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Preparation of various morphological films at nanoscale by phase separation method

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ABSTRACT

A film consisting of nanopore and nanopillar structures was produced from a binary immiscible polymer solution of poly(amic acid) (PAA) and polyimide (PI), which can be used as a potential light extraction layer or flexible substrate in organic light-emitting diode (OLED) devices. A phase separation method was applied to create uniform and random pattern structures in nanoscale via a simple spin-coating technique. Firstly, the binary immiscible polymer solutions of PAA and PI whose precursor is carbazole-based dianiline were prepared with various volume ratios, and then the polymer mixtures were spin-coated onto substrates to form transparent films with various morphologies and dimensions, as observed by a field emission scanning electron microscope technique. In addition, after annealing PAA/PI films at 300 °C, the homogenous and flexible characteristic of nanopore and nanopillar structures could be achieved.

KEYWORDS

Carbazole-based dianiline; nanopillars; nanopores; phase separation; poly(amic acid); polyimide

Introduction

Recently, flexible organic optoelectronic devices are a promising field with the evergrowing rate of display and lighting application. Novel flexible materials must satisfy several crucial requirements. Among various organic polymer materials, a polyimide (PI) is one of the optimum candidates for flexible materials, especially an aromatic PI [1]. PI has extraordinary properties which attract the interest of researchers, such as excellent thermal, mechanical, electrical and chemical performance [2] although it consists of rigid planar imide rings [3]. In addition, PI with heterocycles such as pyridine, benzimidazole, pyrimidine, furan etc. in the backbone can increase their glass transition temperature (T_g) [4]. In optoelectronic parts, the flexible transparent PI is used largely as a substrate instead of a glass in all flexible organic light-emitting diode (OLED) devices [5]. Meanwhile, carbazole and carbazole derivatives also gained much attention from the researchers. They have been applied to OLED devices as an emitting layer or hole transport layer with inherently incredible properties which are high thermal stability [6], easy chemical functionalization, film-forming capability [7], excellent transparency [8], good refractive index [8,9] and high fluorescent quantum yield [10]. The

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strategy for introducing carbazole rings into PI backbones have been proposed in the report of H. M. Wang et al. for the purpose of a hole-transporting and electrochromic materials [11].

Here, we used poly(amic acid) (PAA) and PI made from carbazole based dianiline (CDA) to prepare phase-separated films by a simple and low-cost fabrication process, spin-coating technique. The phase separation phenomenon has been described earlier in our previous reports [12, 13]. The binary polymer solutions were prepared with various ratios to obtain nano-pattern films which were either nanopores or nanopillars. The phase-separated PI films have thermostability, transmittance, high refractive index, flexibility and good light scattering. With these properties, the phase-separated film may be used as a flexible substrate or light out-coupling layer in optoelectronic devices.

Experiment details

Materials

Carbazole (>97.0%), 4-fluoronitrobenzene (>98%), hydrazine monohydrate (79%), acetic anhydride (AA) (>98%), pyridine (>99%) and K_2CO_3 (>99%) were purchased from Tokyo Chemical Industry. 4,4'-(Hexafluoroisopropylidene)-diphthalic anhydride (6FDA) (99%) and palladium 10% on carbon (10% Pd/C) were obtained from Sigma Aldrich. Dimethyl formamide (DMF) (>99%), ethanol (>99%), and dimethyl acetamide (DMAC) (>99%) were purchased from Duksan (South Korea) and used as received.

Preparation of monomers

Step 1: synthesis of 9-(4-nitrophenyl)-9H-carbazole

0.1 mol (16.72 g) of carbazole and 0.1 mol (14.11 g) of 4-fluoronitrobenzene were dissolved in 100 mL of DMF in a 250 mL two-neck round-bottom flask equipped with a stirring hot plate, a condenser and an inlet of inert gas. 0.15 mol (20.7 g) of K_2CO_3 was gradually added into the solution and the reaction was carried out at 100 °C for 12 h. After cooling the reaction solution, crystals were filtered, washed with water and recrystallized by ethanol. The obtained product was light-yellow needle crystals (yield 95%) (Scheme 1).

Step 2: synthesis of 9-(4-aminophenyl)-9H-carbazole

0.08 mol (23.05 g) of 9-(4-nitrophenyl)-9H-carbazole and 0.016 mol (1.7 g) of 10% Pd/C were dispersed in 100 mL of ethanol in a 250 mL two-neck round-bottom flask equipped with a stirring hot plate, a condenser and an inlet of inert gas. The reaction mixture was stirred under nitrogen for 1 h at room temperature before 0.8 mol (40 g) of hydrazine monohydrate was slowly added. The reaction mixture was refluxed at 90 °C for 12 h. The reaction mixture was filtered to get rid of Pd/C, and then ethanol was removed by a vacuum evaporator to leave the white gel product (yield 90%) (Scheme 1).

