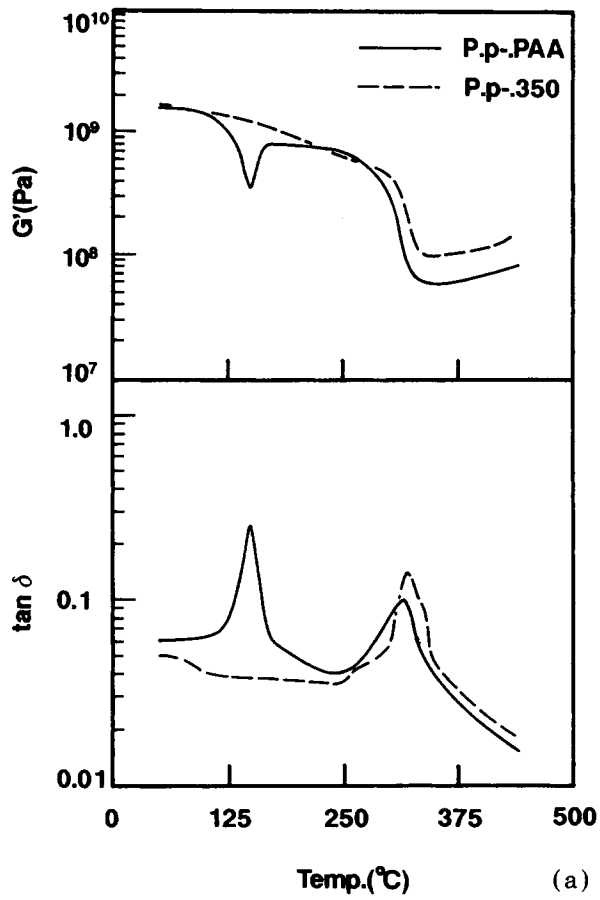
the aromatic polyamic acid does below 150°C. Thereby, P.p-.150 imidized at 150°C shows a relatively high degree of imidization. The degree of imidization of C.m-.150 is higher than that of C.p-.150 because of the higher glass transition temperature and imidization temperature of C.p-.150, compared to C.m-.150.

DSC thermograms of polyamic acids and polyimides studied here are shown in Figure 2(a), (b), and (c) for P.p- series (P.p-.PAA, P.p-.150, P.p-.250, P.p-.350), C.p- series (C.p-.PAA, C.p-.150, C.p-.250, C.p-.350), and C.m- series (C.m-.PAA, C.m-.150, C.m-.250, C.m-.350), respectively. An endothermic peak appeared for all the polyamic acids around their glass transition temperature where the jump (ΔCp) of the difference of heat content between glassy state and liquid state was observed. One can observe separately the jump of heat content of C.m-.PAA at about 125°C, which is ascribed to its glass transition temperature. The lower glass transition temperature of C.m-.PAA corresponds to observations from other reports.[9-11]

The endothermic peak intensity decreases with increasing imidization temperature and does not appear for polyimides imidized at 250°C and 350°C. This peak intensity is assigned to the heat of imidization of an original sample. The endothermic peak of P.p-.PAA appearing at 158°C was relatively *sharp*, but that of alicyclic polyamic acid appearing around 185°C was very *broad*, indicative of very slow imidization of alicyclic polyamic acid. The results obtained here coincide with the results of IR and dynamic viscoelasticity mentioned above. The enthalpy change (ΔH) is tabulated in Table II. The enthalpy change follows the series: C.m-.PAA > C.p-.PAA > P.p-.PAA. The enthalpy change of C.p-.PAA is higher than that of P.p-.PAA, which contains the same diamine moiety but a different ring group. This suggests that an alicyclic polyamic acid needs much more imidization energy than aromatic polyamic acids. Furthermore, it is noted that the enthalpy change of C.m-.PAA is much greater than that of C.p-.PAA, irrespective of a similar primary structure. These differences may be due to the density difference of alicyclic polyimide with p- or m-linkages in the diamine moiety, which will be described later.

