BUTTERWORTH
HEINEMANN

Polymer Vol. 36 No. 13, pp. 2657–2662, 1995

0032-3861/95/\$10.00+0.00

Novel regular network polyimide films from mellitic acid and aliphatic and aromatic diamines or diisocyanates

Minoru Nagata*
Junior Women's College, Kyoto Prefectural University, Shimogamo, Sakyoku, Kyoto 606, Japan

and Tsuyoshi Kiyotsukuri, Takashi Moriya, Naoto Tsutsumi and Wataru Sakai
Department of Polymer Science and Engineering, Kyoto Institute of Technology, Matsugasaki, Sakyoku, Kyoto 606, Japan
(Received 31 August 1994; revised 21 October 1994)

Novel regular network aliphatic–aromatic and aromatic polyimide films were prepared from mellitic acid ($\mathbf{Y_H}$) and aliphatic and aromatic diamines or diisocyanates. Prepolymers prepared by solution polycondensation were cast and successively post-polymerized to form a network. The resultant films were insoluble in any organic solvents. The heat distortion temperature (T_h) and density of network polyimide films increased and then levelled off with increasing post-polymerization temperature and time. Polyimide films prepared from diisocyanates and $\mathbf{Y_H}$ had higher T_h values compared with those prepared from the corresponding diamines and $\mathbf{Y_H}$, which is due to the enhanced degree of reaction of the former films shown by infra-red spectroscopy. On increasing the length of the methylene chain in the diamine component, the T_h values and densities decreased and the intensities of X-ray diffraction peaks increased for network aliphatic–aromatic polyimide films. The T_h values of network polyimide films were somewhat higher than those of the corresponding linear polyimide films and network polyamide films. The $\mathbf{6'Y_H}$ film prepared from $\mathbf{Y_H}$ and hexamethylene diisocyanate ($\mathbf{6'}$) post-polymerized at 370°C for 1 h had a T_h value of 316°C; and the $\mathbf{OY_H}$ film prepared from $\mathbf{Y_H}$ and 4,4′-diaminodiphenyl ether (**O**) post-polymerized at 370°C for 1 h had the highest T_h value of 449°C among the polyimide films studied. Network polyimide films had much higher thermal resistance compared with the corresponding linear polyimide films at higher temperature, suggesting the preferred formation of carbonized structure.

(Keywords: regular network films; polyimides; heat distortion temperature)

INTRODUCTION

As is well known, aromatic polyimides have been recognized as an important class of engineering plastics having outstanding thermal resistance and good mechanical properties. It is expected that their thermal resistance could be further enhanced by the introduction of network structure into the backbone of the polymer.

We have already reported the novel regular network polyester films[1–4] from multifunctional aromatic carboxylic acids and glycols or aromatic diols, and polyamide films[4–6] from trimesic acid and aliphatic or aromatic diamines by solvent casting of prepolymers followed by post-polymerization of cast film. Furthermore, novel regular network polyurethane films[7] were also prepared from aliphatic and aromatic polyols and diisocyanates. The resultant transparent, flexible and insoluble polymer films have a relatively ordered regular network structure and show much higher resistance to thermal distortion compared with the corresponding linear polymer films.

More recently, we have prepared novel regular network polyimide films from mellitic acid and aliphatic and aromatic diamines or diisocyanates, and found that they have remarkably higher resistance to thermal distortion. In this article, we report the preparation of these network polyimide films, and discuss their thermal properties, in relation to their chemical structures, compared with those of the corresponding linear polyimide films.

EXPERIMENTAL

Monomers

Figure 1 shows the structural formulae and codes of the monomers used in this study. Pyromellitic dianhydride was recrystallized from acetic anhydride. Pyromellitic acid tetramethyl ester was obtained by refluxing pyromellitic acid (**X**) in methanol at 60°C for 4 h using sulfuric acid as a catalyst and was recrystallized from methanol. 4,4′-Diaminodiphenyl ether (**O**) was

