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Regular network polyesters from benzenepolycarboxylic acids and glycol

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Regular network polyesters were prepared from trimesic (Y), pyromellitic (X) or mellitic (Y_H) acids and 1,6-hexanediol (6G). Prepolymers prepared by melt-polycondensation were cast from dimethylformamide solution and post-polymerized at 260°C for various times to form a network. The resultant films were transparent, flexible and insoluble in organic solvents. Degrees of reaction estimated from the infra-red absorbance of ester and methylene groups were 95, 95 and 96% for 6GY, 6GX and $6GY_H$ post-polymerized for 12 h, respectively. X-ray diffraction intensity curves showed the formation of some ordered structure owing to the regular networks, and the degrees of ordering were $6GY > 6GX > 6GY_H$. Densities were 1.227, 1.290 and 1.289 $g\,cm^{-3}$ and heat distortion temperatures measured by thermomechanical analysis were 75, 72 and 75°C for 6GY, 6GX and $6GY_H$ post-polymerized for 12 h, respectively. Tensile strengths were in the order $6GY > 6GX > 6GY_H$ and Young's moduli were $6GY_H = 6GX > 6GY$. Dye absorptions were $6GX > 6GY > 6GY_H$, and water absorptions and weight losses in alkali solution were $6GY_H > 6GX > 6GY$. These effects of the number of functional groups on the benzene ring on the structure and properties were discussed, and compared with those of previously reported network polymers.

(Keywords: regular network polyesters; mellitic acid; pyromellitic acid; trimesic acid)

INTRODUCTION

It is expected that the thermal resistance of polymers can be enhanced by the introduction of network structure into the polymer backbone. With this aim, we have prepared novel regular network polyesters[1–4] from tri- or tetrafunctional aromatic carboxylic acids and glycols or aromatic diols, as well as polyamides[4–6] from trimesic acid and aliphatic or aromatic diamines, by solvent casting of prepolymers followed by post-polymerization of cast films. The resultant transparent, flexible and insoluble polymer films had relatively ordered network structure and showed much higher resistance to thermal distortion than the corresponding linear polymer films. We have also reported regular network polyesters[7] from glycerol and aliphatic or aromatic dicarboxylic acids, as well as polyurethanes[8] from glycerol or aromatic polyols and aliphatic or aromatic diisocyanates. More recently, we have prepared regular network polyimides[9] from mellitic acid and aliphatic or aromatic diamines or diisocyanates.

In this paper, we report the preparation, structure and properties of the regular network polyesters from trifunctional trimesic acid, tetrafunctional pyromellitic acid or hexafunctional mellitic acid and 1,6-hexanediol, and elucidate the effect of the number of functional groups on the benzene ring on the structure and properties.

EXPERIMENTAL

Monomers

Structural formulae and codes of the polyfunctional carboxylic acids used in this study are shown in *Figure 1*. Trimesic acid (Y) and hexamethyl ester of mellitic acid (Y_H) were used as received. Dianhydride of pyromellitic acid (X) was recrystallized from acetic anhydride solution. 1,6-Hexanediol (6G) was used without further purification.

Preparation of prepolymers

A mixture of polyfunctional monomer and excess amount of 6G was heated at 200°C for 3 h in a stream of nitrogen. The temperature was then increased to 270°C for 25 min, and the mixture further heated *in vacuo* at 270°C for 4 min for $6GY_H$, for 55 min for 6GY, and for 80 min for 6GX.

Film preparation and post-polymerization

The obtained prepolymer was cast on an aluminium plate from 14 wt% dimethylformamide (DMF) solution

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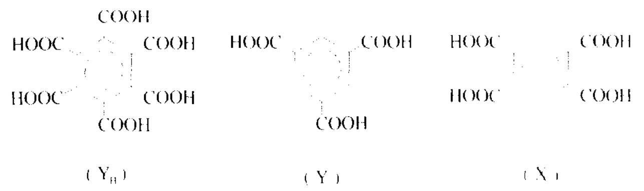

Figure 1 Structural formulae and codes of benzenepolycarboxylic acid monomers

at 80°C for 2 h. The cast film was post-polymerized under a stream of nitrogen at 260°C for a given time up to 12 h. After dissolving off the aluminium substrate with 10% HCl solution, a transparent and flexible film was obtained which was insoluble in organic solvents.