Table II Enthalpy Change on Imidization of Aromatic and Alicyclic Polymides

Sample	ΔH (J/g)
P.p-.PAA	257.1
P.p-.150	85.9
P.p-.250	—
P.p-.350	—
C.p-.PAA	396.5
C.p-.150	248.9
C.p-.250	—
C.p-.350	—
C.m-.PAA	671.8
C.m-.150	366.8
C.m-.250	—
C.m-.350	—

Densities of all the polyamic acids and polyimides are shown in Table III. It was found that density increases with the degree of imidization, indicative of the denser packing of polyimide chains by imidization. Comparing the p- and m-linkages of diamine moiety, the density of both polyamic acids (C.p-.PAA and C.m-.PAA) is approximately the same, but the density of alicyclic polyimide of C.m-.350 is higher than that of C.p-.350. This means that the polyimide with m-linkage has increased chain packing, which results in a denser structure.[10,11] One can say that polyimide of C.m-.350 contains much less free volume compared to C.p-.350 with p-linkage.

Wide-angle X-ray diffraction patterns in the out-of-plane direction were performed to clarify the structure of polyamic acid and polyimide. The diffraction profiles of P.p- series (P.p-.PAA, P.p-.150, P.p-.250, P.p-.350), C.p- series (C.p-.PAA, C.p-.150, C.p-.250, C.p-.350), and C.m- series (C.m-.PAA, C.m-.150, C.m-.250, C.m-.350) are shown in Figure 3(a), (b), and (c), respectively. The diffraction peak was observed around $2\theta = 18°$ for all the polyamic acids and polyimides. Peak intensity increased and became sharper with increased imidization temperature.[12,13] This peak has been assigned to an intermolecular spacing of polyamic acid and polyimide,