Step 3: synthesis of N-4-(9H-carbazol-9-yl)-4-nitro-N-(4-nitrophenyl)aniline

The process is the same as that of step one but with the ratio of reactants; one equiv., two equiv., and 1.5 equiv. for 9-(4-aminophenyl)-9H-carbazole, 4-fluoronitrobenzene



Scheme 1. The structures of PAA and PI prepared from CDA.

and K_2CO_3 , respectively. The obtained product was dark-yellow needle crystals (yield 91.4%) (Scheme 1).

Step 4: synthesis of N^1 -(4-(9H-carbazol-9-yl)phenyl)- N^1 -(4-aminophenyl)benzene-1,4-diamine

The process is the same as that of step two but with the ratio of reactants; 1 equiv., 0.Two equiv., and 20 equiv. for N-4-(9H-carbazol-9-yl)-4-nitro-N-(4-nitrophenyl)aniline, 10% Pd/C and hydrazine monohydrate, respectively. The obtained product was light-grey needle crystals (yield 89.3%) (Scheme 1).

Preparation of polymers

Step 1: preparation of PAA

0.05 mol (22.01 g) of N^1 -(4-(9H-carbazol-9-yl)phenyl)- N^1 -(4-aminophenyl)benzene-1,4-diamine and 0.05 mol (22.22 g) of 6FDA were dissolved in 80 mL of DMAC in a 250 mL two-neck round-bottom flask equipped with a stirring hot plate, a condenser and an inlet of inert gas. The reaction mixture was stirred under nitrogen at 0 °C for 1 h. Then, stirring was continued at room temperature for 24 h. Finally, PAA was collected by precipitation of the one-half reaction solution into excess deionized water (Scheme 1). 130 👄 T. T. K. TU ET AL.

Step 2: preparation of PI

0.025 mol (2.55 g or 2.36 ml) of AA and 0.025 mol (1.98 g or 2.02 ml) of pyridine were added into the rest of the PAA solution. The reaction was continually stirred at $100 \degree \text{C}$ for 24 h to produce PI. Finally, PI was collected by precipitation of the reaction solution into methanol (Scheme 1).

Step 3: preparation of phase separated film. PAA and PI were separately dissolved into DMAC, where the concentration of solutions was 5%. The PAA and PI solution were mixed with the following ratios: 1:9; 3:7; 5:5; 7:3 and 9:1. The mixtures were spin-coated on a glass substrate with a speed of 1200 rpm for 30 s in the first step and 2500 rpm for 3 s in the second step. The phase-separated films were annealed at $50 \,^{\circ}$ C for 10 min under vacuum, and the temperature was gradually increased to $150 \,^{\circ}$ C at intervals of 10 min/time to form polymer films on the glass substrate. Afterwards, the temperature was gradually increased at $50 \,^{\circ}$ C to gain phase-separated PI films.

Characterization

Proton nuclear magnetic resonance (¹H-NMR) spectra were measured on a JEOL JNM ECP-600 MHz. Fourier-transform infrared spectroscopy (FT-IR) spectra were recorded on an Agilent Tech spectrometer. Thermogravimetric analysis (TGA) was conducted on a Perkin - Elmer Pyris 1 analyzer (USA). Field emission scanning electron microscopes (FE-SEM) images were performed on a JEM-2100F (JEOL). Ultraviolet-visible spectroscopy (UV-Vis) spectra were carried out on an Optizen POP UV-Vis spectrophotometer. Refractive index (RI) was characterized by a J. A. Woollam M-2000D Spectroscopic Ellipsometer.

Results and discussion

To prepare PAA and PI from CDA, we have referred to the report of H.M. Wang et al. [11] (Scheme 1). Carbazole was transformed repeatedly into the corresponding nitro and amino compounds in sequence by using simple and mild processing conditions to produce CDA. In the next step, the step-growth polymerization was conducted by the reaction between CDA and 6FDA, resulting in PAA. The chemical imidization reaction was used to produce PI powder for the preparation of phase separated films. The thermal imidization was also used, however, in the step of completing the homogeneous PI film.

The FT-IR spectra were studied to examine the presence of the functional groups on the backbone of polymers. The principal difference of structure features between PAA and PI is the appearance and disappearance of O–H and N–H links, as shown in Fig. 1. The spectrum of PAA shows the O–H stretch and N–H stretch (secondary amine) in the range $3683-3166 \text{ cm}^{-1}$, which almost overlap the C–H stretch at 3070 and 2932 cm^{-1} . The characteristic imide group absorptions are exhibited by the presences of imide carbonyl symmetrical stretch (C=O) around 1784 cm^{-1} and tertiary amine stretch (C–N) around 1382 cm^{-1} . It is also clearly observed that the intensity of imide



Figure 1. FTIR spectra of PAA and PI.

carbonyl asymmetrical stretch (C=O) around 1728 cm⁻¹ increases strongly and the N-H bend in secondary amine around 1512 cm⁻¹ disappears.