Characterization

Infra-red spectra were recorded on a Jusco model IRA-1 spectrophotometer using a thin cast film of 10–20 μm thickness.

The wide-angle X-ray intensity curve was determined with a Toshiba model ADG-301 X-ray diffractometer with nickel-filtered Cu $K\alpha$ radiation.

Density was measured in aqueous KI solution at 30°C by the floating method.

Thermomechanical analysis was performed in the penetration mode under a pressure of 10 kg cm^{-2} and a heating rate of 20°C min^{-1} in a nitrogen atmosphere, using a Shimadzu model DT-30 thermomechanical analyser.

Tensile properties were measured with a Iwamoto tensile tester at an extension rate of 125% min^{-1}.

Dyeing was carried out at 80°C for 24 h using 1,4-diaminoanthraquinone disperse dye. The absorbed dye was extracted in *o*-chlorophenol at 70°C for 6 h and dye absorption was measured with a Kohdensha model ANA-18 calorimeter.

Water absorption was determined by immersing a film in water at 30°C for 24 h, followed by removing surplus surface water with a filter paper and immediate weighing.

Alkali hydrolysis was carried out in a 10% NaOH aqueous solution at 60°C for 4 h.

RESULTS AND DISCUSSION

Degree of reaction

Figure 2 shows the change in the infra-red spectra of films post-polymerized at 260°C for 30 min and 12 h. Absorption at 3460 cm^{-1} due to hydroxyl groups decreases remarkably with increased post-polymerization time, while absorption at 2959 cm^{-1} due to methylene groups remains unchanged. Since the post-polymerization proceeds through the elimination of $-OC-O-(CH_2)_6-OH$ terminal groups by the ester-exchange reaction, the change of absorption intensity ratio between hydroxyl and methylene groups is a measure of the degree of reaction.

For $6GY_H$, at the intial stage of polymerization the ratio of hydroxyl to methylene groups in a monomeric unit, $[OH]/[CH_2]$, is $6/(6\times 6)$, and varies with the progress of reaction to become $(6-6)/(6\times 6-3\times 6)$ when the network structure is completely developed. Thus the following equation is defined:

$$[OH]/[CH_2] = (6-y)/(36-3y) \qquad (1)$$

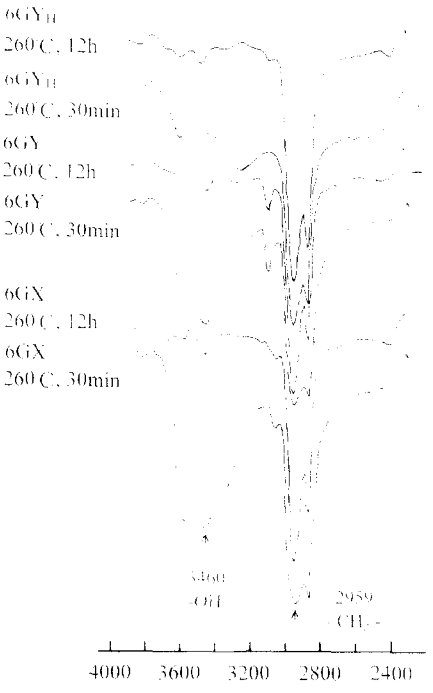

Figure 2 Infra-red spectra of films post-polymerized at 260°C for 30 min and 12 h

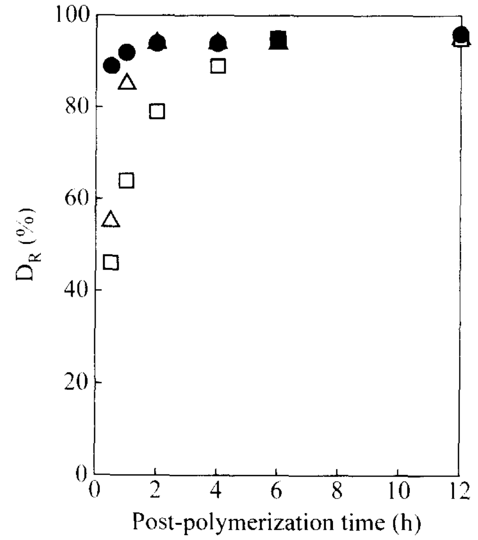

Figure 3 Post-polymerization time dependence of degree of reaction for films post-polymerized at 260°C: △, 6GY; □, 6GX; ●, $6GY_H$