Figure 1 (a) Temperature-dependence of storage shear modulus (G') and loss tangent (tan δ) at the frequency of 1 Hz of P.p-.PAA (——) and P.p-.350 (- - -). (b) Temperature-dependence of storage shear modulus (G') and loss tangent (tan δ) at the frequency of 1 Hz of C.p-.PAA (——) and C.p-.350 (- - -). (c) Temperature-dependence of storage shear modulus (G') and loss tangent (tan δ) at the frequency of 1 Hz of C.m-.PAA (——) and C.m-.350 (- - -).
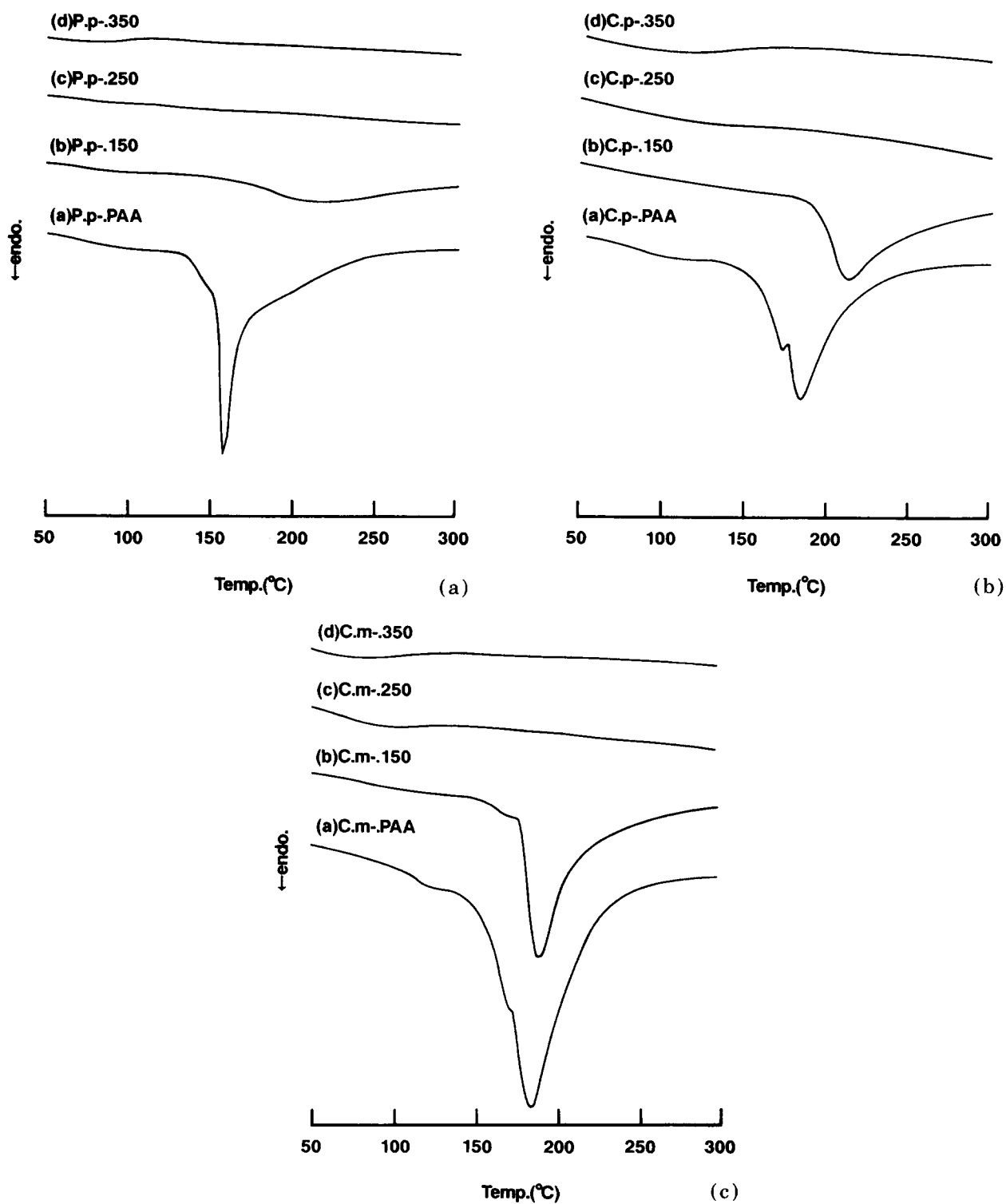
Figure 2 (a) DSC thermograms of P.p-.PAA (a), P.p-.150 (b), P.p-.250 (c), and P.p-.350 (d). (b) DSC thermograms of C.p-.PAA (a), C.p-.150 (b), C.p-.250 (c), and C.p-.350 (d). (c) DSC thermograms of C.m-.PAA (a), C.m-.150 (b), C.m-.250 (c), and C.m-.350 (d).
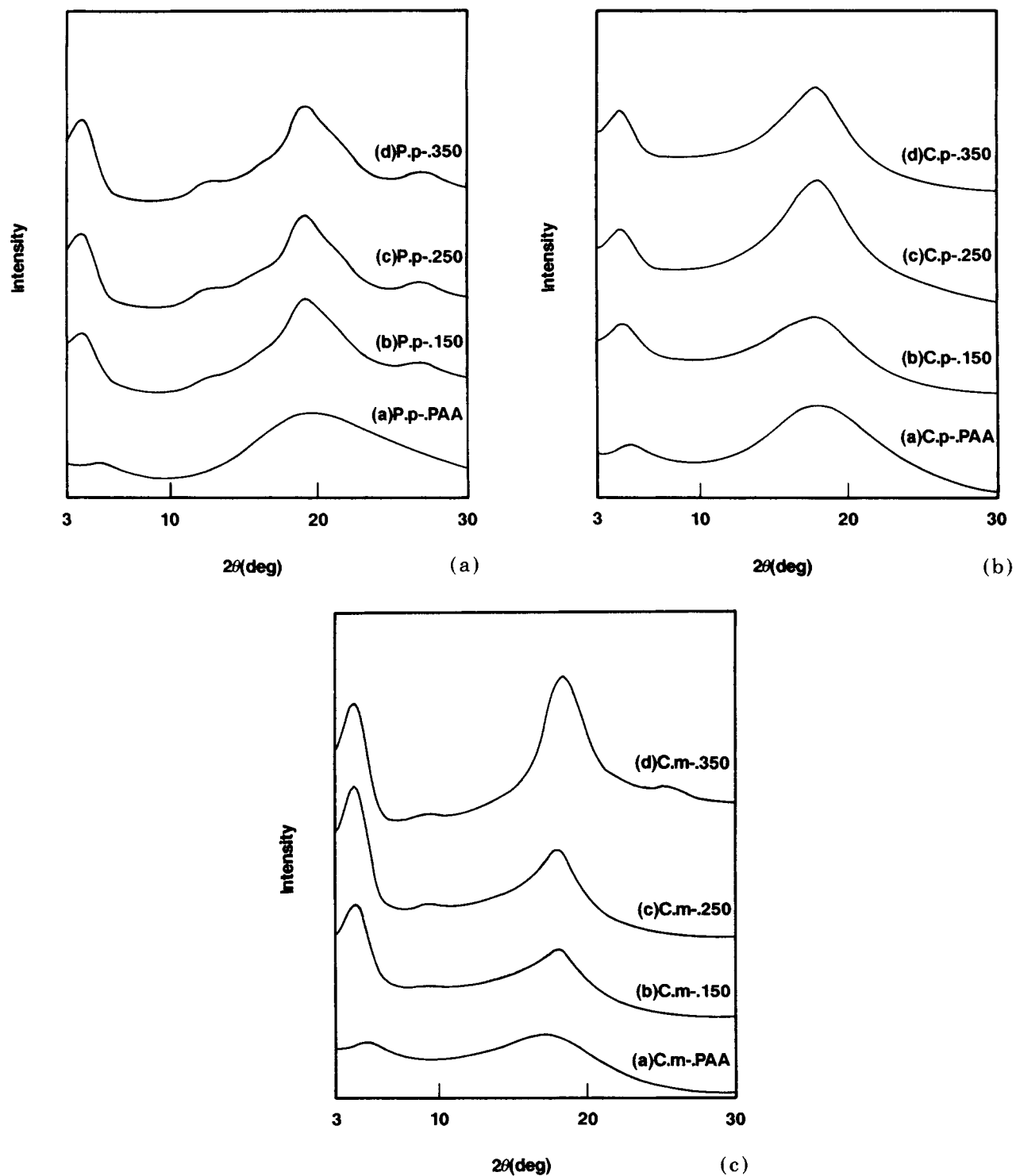
Figure 3   (a) X-ray diffraction profiles of P.p-.PAA (a), P.p-.150 (b), P.p-.250 (c), and P.p-.350 (d). (b) X-ray diffraction profiles of C.p-.PAA (a), C.p-.150 (b), C.p-.250 (c), and C.p-.350 (d). (c) X-ray diffraction profiles of C.m-.PAA (a), C.m-.150 (b), C.m-.250 (c), and C.m-.350 (d).

