High-Modulus Positive-type Photosensitive Poly(amide-benzoxazole)s

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A new type of high modulus poly(amide benzoxazole)s (PABO) was derived from trans-1,4-cyclohexanedicarboxylic acid (CHDCA), bis(3-hydroxy-4-amino) biphenyl (p-HAB), bis(4-hydroxy-3-amino)biphenyl (m-HAB), and 2,2'-bis(trifluoromethyl) benzidine (TFMB). A stiff structure of cycloaliphatic CHDCA and fluorine-containing rod-like TFMB play a great role for the generation of high modulus in the PABO films with a significantly improved transparency at 365 nm for the PABO precursor film. A PABO possessing a copolymer composition of m-HAB60, TFMB40, and CHDCA100 achieved a high modulus of 4.9 GPa, a low coefficient of thermal expansion (CTE) of 19.8 ppm/K, a high T_g at 294°C, sufficient film toughness (elongation at break = 12.5 %), and high transparency at 365 nm (light transmittance = 73 %) for a 10 μ m thick PABO precursor film. The molecular weight control allowed the formation of fine positive-tone patterns by development using a 2.38 wt% TMAH aqueous solution at room temperature.

Keywords: Transparent Polybenzoxazoles / High modulus / Positive-type Photo-patterning

1. Introduction

High temperature polymeric materials, typically, polyimides (PIs) have been widely utilized in a variety of micro- and optoelectronic applications, for example, as the base films for flexible printed circuit boards (FPC) and the tape-automated bonding (TAB), the chip-on-film (COF) assembling systems, the buffer-coating films and interlayer dielectrics for LSI chips, high temperature adhesives, light wave guides for their combined excellent properties, i.e., high glass transition temperature (T_g), high resistance to chemicals and radiation, relatively low dielectric constant, and good mechanical properties [1]. We have developed novel PIs possessing both low coefficient of thermal expansion (CTE) and low extent of water absorption, i.e., poly(ester imide)s (PEsI) and proposed how our PEsI systems are useful as the base films in FPC and COF [2,3].

The present work concerns with a new type of buffer-coating materials. The most important properties required for the buffer-coating films are heat resistance and high-resolution patterning ability. We have been so far studied some photosensitive heat resistant polymeric materials: negative- and positive-working semi-alicyclic PI systems [4], positive-working PEsI systems [5], and hydroxyamide-containing PI systems which

can be thermally converted to poly(imide benzoxazole)s [6].

One of the most reliable high-resolution positive-working photosensitive heat resistant materials, which can be developed by an environmentally friendly alkali-solution, typically, a 2.38 wt% tetramethylammonium hydroxide (TMAH) aqueous solution, is formulated from PBO precursor (polyhydroxyamides, PHAs) and diazonaphthoquinones (DNQ). This is attributed to sufficiently large difference of the dissolution rates between the exposed and unexposed areas, which is based on adequate TMAH-solubility of phenolic OH-pendant PHAs.

A very recent demand in photosensitive PBO systems is high modulus. This is a very important property to protect LSI chips and very brittle inorganic passivation layers from various external stress, for example, from hard silica additives contained in packaging composite materials. We have previously studied high-modulus PBO films with great difficulty in the film-forming processes [7]; the most important structural factor is basically their stiff/linear backbone structures to achieve high modulus of PBO films, which often inhibit solution-casting processes of PHA films owing to rigid chain-induced poor solubility of PHAs in common organic solvents such as

N-methyl-2-pyrrolidone (NMP). For example, a PHA prepared from bis(3-hydroxy-4-amino) biphenyl (p-HAB) with terephthalic acid (TPA) is quite insoluble in any organic solvents (see Fig.1 for the monomer structures). Even a bent structure of an isomeric PHA derived from bis(4-hydroxy-3-amino)biphenyl (m-HAB) with TPA, which can be thermally converted to a rod-like PBO with a similar shape to the p-HAB/TPA PBO, was insoluble in NMP, instead, soluble only in toxic hexamethylphosphoramide or its mixed solvents.

Our initial approach was to incorporate p-aromatic ester linkage into these PHA main chains to accomplish both the solution processability of PHAs and high modulus of PBOs. This attempt was effective for this purpose, however, another problem to be solved still remained, namely, its poor transparency at 365 nm (i-line of high-pressure mercury lamp as a standard light source for lithographic processes). Higher i-line transparency of PHA films is strongly desired to enhance the sensitivity.