---

* To whom correspondence should be addressed

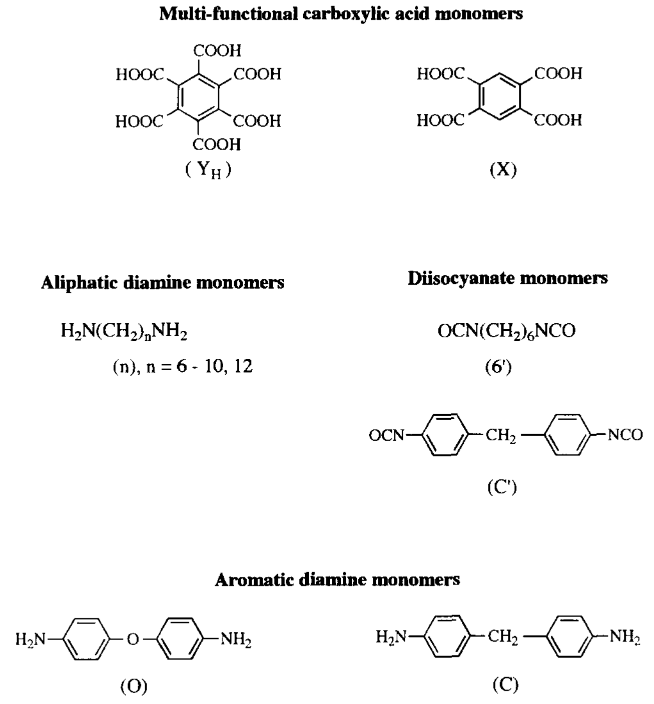

Figure 1 Structural formulae and codes of monomers used in this study

purified by vacuum sublimation. Mellitic acid (**Y_H**), its hexamethyl ester, two diisocyanates (**6′** and **C′**), various aliphatic diamines (**6–10, 12**) and 4,4′-diaminodiphenylmethane (**C**) were used as received.

Preparation of prepolymers

A mixture of 1 mmol of mellitic acid hexamethyl ester and 1.5 mmol of diamines was dissolved in 1 g of *o*-xylenol for aliphatic diamines and 1 g of *N,N′*-dimethylacetamide (DMAc) for aromatic diamines, respectively. The solution was heated at 160°C for 10–30 min in a stream of nitrogen. Prepolymer from **Y_H** and diisocyanate was prepared as follows. A mixture of 1.5 mmol of diisocyanates and 1 mmol of **Y_H** was dissolved in 2.5 g of *N*-methyl-2-pyrrolidone (NMP) in a stream of nitrogen and the solution was heated at 100°C for 5–15 min in a stream of nitrogen. The polyimides obtained were named by the monomer codes. For example, the polyimide from **Y_H** and diamine ***n*** is called **nY_H**, and the polyimide from **Y_H** and diisocyanate **6′** is called **$6'Y_H$**.

Preparation and post-polymerization of network polyimide films

The obtained prepolymer solution was cast on an aluminium plate at 80°C for DMAc and NMP, and at 120–200°C *in vacuo* for *o*-xylenol, respectively. The cast film was post-polymerized at the given temperature and time in an electric furnace. The post-polymerized film was then peeled off from the aluminium plate. The obtained films were deeply coloured and insoluble in any organic solvents.

Preparation of linear polyimide films

The **9X** and **12X** films were prepared by melt polycondensation. First, 5 mmol of pyromellitic dianhydride was dissolved in 12 ml of methanol at 60°C, and to the solution was added 5 mmol of diamine and the solution was stirred at 60°C for 2 h. The 1:1 salt was isolated by evaporation of methanol and was heated at 140°C for 2 h *in vacuo* and successively heated at 310–325°C for 2 h. The obtained polyimide was cast from dichloroacetic acid solution on a Teflon plate at 80°C for 6 h and finally at 300°C for 1 h *in vacuo*.

The **OX** and **CX** films were prepared via poly(amic acid)[8]. The polymerization was carried out in nitrogen