where y is the number of reacted functional groups per benzene ring. Then

$$y = 6(1-6[OH]/[CH_2])/(1-3[OH]/[CH_2]) \qquad (2)$$

The extended general expression for $6GY_H$, 6GX and 6GY is

$$y = n(1-6[OH]/[CH_2])/(1-3[OH]/[CH_2]) \qquad (3)$$

where n is the number of carboxylic acid groups per benzene ring. The degree of reaction D_R is calculated as

$$D_R = (y/n)\times 100\,(\%) \qquad (4)$$

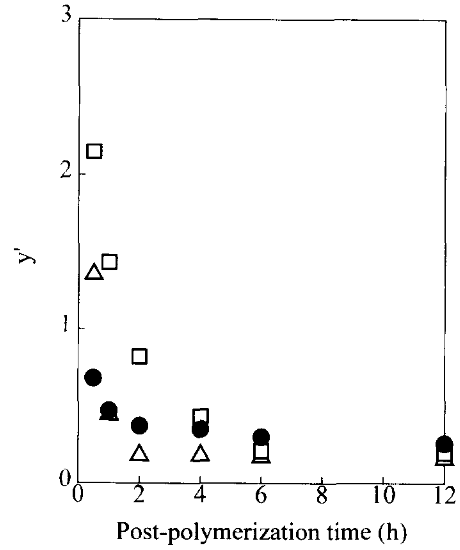

Figure 4 Post-polymerization time dependence of number of unreacted functional groups per benzene ring for films post-polymerized at 260°C: △, 6GY; □, 6GX; ●, $6GY_H$

and the number of unreacted functional groups per benzene ring is obtained as

$$y' = n - y \quad (5)$$

y is determined from the measured absorption intensity ratio by using the calibration curve obtained for various diols and alcohols[3].

Figure 3 shows the plot of D_R against post-polymerization time. D_R increases with increasing post-polymerization time and levels out after 2–6 h. D_R values after 12 h are almost the same and are 96, 95 and 95% for $6GY_H$, 6GX and 6GY, respectively. D_R values after 12 h for 2GX and 2GY, prepared previously with ethylene glycol (2G) as glycol monomer, are 87 and 95% respectively[3]. Thus, the D_R value is smaller for 2GX than for 6GX, suggesting that the shorter methylene chain of glycol is less favourable for the reaction when the number of functional groups on the benzene ring becomes larger. This is also observed for the preparation of $2GY_H$, which could not form a good film probably due to the lower reactivity.

Figure 4 shows the plot of y' against post-polymerization time. Values of y' after 12 h are 0.26, 0.20 and 0.16 for $6GY_H$, 6GX and 6GY, respectively, showing that more functional groups on the benzene ring gives rise to more unreacted terminal groups.

Structure of post-polymerized films

X-ray diffraction intensity curves of films post-polymerized for 6 h are shown in *Figure 5*. Two broad but strong diffraction peaks appear for 6GY, showing the formation of a relatively ordered structure owing to the regular network of symmetric trimesic acid moieties as reported before[1]. The degree of this ordering decreases with increasing number of functional groups on the benzene ring, reflecting the increase of unreacted terminal groups.

Change of density when increasing the post-polymerization time is shown in *Figure 6*. The densities of these films decrease with increasing post-polymerization time and level out after 6 h. This decrease of density was also observed for 2GY, and was explained by the increase of free volume with the elimination of glycol by the ester-exchange reaction[1]. The densities after post-polymerization for 12 h are 1.289, 1.290 and 1.227 g cm^{-3} for $6GY_H$, 6GX and 6GY, respectively. The higher density of $6GY_H$ and 6GX than 6GY is explained by the higher concentration of the heavy benzene ring, as shown in *Figure 7*. It is expected from *Figure 7* that the density of $6GY_H$ is higher than that of 6GX, but the density obtained is a little higher for 6GX than for $6GY_H$. This peculiar result may be explained by the expansion of network structure for $6GY_H$, as shown by the shift of diffraction peak in *Figure 5*. It has already been pointed out that the spacing from the left peak relates to the length of methylene chain and the spacing from the right peak relates to the intermolecular distance of benzene rings[6]. The shift of the right peak to lower scattering angle implies the increase of the distance between benzene ring planes, which causes the decrease of

