The Structure-Property Relationship of Porous Alicyclic Copolyimide Thin Films having PPG Side Chains

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Abstract

Two types of copolyimides(coPIs) were synthesized using a dianhydride ODST (1.00 eq.), oxydianiline (0.95 eq.), and PPG (M_w.2400)-containing diamine (PPGDA, 0.05 eq.) by different synthetic method. Structural difference of the two coPIs was confirmed by ^{1}H-NMR. The coPI film resulted in the formation of nanopores upon heating due to thermal decomposition of microphase-separated PPG moieties. Although the two types of coPIs have same content of PPG, the size of pores was significantly different to each other. This difference was attributed to the discrepancy of the distribution of PPG side chains on the PI main chain.

Introduction

The insulating material in LSI is required to show both high thermal stability and low dielectric constant. We have investigated one of such material, the nanoporous alicyclic copolyimide (coPI) film. The coPI contains a monomer having thermally degradable poly(propylene glycol) (PPG) side chain, thus the heat treatment of the film affords the nanopores. So far, we have been tried to clarify the relationship between the pore size and the molecular structure such as length/content of PPG chain and the structure of the copolymer, PPG-*graft*-PI / PPG-*block*-PI. Such a study is of significance from the viewpoint of obtaining structure-property relationship of nanoporous film which is applicable to the control of the pore size and distribution. This time, we report a new insight of nanopore forming behavior of coPIs having side chain PPG groups (Figure 1).
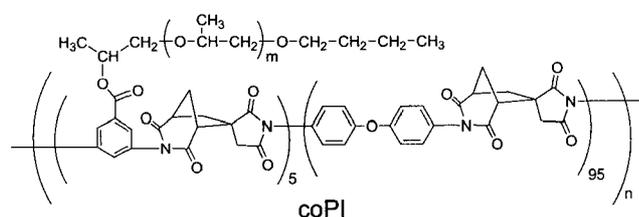

Figure 1.The structure of coPIs.

Experimental

Synthesis of coPIs. Two types of coPIs were prepared using *Rel*-[1*S*,5*R*,6*R*]-3-oxabicyclo

[3,2,1]octane-2,4-dione-5-spiro-3'-(tetrahydrofuran-2',5'-dione) (ODST, 1.00 eq)[11],oxydianil-ine (ODA, 0.95 eq) and PPG (M_w.2400)-containing diamine (PPGDA, 0.05 eq). The coPI1 was obtained by the following procedure. To a DMF solution of ODST (0.2289 g, 1.02 mmol) was added drowise DMF solution of PPGDA (0.1498 g, 0.05 mmol) under nitrogen atmosphere at 0 °C. The mixture was stirred for 4 hours at 60 °C. Then the solution was cooled to 0 °C and a DMF solution of ODA (0.1942 g, 0.97 mmol) was added dropwise. The mixture was again stirred at 60 °C for 5 hours. The resulting poly(amide acid), coPAA1, was precipitated by a slow addition of the reaction mixture into water. The solid was filtered off and dried in vacuum for 5 hours at 60 °C (0.4927 g, 86 % yield). Acetic anhydride (0.50 mL) and triethylamine (1.00 mL) were added to the DMF solution of coPAA1 (0.40 g) and the mixture was heated to reflux at 150 °C for 6 hours under nitrogen atmosphere. The mixture was poured into 500 mL of water, and coPI1 was obtained by filtration (0.3920 g, 94 % yield).

For the synthesis of coPI2, ODST was added to the mixture of the two diamines dissolved in anhydrous DMF solution in one portion. The isolation and the imidization of the corresponding poly(amide acid), coPAA2, was carried out in the same manner as above (85 % yield).

Fabrication of porous film. The coPI solution in DMF (50 mg/mL) was spin cast on a glass substrate. The film was dried at 140 °C under nitrogen atmosphere and the porous film was prepared through annealing process at 200 °C for 9 hours under reduced vacuum conditions (710 mmHg).

Results and Discussion

The two types of coPIs were prepared by different synthetic method; coPI1 was synthesized by a two-step addition of PPGDA/ODA to the ODST solution, and coPI2 was synthesized by mixing the monomers in an "all-at-once" fashion. In both cases, the molar ratio of the two diamine monomers was PPGDA/ODA=5/95. Structural difference between coPI1 and coPI2 was confirmed by ^{1}H-NMR of the corresponding copoly(amide acid)s; a distinct difference was observed in the aromatic region (6.5-7.7 ppm) whereas the peaks in the aliphatic region were completely identical (1.8-3.6 ppm) for coPIs. The properties of the coPIs are shown in the table 1.