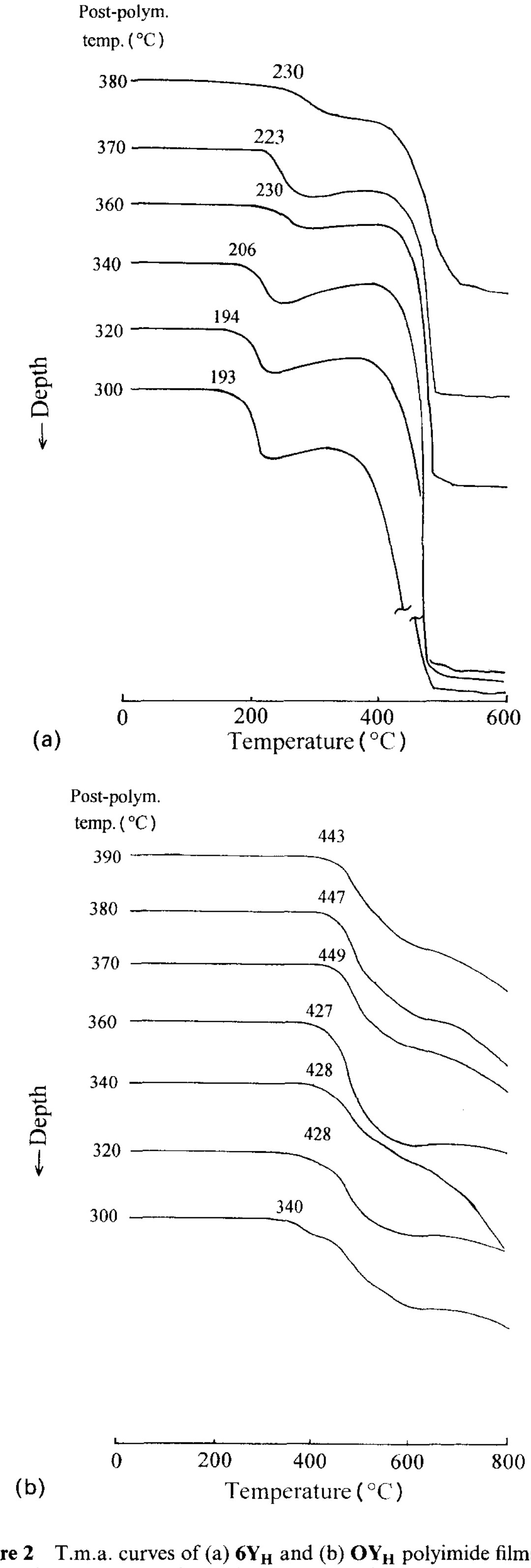

Figure 2 T.m.a. curves of (a) **$6Y_H$** and (b) **OY_H** polyimide films post-polymerized at various elevated temperatures for a constant time of 1 h

atmosphere by the addition of equimolar pyromellitic dianhydride to the stirred solution of diamines in DMAc. The resulting solution was stirred at ambient temperature for 1 h. The obtained poly(amic acid) solution was cast on an aluminium plate at 80°C for 2 h *in vacuo* and then imidized at 370°C for 1 h.

Characterization

Infra-red spectra were recorded on a Jasco model A-1 i.r. spectrophotometer by using a KBr pellet.

Thermomechanical analysis (t.m.a.) was performed in penetration mode under a pressure of $10\,\mathrm{kg\,cm^{-2}}$ and a heating rate of $20^{\circ}\mathrm{C\,min^{-1}}$ in nitrogen atmosphere, using a Shimadzu model DT-30 thermomechanical analyser.

Density was measured in a heptane–carbon tetrachloride density gradient column at 30°C within ±0.1°C accuracy.

The X-ray diffraction intensity curve was measured with a Toshiba model ADG-301 X-ray diffractometer with nickel-filtered Cu K_{α} radiation.

Thermogravimetry (t.g.) was performed on a Shimadzu model DT-30 thermogravimetric analyser at a heating rate of $20^{\circ}\mathrm{C\,min^{-1}}$ in nitrogen atmosphere.

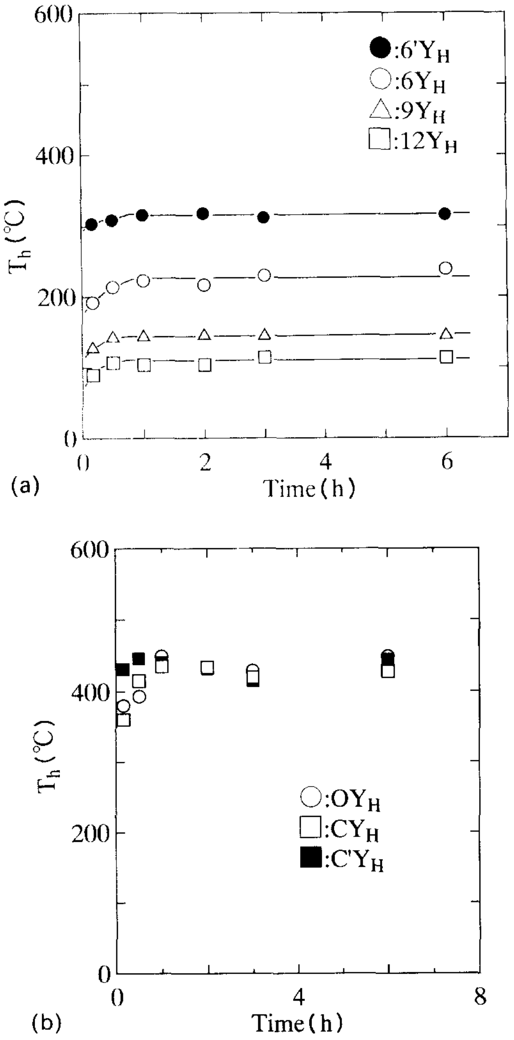

Figure 3 Effect of post-polymerization time at a constant temperature of 370°C on T_h for network (a) aliphatic–aromatic and (b) aromatic polyimide films