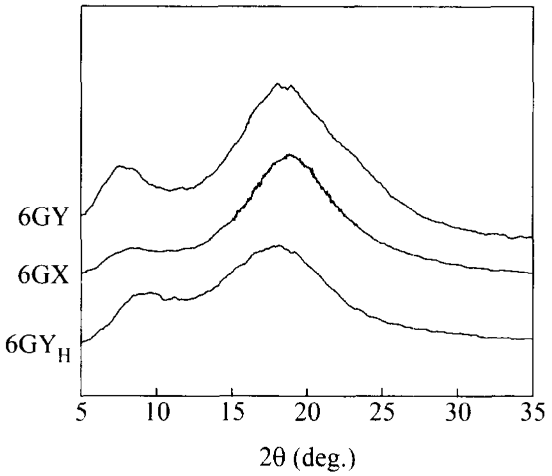

Figure 5 X-ray diffraction intensity curves of films post-polymerized at 260°C for 6 h

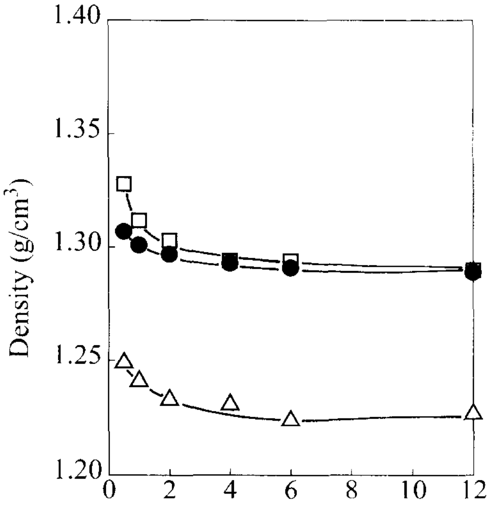

Figure 6 Post-polymerization time dependence of density for films post-polymerized at 260°C: △, 6GY; □, 6GX; ●, $6GY_H$

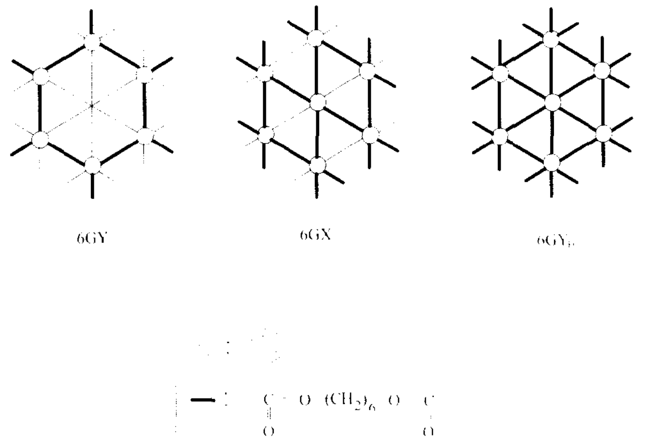

Figure 7 Model of network structures for 6GY, 6GX and 6GY$_H$

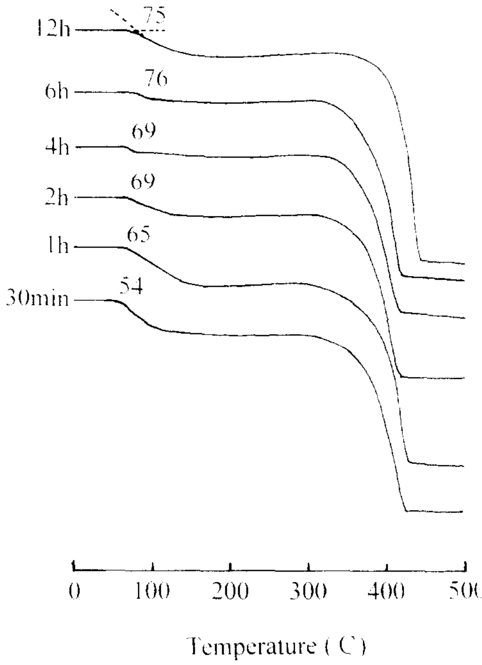

Figure 8 Thermomechanical analysis curves of 6GY$_H$ post-polymerized at 260°C for various times