The ¹H-NMR spectra of PAA and PI confirmed the polymer structures (Fig. 2). The most contrast difference between the two polymers figured out in the spectra is the presence of a proton peak at 4.32 ppm that characterizes the proton of amide groups on the PAA backbone. The proton peak of the carboxyl group in PAA is hardly detected because the strong hydrogen bonding between the carboxyl group and deuterium in DMSOd₆. After the chemical imidization, the protons in aromatic rings of 6FDA moieties (position a, d, k) and aniline moieties (position j) are not much affected by ones in the amide groups. Thus, all these protons are shielded, in other words, their chemical shifts move to the lower field.

To investigate the optical characteristics of PAA and PI materials, we measured the refractive index and transparency of their samples which were coated on a silicon wafer or glass substrate with 5% concentration (Fig. 3). The refractive index was collected by the spectroscopy ellipsometry using the Cauchy and Si_jaw layer in the range wavelength from 400 to 900 nm. The index of PAA is measured to be like common polymer materials (around 1.68), whereas the index of PI jumps to around 1.73 which is similar to the value of typical organic layers in OLEDs. Besides, UV-vis spectra were recorded in the wavelength range from 300 to 1000 nm to determine the percentage of transmittance of the light ray through the PAA and PI films coated on the glass substrate. As a result, the transmittances starting from 450 nm onwards are 80% and 85% for PAA and PI, respectively. Although these results are not high as compared to other polymer



Figure 2. ¹H-NMR spectra of PAA and PI.



Figure 3. (a) Refractive index of PAA and PI in the wavelength range from 400 nm to 900 nm, (b) The percentage of transmittance of PAA and PI in the wavelength range from 300 nm to 1000 nm.

materials, the combination of high refractive index and transparency of the PI film is suitable enough for optoelectronic devices.

The thermal stability was evaluated by TGA, as shown in Fig. 4. Both TGA curves of PAA and PI exhibited similar shapes and good thermal stability. While the weight loss curve of PI remained until 400 °C under nitrogen, the curve of PAA diminished over 4% by weight. The curves of both polymers continued to fall sharply at the same temperature 417 °C. It means that during the first 400 °C the thermal imidization has occurred to transform PAA to PI. The first weight loss of PI and the second weight loss of PAA started to take place at 417 °C. Approximately 16% by weight of PAA and over



Figure 4. TGA diagram of PAA and PI in temperature range from 50 °C to 1200 °C.



Figure 5. SEM images of phase-separated PI films from various PAA/PI binary solutions with volume ratios (a) 1/9; (b) 3/7; (c) 5/5; (d) 7/3; (e) 9/1.

20% by weight of PI were lost steadily over a quite long temperature range from 417 $^{\circ}$ C to 776 $^{\circ}$ C, which was attributed to the contribution of the high aromatic ring content in the backbone of PAA and PI. Meanwhile, the remaining 80% weight loss of PAA and PI took place at the next stage from ca. 800 $^{\circ}$ C. As a result, the PAA and PI possess inherently excellent thermal stability.

The topography of surficial phase-separated PI films was surveyed by using the FE-SEM technique after transforming the PAA:PI blend films to PI films by thermal imidization. The formation of nanopores and nanopillars at various ratios of binary polymer mixtures were observed on SEM images as shown in Fig. 5. The surficial morphologies 134 👄 T. T. K. TU ET AL.

that were formed from the PAA: PI solution with a volume ratio of 1:9 exhibited nanopore patterns whose size and shape are not uniform and well distributed (Fig. 5a). At the volume ratio of 3:7, sharper and larger nanopores were formed on the surface of polymer films as shown in Fig. 5b. However, inside and outside the big pores, there were countless nanopillars which were not the same size. Interestingly, the morphologies of the film surface became opposite in comparison to ones with the lower PAA contents when the PAA content increased until equal to or greater than the PI content in the binary polymer solution. That is, the shapes of patterns were nanopillars from the PAA: PI solutions with volume ratios of 5:5 and 7:3. Although the surfaces were nanopillars, their distributions, tightness and sizes of nanopillars were different from each other. For the volume ratio of 5:5, the nanopillars were ununiform and had various sizes in the range from 50 to 200 nm. Whereas, nanopillars of well-distribution and smaller size were formed for 7:3. Finally, a nearly flat surface was observed in the case of the PAA:PI mixture of 9:1.

Conclusion

In conclusion, the nanopore and nanopillar patterned surfaces of PI films were prepared successfully by the simple and low-cost spin-coating technique. The PI film showed outstanding properties with the high refractive index of 1.73, good transparency of 85%, excellent thermal stability and flexibility. It is supposed that the PI can be one of promising materials for the optoelectronic or photovoltaic fields in general and OLED devices in particular.

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