RESULTS AND DISCUSSION

Conditions of post-polymerization

Figure 2 shows t.m.a. curves of $\mathbf{6Y_H}$ and $\mathbf{OY_H}$ polyimide films when post-polymerized at various elevated temperatures for a constant time of 1 h. Two-step penetration behaviour is observed for $\mathbf{6Y_H}$ film; whereas for $\mathbf{OY_H}$ film, heat distortion is not observed until the final penetration by thermal decomposition. The heat distortion temperature T_h is defined by the first inflection point in the t.m.a. curve. The T_h values of both $\mathbf{6Y_H}$ and $\mathbf{OY_H}$ films increase on increasing the post-polymerization temperature and then levelled off. The effect of post-polymerization time on T_h is shown in *Figure 3* for various network polyimide films. The T_h values of both aliphatic–aromatic and aromatic polyimide films increase with increasing post-polymerization time and then level off after ca. 1 h. The increase of T_h values implies that the mobility of molecular chains is more suppressed by the network formation. It is noted that $\mathbf{6'Y_H}$ film, having the same chemical structure as $\mathbf{6Y_H}$ film, has much higher T_h value compared with $\mathbf{6Y_H}$ film. This may be ascribed to the enhanced degree of reaction of $\mathbf{6'Y_H}$ film caused by more reactive diisocyanate as shown below. T_h increase is also observed for $\mathbf{C'Y_H}$ film.

Structure and thermal properties

Figure 4 shows infra-red spectra of $\mathbf{6Y_H}$ prepolymer and $\mathbf{6Y_H}$ and $\mathbf{6'Y_H}$ films. The prepolymer shows the absorption at $1620\,\mathrm{cm^{-1}}$ due to the amide group and those at 1780 and $1380\,\mathrm{cm^{-1}}$ due to the imide group, implying that the imidization reaction has already occurred at the prepolymer preparation stage. *Table 1* gives the change of absorption intensity ratio of imide

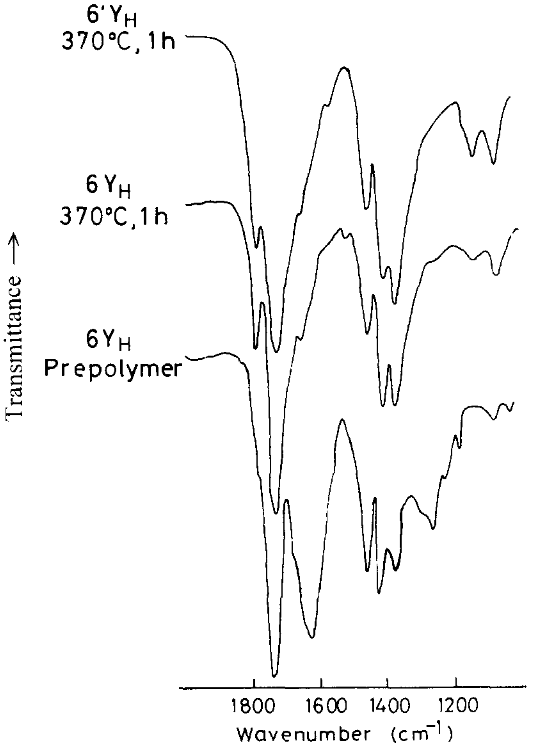

Figure 4 Infra-red spectra for $\mathbf{6Y_H}$ prepolymer and $\mathbf{6Y_H}$ and $\mathbf{6'Y_H}$ films post-polymerized at 370°C for 1 h

Table 1 Absorbance intensity ratios for **6Y$_H$** and **6′Y$_H$** films post-polymerized at 370°C for various times

Sample		Absorbance intensity ratio	Post-polymerization time (min) 0	10	60
6Y$_H$	imide	A_{1350}/A_{1440}	1.0	1.9	1.8
	imide	A_{1780}/A_{1440}	0.4	1.2	1.1
	amide	A_{1620}/A_{1440}	1.7	1.2	1.0
6′Y$_H$	imide	A_{1350}/A_{1440}	1.0	2.3	2.1
	imide	A_{1780}/A_{1440}	0.9	1.3	1.4
	amide	A_{1620}/A_{1440}	1.8	1.0	1.0