Table III Density and Intermolecular Spacing (d₁) and Intermolecular Spacing (d₂) of Aromatic and Alicyclic Polyimides

Sample	Density (g/cm^3)	d_1 Spacing (Å)	d_2 Spacing (Å)
P.p-.PAA	1.335	4.6	17.3
P.p-.150	1.353	4.6	22.4
P.p-.250	1.374	4.6	22.4
P.p-.350	1.377	4.6	22.4
C.p-.PAA	1.313	4.9	16.8
C.p-.150	1.339	5.0	19.0
C.p-.250	1.365	5.0	19.2
C.p-.350	1.372	5.0	19.6
C.m-.PAA	1.314	5.2	17.1
C.m-.150	1.352	4.9	20.3
C.m-.250	1.375	4.9	20.8
C.m-.350	1.384	4.8	21.0

and is considerably influenced by the diamine moiety.[12-14] The spacing (d_1) calculated from a maximum peak diffraction using the Bragg equation is also shown in Table III. The spacing of P.p- and C.p- series containing p-linkage in the diamine moiety did not vary substantially by imidization, but that of C.m- series containing m-linkage decreases by imidization. These results suggest that no rotation of the aromatic ring around the main chain causing a change in packing occurs for P.p- and C.p-series. On the other hand, rotation must occur to cause the increased chain packing for C.m- series.

Another diffraction peak was observed in the scattering angle range of $2\theta = 4 \sim 5°$, and its intensity increased with imidization temperature as well. This peak has been assigned to the intramolecular spacing along the polyimide chain.[12-14] The peak of C.m-.350 was much more intense compared to P.p-.350 and C.p-.350, which indicates a very packed and out-of-plane ordered structure for the C.m-.350. Similarly, the spacing (d_2) was calculated from the scattering angle of the peak maximum and also tabulated in Table III. The spacing (d_2) of alicyclic polyimide increased with imidization temperature. This supports the idea that the main chain adopts a much more rigid extended form by imidization, which was considered to be intrinsic conformation of alicyclic polyimide studied here.

CONCLUSION

The alicyclic polyamic acid and polyimide containing cyclobutane ring in dianhydride moiety and aromatic ring with p- or m-linkages in diamine moiety were characterized by infrared spectroscopy, dynamic viscoelasticity, differential-scanning calorimetry, density, and wide-angle X-ray diffraction analyses. Partially and fully imidized polyimides were obtained by varying the imidization temperature, e.g., 150°C, 250°C, and 350°C. The rate of imidization of alicyclic polyamic acid was reduced at about 150°C compared to aromatic polyamic acid. Compared to alicyclic polyimides with p-linkage in the diamine moiety, those with m-linkage had higher density, much more packing, and took an out-of-plane ordered structure.

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