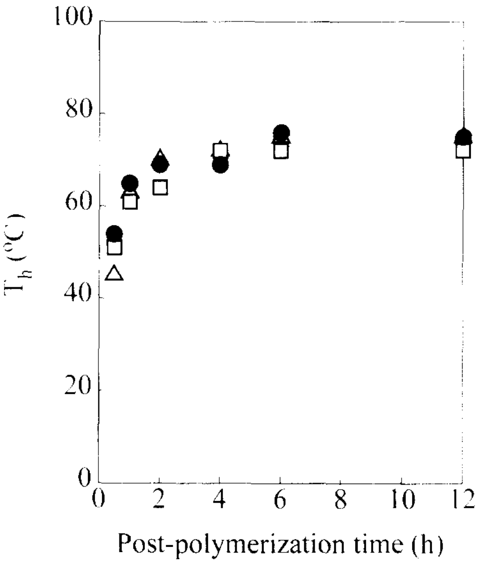

Figure 9 Post-polymerization time dependence of heat-distortion temperature for films post-polymerized at 260°C: △, 6GY; □, 6GX; ●, 6GY$_H$

Table 1 Mechanical properties of films post-polymerized at 260°C for 6 h

Polymer	Tensile strength (kg mm^{-2})	Elongation (%)	Young's modulus (kg mm^{-2})
6GY$_H$	0.6–1.3	1.8–2.4	110–140
6GX	1.3–2.1	2.3–3.2	110–130
6GY	2.8–3.8	6.1–9.7	70–110

concentration of the benzene ring, and thus density decreases for 6GY$_H$.

Properties of post-polymerized films

Figure 8 shows thermomechanical analysis curves of 6GY$_H$ post-polymerized for various times. Heat distortion temperature, T_h, the inflection point of the curve, increases with increasing post-polymerization time and levels out after 6 h, which is consistent with changes of the degree of reaction and density shown above. The T_h values are plotted against the post-polymerization time in *Figure 9*. The T_h values after 12 h are almost the same and are 75, 72 and 75°C for 6GY$_H$, 6GX and 6GY, respectively. The T_h value of 2GY after 12 h was 222°C, while that of 2GX disappeared above a post-polymerization time of 30 min[3]. This suggests that the chain mobility of 2GX was largely restricted by the higher network formation with benzene ring as shown by the γ value, which was 3.15 and 2.85 for 2GX and 2GY, respectively[3]. While the γ values of 5.74 for 6GY$_H$ and 3.80 for 6GX are much higher than that of 2.84 for 6GY, their T_h values are almost the same, which suggests that the chain mobilities of these polyesters are governed by the long flexible chain of the glycol component.

Tensile properties are summarized in *Table 1* for films post-polymerized for 6 h. It was previously observed for 2GY and 2GX that tensile strength is higher for 2GY and Young's modulus is higher for 2GX[3]. The higher tensile strength of 2GY was ascribed to the higher ordering of network structure, and the higher Young's modulus of 2GX was ascribed to the higher concentration of benzene rings per unit volume[3]. Similar results are also observed for 6GY$_H$, 6GX and 6GY. The tensile strength is the following order: 6GY > 6GX > 6GY$_H$, corresponding to the higher ordering of network as shown in *Figure 5*. The Young's modulus is in the following order: 6GY$_H$ = 6GX > 6GY, corresponding to the higher concentration of benzene rings shown by the density in *Figure 6*.