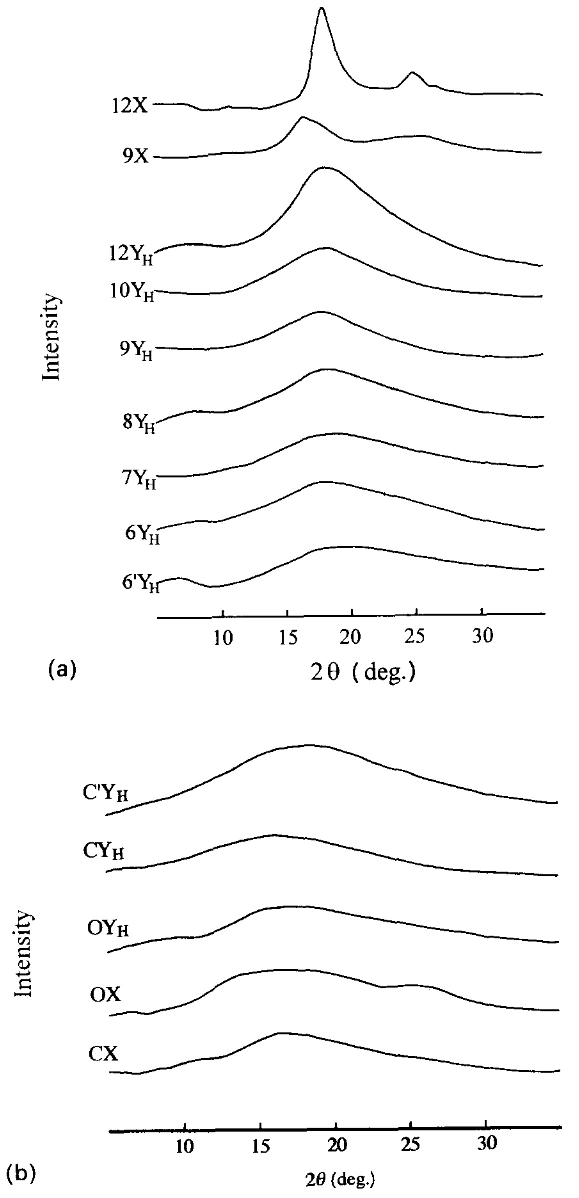

Figure 5 X-ray diffraction intensity curves of network (a) aliphatic–aromatic and (b) aromatic polyimide films post-polymerized at 370°C for 1 h, as well as linear polyimide films

(A_{1350}, A_{1780}) to benzene ring (A_{1440}) and amide II (A_{1620}) to benzene ring (A_{1440}) against the post-polymerization time for **6Y$_H$** and **6′Y$_H$**. On increasing the post-polymerization time, imide intensity ratio (A_{1350}/A_{1440} and A_{1780}/A_{1440}) increases and amide intensity ratio (A_{1620}/A_{1440}) decreases, which confirms that post-polymerization promotes the imidization reaction, and levels off after post-polymerization at 370°C for 1 h. This is also consistent with the results of T_h values in *Figure*

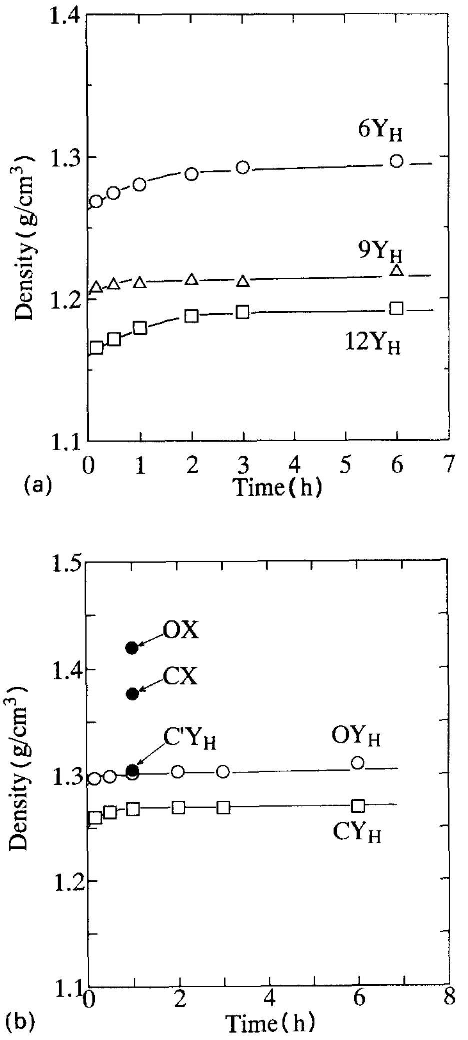

Figure 6 Effect of post-polymerization time at a constant temperature of 370°C on densities of (a) network aliphatic–aromatic and (b) network and linear aromatic polyimide films