Our second approach was the incorporation of cycloaliphatic units using trans-1,4-cyclohexane dicarboxylic acid (CHDCA, Fig.1) into the PHA main chains, thereby electronic conjugation through the amide linkages can be inhibited without significantly sacrificing its chain stiffness/linearity. But unfortunately, this approach caused poor solution-processability.

Fig.1 Structures of monomers used.

Our previous work gives a hint to solve the present problems, that is, to achieve the high i-line transparency, the solution-processability, and high modulus at the same time: a PEsl precursor derived from an ester-containing tetracarboxylic dianhydride with rod-like 2,2'-bis(trifluoromethyl) benzidine (TFMB) could be solution-processed from NMP and γ -butyrolactone, and its film displayed a high transmittance at 365 nm. In

addition, its thermally imidized film accomplished a high tensile modulus exceeding 5 GPa. The results suggest that TFMB was a very useful monomer in PI systems for the present purpose.

Our idea in the present work is to use TFMB for copolymerization with the semi-cycloaliphatic PHA systems mentioned above. In this work, we propose high-modulus photosensitive poly(amide benzoxazole) (PABO) systems. Our temporal target is modulus higher than 5 GPa.

2. Experimental Section

2.1. Preparation of PABOs and their Precursors

The structures and abbreviations of the monomers used are shown in Fig.1. A typical procedure in the polymerization of PABO precursors is as follows: m-HAB was dissolved in dried NMP containing pyridine as an HCl acceptor. Four molar amount of chlorotrimethylsilane as a silylation reagent were added into the solution, then stirred for 1 h at room temperature to ensure silylation of all the functional groups ($-\text{NH}_2$ and $-\text{OH}$) in m-HAB. To this solution, TFMB powder was added. After LiCl as a dissolution promoter was dissolved into the solution, an equimolar amount of dichlorinated CHDCA ($= [\text{m-HAB}] + [\text{TFMB}]$), prepared by the reaction of CHDCA and thionyl chloride in the presence of DMF as a catalyst, was gradually added with continuous stirring at room temperature. A viscous and homogeneous solution was obtained after 24 h.

The polymerization solution of silylated PABO precursor was diluted with NMP, then dropped into a large amount of fresh water. This procedure allowed almost complete desilylation. The precipitated PABO precursor was repeatedly washed with fresh water to ensure complete removal of the salt until the absence of chloride ion was confirmed on a convenient test using a silver nitrate aqueous solution indicator. The precipitate was collected by filtration and vacuum-drying at 120°C for 12 h. The PABO precursor powder was dissolved in pure NMP and cast on a glass plate at 120°C. The formed PABO precursor film was cured at 350°C as adhered on the substrate and finally annealed at 280°C in a free-standing state to remove residual stress.

For positive-type patterning, DNQ (NT-200, Toyo Gosei) was dissolved into the NMP solution of PABO precursor. The DNQ-containing PABO precursor film (DNQ = 30 wt %) at 80°C/1h, was pre-baked at 100°C/10min then irradiated on a high-pressure mercury lamp (Toscore 251) through

a photo-mask, and finally developed by a 2.38 wt% TMAH aqueous solution. The pattern was observed on a scanning electron microscope.

2.2. Measurements

The reduced viscosities (η_{red}) of PABO precursors were measured at 0.5 wt% in DMAc at 30°C using an Ostwald viscometer. η_{red} can be practically regarded as inherent viscosity (η_{inh}).

CTEs of the PABO specimens (20 mm long, 5 mm wide, and typically 15 μm thick) were measured at a heating rate of 5°C/min as an average within 100–200°C for the film plane direction on a thermomechanical analyzer (Bruker-AXS TMA 4010) with a load (0.5 g per film thickness in μm) in a nitrogen flow. In this case, the data were collected from the second heating run after pre-heating up to 120°C to eliminate the adsorbed water since the first run occasionally shows an abnormal TMA curve. Storage modulus (E') and loss energy (E'') were measured as a function of temperature to determine T_g from a peak temperature of the E'' curve using the same instrument at a heating rate of 5°C/min with a sinusoidal load frequency of 0.1 Hz in a nitrogen atmosphere.

Thermogravimetric analysis (TGA) was conducted to evaluate the thermal stability of PABO films at a heating rate of 10°C/min in nitrogen and air. Thermal stability of PABO films was estimated from the 5 % weight loss temperatures (T_d^5).

The transparency of PABO precursor films was evaluated from the transmittance ($T\%$) at 365 nm.

The extent of water absorption ($W_A\%$) for PABO films were determined from the relation:

$$W_A = (W - W_0)/W_0 \times 100 \quad (\%)$$

where W_0 is the weight of the sample vacuum-dried at 50°C for 24 h, and W is the weight of the sample immersed in water at 23°C for 24 h and subsequently wiped with tissue paper.