Table 1. The properties of polymers

| Name | M_w [a] | PDI | PPG content(wt%) | | T_g(°C) | T_d(°C) [d] | Pore size(nm) |
			charge	TGA [b]			
Homo-PI	69,200	2.94	0	0	270	370	0
coPI1	104,700	2.36	26.6	25.3	N.M [c]	207	50 – 210
coPI2	132,000	2.84	26.6	25.6	N.M [c]	212	50 – 430

[a] The weight-average molecular weight (M_w) and poly dispersity index (PDI) were determined by gel permeation chromatography using DMF solution. [b] Estimated by isothermal treatment at 250 °C for 3 hr., [c] N.M = not measurable, [d] 5 wt% decomposition temperature for polyimide measured by TGA under nitrogen (10°C/min).
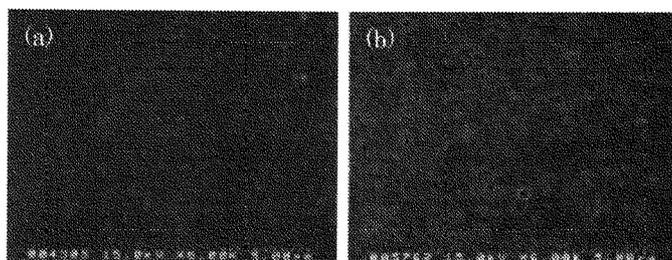
Figure 2. SEM images of (a) coPI1 and (b) coPI2 porous film.

Thermal decomposition of the coPIs was monitored by ^{1}H-NMR spectral change. After heating the coPI at 200 °C, the $-CH_3$ peak of PPG side chains at 1.1 ppm almost disappeared indicating that PPG moiety was decomposed to be volatile small molecules, presumably propylene glycols while the PI main chain remained intact.

Content of PPG in coPIs was also analyzed by isothermal thermogravimetry at 250 °C for 3 hours in air to be 25.3 and 25.6 wt% for coPI1 and coPI2, respectively. These values were a little smaller than the feed amount. This might be due to the loss of low molecular weight fraction during polymer isolation process.[3] It was clarified that the thermal treatment of coPIs at 200 °C for 9 hours also resulted in the decomposition of PPG moiety up to 98.6 %. This is of importance from the viewpoint of nanopore formation because the glass transition temperature (T_g) of the PI main chain was 270 °C and high PPG decomposition temperature (> 250 °C) might bring about the collapse of nanopores due to the movement of PI main chain.

In preparing porous film, thermal treatment was performed under reduced pressure to prevent a collapse of formed pores inside the film (Figure 2 and Table 1).[2] Both coPI films gave the pores with 50 to 200 nm in diameter, but the formation of larger-sized pores up to 400 nm in diameter was accompanied only in the case of coPI2 porous film.

The above observation should arise from the structural difference of the coPIs. Therefore, we further investigated on the macromolecular structure of the coPIs by model reaction approach. A monoanhydride 1 was treated with equimolar mixture of ODA and PPGDA to give a mixture of adducts in the ratio shown in scheme 1. This result indicates that PPGDA was 16 times less reactive compared to ODA presumably due to the difference in the molecular size and/or the difference in electron density on amino group which was affected by the substituent on the phenyl
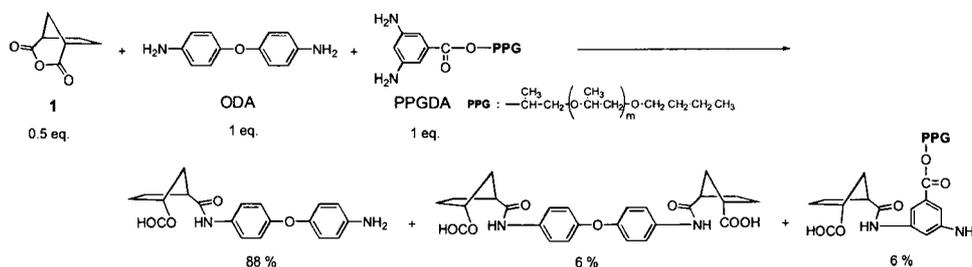
Scheme 1.

ring. From the model study, it might be concluded that the coPI1 has a macromolecular structure in which PPG group is randomly distributed on the PI main chain, whereas the molecular structure of coPI2 is much like that of ABA-type triblock copolymer of which the A-unit is PPGDA and B-unit is ODA. The latter was confirmed by ^{1}H-NMR of coPI2 and a separately synthesized ABA-block type coPI.

The different polymer structure might have influenced the PPG domain formation in film state. It has been shown that the behavior of microphase separation in graft polymer is affected by various factors such as the number of grafted chains or distance between grafted chains.[4,5] Two types of the coPIs have same number of PPG chains, but distribution of PPG moiety on the PI main chain is different. As the distance between PPG chains becomes shorter, PPG chains are easy to aggregate leading to formation of larger domain in the film state. Therefore, after decomposition of PPG domain, larger sized of pores were observed in coPI2 porous film.

Conclusion

The synthetic method for the coPI influenced on the polymer structure, namely, the different distribution for PPG moiety in the polyimide chain, and this resulted in the formation of different size distribution of nanopores upon heating in the film state.

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