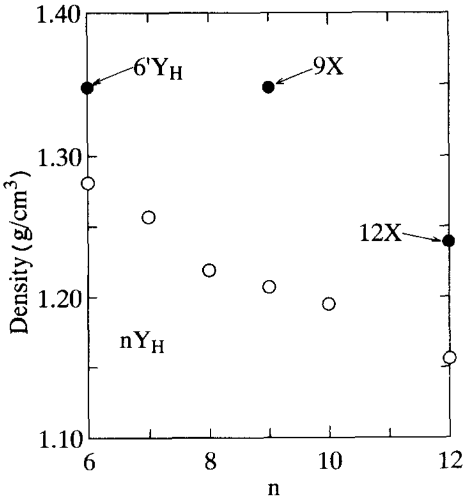

Figure 7 Density *versus* number of methylene units in the diamine component of ***n*Y$_H$** and **6′Y$_H$** post-polymerized at 370°C for 1 h, as well as linear polyimide films

3a. Imide intensity ratio of $\mathbf{6'Y_H}$ is larger than that of $\mathbf{6Y_H}$, suggesting the higher degree of reaction of $\mathbf{6'Y_H}$. Similar behaviour was observed between $\mathbf{C'Y_H}$ and $\mathbf{CY_H}$ films.

Figure 5 shows X-ray diffraction intensity curves of various network aliphatic–aromatic and aromatic polyimide films post-polymerized at 370°C for 1 h and the corresponding **9X** and **12X** linear polyimide films. Two diffraction peaks have already been observed for network polyester, polyamide and polyurethane films, suggesting some ordered structure due to regular networks caused by the symmetric structure of multifunctional monomers[1–7]. The formation of some ordered structure is also assumed for network aliphatic–aromatic and aromatic polyimide films, but the degree of ordering appears to be lower for these films. The intensities of the peaks of network aliphatic–aromatic polyimide films become higher with increasing length of methylene chain in diamine component, suggesting that a flexible, longer methylene chain reduces the distortion of the network structure. Similar behaviours have also been observed for network polyester[2] and polyamide[5] films having longer methylene chain.

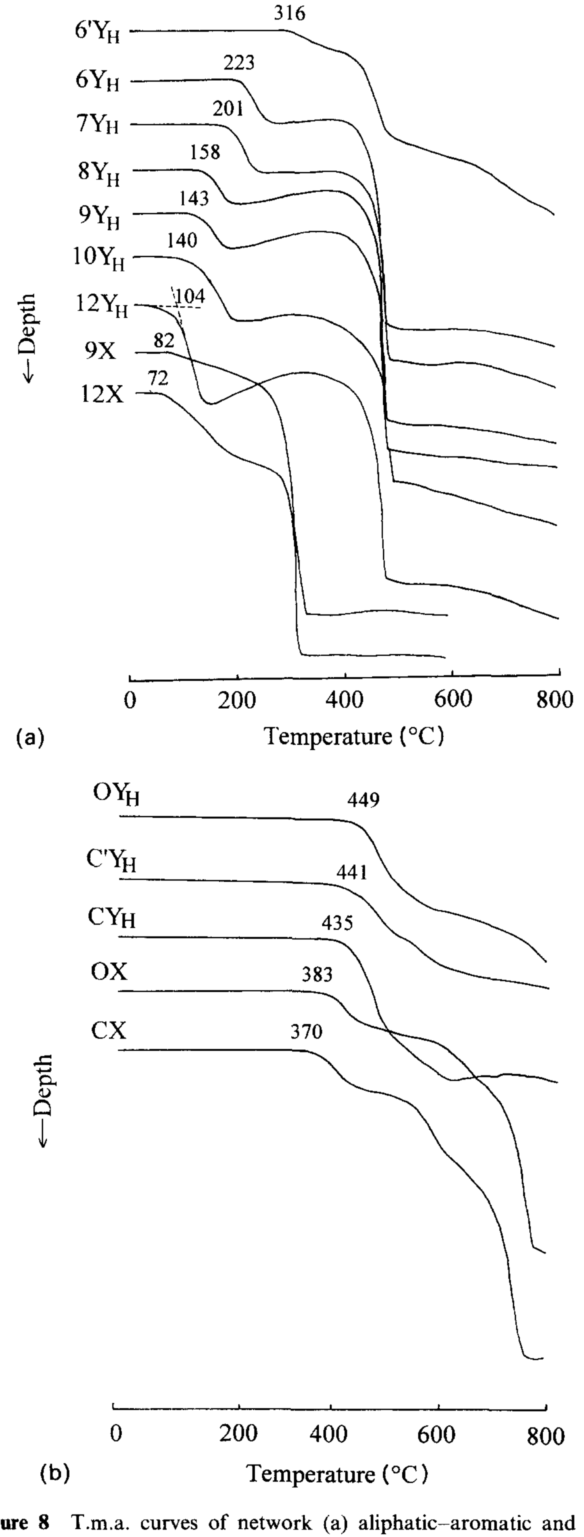

Figure 8 T.m.a. curves of network (a) aliphatic–aromatic and (b) aromatic polyimide films, as well as linear polyimide films