Tensile modulus (E), elongation at break (ϵ_b), and tensile strength were measured on a stretching testing machine (Toyo Baldwin, Tensilon UTM-II) with a crosshead speed of 8 mm/min.

The dissolution rates were measured from the thickness changes monitored on a Filmetrics F-20 thin-film analyzer. The photosensitivity and the γ value were determined on the basis of the plots of normalized thickness as a function of exposure dose (i-line).

3. Results and Discussion

3.1. PABO system derived from p-HAB, TFMB, and CHDCA.

Table 1 lists the properties of PABO system with a copolymer composition of p-HAB50, TFMB50, and CHDCA100. The PABO film showed a relatively low CTE of 21.5 ppm/K and a high T_g at 302°C. It should be noted that this system achieved a very high modulus of 6 GPa exceeding our temporal target. However, the transparency at 365 nm ($T = 26.6\%$) of the PABO precursor film (10 μm thick) was insufficient. A slight increase in the p-HAB content from 50 to 60 mol % caused a drastic decrease in the solubility of the PABO powder in NMP, as a result, the solution-casting process itself was inhibited.

3.2. PABO systems derived from m-HAB, TFMB, and CHDCA.

m-HAB was also used instead of p-HAB with expectation of improvement of the film transparency. **Table 2** summarizes the properties of PABO system with a copolymer composition of m-HAB50, TFMB50, and CHDCA100. A pronounced effect of the use of m-HAB was observed in the drastically improved i-line transparency ($T = 70.2\%$) of the PABO precursor film with a still sufficiently high T_g at 292°C. A possible explanation is that the significantly improved transparency results from a much lower degree of coloration of m-HAB monomer than p-HAB, which probably originates from some oxidized colored impurity present in the monomers. On the other hand, the modulus (4.2 GPa) was lower than expected. The result suggests that the precursor chain structures affect the modulus of the resulting PABO films. In contrast to the p-HAB system mentioned above, even at 60 mol % m-HAB, the solution-processability was maintained, reflecting much higher solubility of the m-HAB system. It should be noted that this PABO exhibited a relatively high modulus (4.9 GPa) approximate to our temporal target in addition to its very high transparency exceeding to 70 %.

3.3. Positive-tone patterning

We first attempted the formation of positive-tone pattern using DNQ-containing PABO precursor with a composition of m-HAB60, TFMB40, and CHDCA100. However, poor solubility of the exposed area in the photosensitive film in 2.38 wt% TMAH at room temperature disturbed the formation of fine pattern. This is

Table 1 Properties of PABO film derived from p-HAB50, TFMB50, and CHDCA100.

p-HAB	η_{inh} (dL/g)	CTE (ppm/K)	T _g (°C)	T _d ⁵ in N ₂ (°C)	ϵ_b (%)	E (GPa)	W _A (%)	T% (365nm)
50 %	4.02	21.5	302	460	9.1	5.98	1.29	26.6

Table 2 Properties of PABO film derived from m-HAB, TFMB, and CHDCA.

m-HAB	η_{inh} (dL/g)	CTE (ppm/K)	T _g (°C)	T _d ⁵ in N ₂ (°C)	ϵ_b (%)	E (GPa)	W _A (%)	T% (365nm)
50 %	1.05	33.7	292	434	7.9	4.18	1.11	70.2
60 %	1.73	19.8	294	419	12.5	4.90	1.03	73.3

probably due to a high fluorine content and a high molecular weight of the PABO precursor as suggested from its high inherent viscosity of 1.73 dL/g. This PABO film showed the water absorption of 1.03 %. This relatively high value is probably related to the presence of the hydrophilic amide linkages in the structure. The molecular weight control using an end-capper (η_{inh} = 0.67 dL/g) enabled us to form fine pattern with L & S = 20 μ m by development using 2.38 wt% TMAH at room temperature as shown in **Figure 2**.

Fig.2 SEM photograph of positive-tone pattern for PABO (m-HAB60;TFMB40/CHCCA)

4. Conclusions

The PABO system consisting of m-HAB60, TFMB40, and CHDCA100 achieved a high modulus of 4.9 GPa, a low CTE of 19.8 ppm/K, a

high T_g at 294°C, sufficient film toughness (ϵ_b = 12.5 %), and high i-line transparency (T = 73 %) for its precursor film. The molecular weight control allowed the formation of fine positive-tone patterns by development using a 2.38 wt% TMAH aqueous solution at room temperature.

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