Figure 10 shows dye absorption of films post-polymerized for various times. The dye absorption decreases for 6GX and 6GY with increasing post-polymerization time and levels out after 6 h. This is probably because the progress of network formation disturbs the penetration of large dye molecules through the networks, thus the dye absorption decreases. The dye absorption after 12 h is 0.20, 0.52 and 0.85 g m^{-2} for 6GY$_H$, 6GY and 6GX, respectively. The smallest dye absorption of 6GY$_H$ can be ascribed to the highest

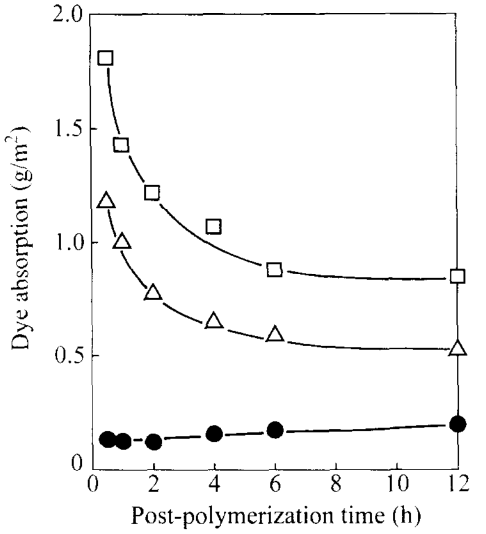

Figure 10 Post-polymerization time dependence of dye absorption for films post-polymerized at 260°C: △, 6GY; □, 6GX; ●, 6GY$_H$

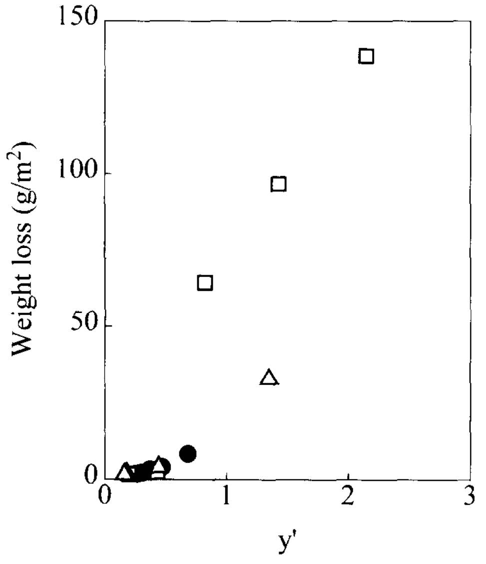

Figure 11 Weight loss in alkali solution *versus* numer of unreacted functional groups per benzene ring for films post-polymerized at 260°C: △, 6GY; □, 6GX; ●, 6GY$_H$

network density as shown in *Figure 7*. It is expected from the network density that the dye penetration is easier for 6GY than for 6GX, but the dye absorption obtained is higher for 6GX. This higher dye absorption of 6GX is probably due to the higher concentration of benzene rings, which is the dye site for the aromatic disperse dye. It was found that 2GY post-polymerized for 2 h has little dye absorption. This film has a short methylene chain length between crosslinked sites, which disturbs the penetration of dye molecules through the networks. These behaviours of dye absorption are important to show the utilization of our regular network films as membranes for the separation of molecules by varying the chain length between crosslinked sites.

The water absorption decreased with increasing post-polymerization time and levelled out after 12 h to 0.62, 0.55 and 0.39 wt% for 6GY$_H$, 6GX and 6GY, respectively. The decrease of water absorption can be ascribed to the decrease of the concentration of unreacted hydroxyl groups, the water absorbing site, and thus the decrease of water absorption corresponded well to the decrease of y' in *Figure 4*.

The weight loss in alkali solution decreased with increasing post-polymerization time and levelled out after 12 h to 1.90, 1.75 and 1.58 g m^{-2} for 6GY$_H$, 6GX and 6GY, respectively. *Figure 11* shows the plots of these weight losses against the y' values. An almost linear relationship is obtained between the weight loss and y', suggesting that the alkali hydrolysis is controlled by the concentration of unreacted hydroxyl groups similar to the water absorption.

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. Part A, Polym. Chem.* 1990, **28**, 1197
3 Tsutsumi, N., Chen, Y. and Kiyotsukuri, T. *J. Polym. Sci. Part 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., Kanaboshi, M. and Tsutsumi, N. *Polym. Int.* 1994, **33**, 1
8 Kiyotsukuri, T., Nagata, M., Okada, H., Miura, D. and Tsutsumi, N. *Macromol. Chem. Phys.* 1994, **195**, 1797
9 Nagata, M., Kiyotsukuri, T., Moriya, T., Tsutsumi, N. and Sakai, W. *Polymer* 1995, **36**, 2657