The densities of various network aliphatic–aromatic and aromatic polyimide films post-polymerized at 370°C are plotted against the post-polymerization time in *Figure 6*. *Figure 7* shows the density of network aromatic–aliphatic polyimide films against the length of methylene chain in the diamine component. The densities of the corresponding **9X** and **12X** linear polyimide films are also given. The densities of network aliphatic–aromatic and aromatic polyimide films increase with increasing post-polymerization time and level off after ca. 1 h, which is comparable with the results of T_h values in *Figure 3*. The densities of network aliphatic–aromatic polyimide films decrease gradually on increasing the length of methylene chain in diamine component, which is explained by the decrease of the total amount of heavy benzene rings per unit volume. Similar behaviours have also been observed for network polyamide films[5,6]. The densities of $\mathbf{6'Y_H}$ and $\mathbf{C'Y_H}$ films are markedly higher than those of the corresponding $\mathbf{6Y_H}$ and $\mathbf{CY_H}$ films, which supports the formation of the more packed network structure caused by their enhanced degree of reaction as mentioned above. The densities of $\mathbf{9Y_H}$, $\mathbf{12Y_H}$, $\mathbf{OY_H}$ and $\mathbf{CY_H}$ ($\mathbf{C'Y_H}$) films are lower than those of the corresponding linear **9X**, **12X**, **OX** and **CX** films, reflecting the lower packing of molecular chains due to the network structure.

Figure 8 shows t.m.a. curves of various network aliphatic–aromatic and aromatic polyimide films post-polymerized at 370°C for 1 h together with the corresponding linear polyimide films. The T_h values of the network aliphatic–aromatic polyimide films decrease remarkably on increasing the length of methylene chain in diamine components. This behaviour has also been observed for network polyester[1,2] and polyamide[5,6] films. As expected, network aromatic polyimide films

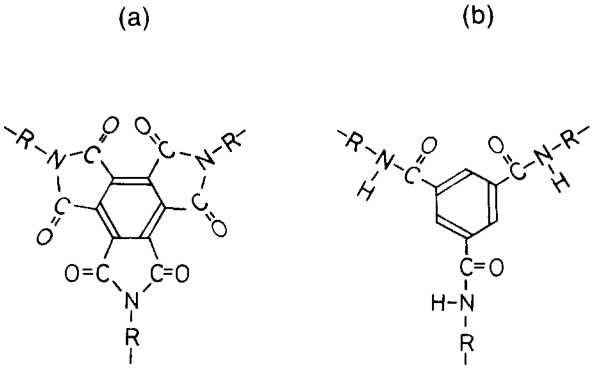

Figure 9 Structural units of (a) polyimide and (b) polyamide networks

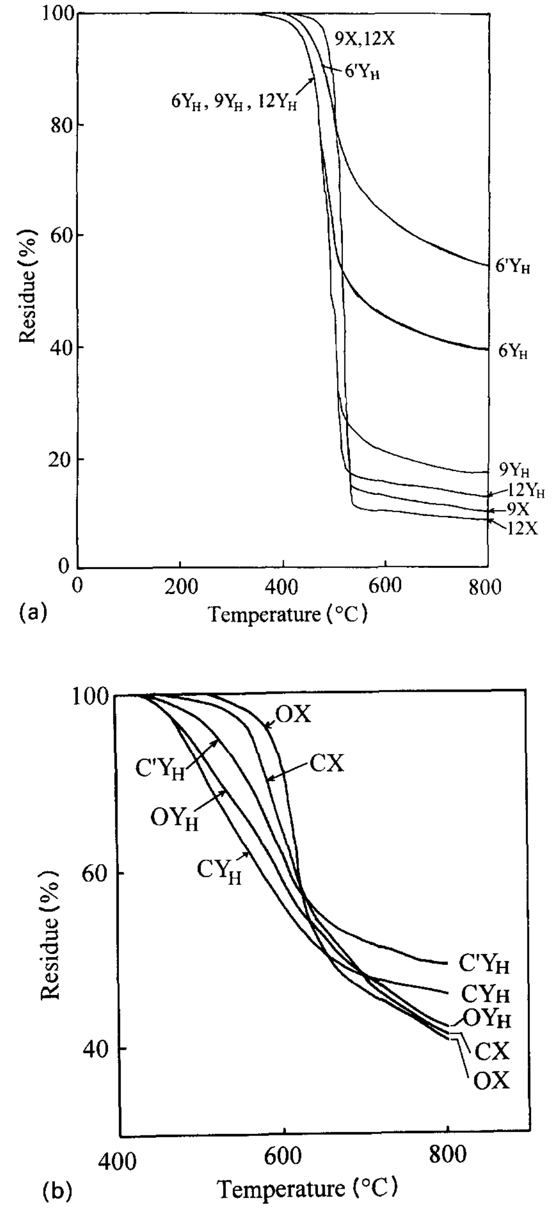

Figure 10 T.g. curves of network (a) aliphatic–aromatic and (b) aromatic polyimide films, as well as linear polyimide films

exhibit much higher T_h values than network aliphatic–aromatic polyimide films, reflecting the rigidity of the benzene ring. $\mathbf{OY_H}$ has the highest T_h value of 449°C among the polyimide films studied. It is noted that the T_h values of $\mathbf{9Y_H}$, $\mathbf{12Y_H}$, $\mathbf{OY_H}$ and $\mathbf{CY_H}$ ($\mathbf{C'Y_H}$) films are somewhat higher than those of the corresponding linear **9X**, **12X**, **OX** and **CX** films, indicating that the resistance to thermal distortion is greatly enhanced by network formation. It is also noted that network polyimide films show higher thermal stability at higher temperature. The $\mathbf{9Y_H}$ and $\mathbf{12Y_H}$ films are not penetrated by a probe until ca. 500°C, whereas the corresponding linear **9X** and **12X** films are penetrated around 300°C, owing to melting, and $\mathbf{OY_H}$ and $\mathbf{CY_H}$ ($\mathbf{C'Y_H}$) films are not penetrated at 800°C, whereas the corresponding linear **OX** and **CX** films are penetrated below 800°C.

It is important that the network polyimide films have higher T_h values than the corresponding network polyamide films, in spite of the lack of intermolecular hydrogen bonding. Thus, the T_h value of 316°C for $\mathbf{6'Y_H}$ network polyimide film is remarkably higher than that of 232°C for the **6Y** network polyamide film[5,6] prepared from trimesic acid (**Y**) and hexamethylene diamine (**6**). The T_h values of 449°C for $\mathbf{OY_H}$ and 441°C for $\mathbf{C'Y_H}$ network polyimide films are also higher than those of 444°C and 416°C for the **OY** and **CY** network polyamide films[4] prepared from **Y**, 4,4'-diaminodiphenyl ether (**O**) and 4,4'-diaminodiphenylmethane (**C**). The structural units of these polyimide and polyamide networks are shown in *Figure 9*. The higher T_h values of network polyimide films could be ascribed to the more rigid ring structures formed by the imide linkages.

Figure 10 shows t.g. curves of various network aliphatic–aromatic and aromatic polyimide films post-polymerized at 370°C for 1 h together with the corresponding linear polyimide films. The residues of $\mathbf{9Y_H}$, $\mathbf{12Y_H}$, $\mathbf{OY_H}$ and $\mathbf{CY_H}$ ($\mathbf{C'Y_H}$) films at 800°C are larger than those of the corresponding linear **9X**, **12X**, **OX** and **CX** films. This result suggests that the formation of carbonized structure at higher temperature would be promoted by the network structure. However, the initial decomposition temperatures of these network polyimide films are lower than those of the corresponding linear polyimide films. The initial decomposition temperatures of $\mathbf{6Y_H}$ and $\mathbf{CY_H}$ films are lower than those of the corresponding more reacted $\mathbf{6'Y_H}$ and $\mathbf{C'Y_H}$ films. This suggests that the initial decomposition temperature is decreased by the presence of unreacted terminal functional groups.

REFERENCES

1 Kiyotsukuri, T., Tsutsumi, N. and Chen, Y. *Polym. Commun.* 1990, **31,** 17

2 Kiyotsukuri, T., Tsutsumi, N. and Chen, Y. *J. Polym. Sci. (A) Polym. Chem.* 1990, **28,** 1197

3 Tsutsumi, N., Chen, Y. and Kiyotsukuri, T. *J. Polym. Sci. (A) Polym. Chem.* 1991, **29,** 1963

4 Kiyotsukuri, T., Tsutsumi, N., Okada, H. and Nagata, M. *Polymer* 1992, **33,** 4990

5 Kiyotsukuri, T., Tsutsumi, N., Sugimoto, M. and Saito, N. *Polym. Commun.* 1990, **31,** 56

6 Kiyotsukuri, T., Murata, M., Sugimoto, M. and Tsutsumi, N. *Polym. Int.* 1994, **34,** 173

7 Kiyotsukuri, T., Nagata, M., Okada, H., Miura, D. and Tsutsumi, N. *Macromol. Chem. Phys.* 1994, **195,** 1797

8 Sroog, C. E., Endrey, A. L., Abramo, S. V., Berr, C. E., Edwards, W. M. and Olivier, K. L. *J. Polym. Sci. (A)* 1965, **3,** 1373