Synthesis and Characterization of a Kind of Soluble Photosensitive Copolyimides

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Abstract: Two kinds of monomers with hydroxyl group, 4,4'-diamino-4''-hydroxyphenyl triphenylmethane (DHTM) and 3,3',4,4'-benzhydrol tetracarboxylic dianhydride (BHTDA) were synthesized, respectively. Based on these two synthetic monomers and some other commercial monomer, a kind of copolyimide containing hydroxyl (polymer I) was prepared and characterized. Polymer I was prepared utilizing the DHTM as diamine and both BHTDA and 4, 4'-(Hexafluoroisopropylidene) diphthalic anhydride (6FDA) as dianhydrides with the diverse molar ratio. The DNQ, o-diazonaphthoquinone derivative, was introduced into the polymer I as an important and effective photosensitive group and lithography behaviors of PSPIs were investigated. These polyimides show unique lithographic behavior with an aqueous base developer. The result shows that the photoreaction mechanism after exposing to UV light depends on the moisture and content of hydrophilic group (-OH).

Key words: DHTM, BHTDA, Polyimide, NQD, Photosensitive

Introduction

Polyimides (PIs) have been widely applied into different fields, especially in the manufacturing of semiconductors, as an important class of advanced material due to the high thermal stability and low dielectric constant since 1960s. However, the process for multilayer fabrication using conventional polyimides is complicated. [1] Photosensitive polyimides (PSPIs) are occupying the prevalent position used as protection and insulation layers in electronic appliances since the number of processing steps can be reduced by avoiding the use of classical photoresists. [2] Usually, PSPIs can be divided into negative type and positive type according to the differences of developing mechanism and the imagination obtained. Most of the negative PSPIs are prepared from poly(amic acid)s, where cross-linking sites are introduced to amic acids through ester and acid amine ion linkages. [3,4] Additionally, the positive PSPIs are composed by poly(amic acid) and DNQ [5] or 1,4-dihydropyridine derivatives, [6] polyimide containing hydroxyl groups and DNQ, [7] or o-nitrobenzyl esters of polyamic acid. [8]

When exposed into certain wavelength ultraviolet rays, the hydrophobic DNQ can converse into hydrophilic indenecarboxylic acid via ketocarbene and ketene intermediates. [9-11] The photochemical reaction offers a route to prepared PSPIs. Moreover, the deep color caused by charge transfer complex formation and insolubility of conventional PIs tremendously restricts their practice application. Based on those disadvantages mentioned above, the PIs containing fluoroalkyl and hydroxyl groups were prepared utilizing the DHTM as diamines and both 6FDA and BHTDA as dianhydrides in our experiment. Then the DNQ was introduced into the PIs to synthesize the PSPIs (PI-DNQ). The structure and properties of PSPIs was characterized and studied.

Experiment Section

Materials. The DHTM and BHTDA were synthesized according to the reports by Bor-Kuan Chen [12] and Der-Jang liaw [13], respectively. The 6FDA was purified by vacuum sublimation. The solvent diglyme was distilled before use and stored over molecular sieves. The DNQ was kindly provided by Liaoning Huahai-Lanfan chemical technology Co., Ltd and used as received, and other materials were obtained from commercial sources and used without further purification.

Instrumentation. IR spectra were measured with a Nicolet Nexus 670 spectrometer. NMR spectra were recorded with a Bruker AMX-600M spectrometer using DMSO-d6 as a solvent and tetramethylsilane as internal standard. The water contact angle values were measured on a Dataphysics OCA20 contact-angle system at ambient temperature.

Synthesis of DHTM. The DHTM was synthesized as follows: A mixture of 4-hydroxybenzaldehyde 12g (0.1mol), aniline 28 g (0.3 mol), and aniline hydrochloride 1.30 g (0.01 mol) was charged into three necked flask and stirred at 120℃ under nitrogen atmosphere for 3h. After the completion of the reaction, a pink crude product was isolated and dried. Further recrystallization from ethanol (three times) produced a purple needle crystalline product of DHTM. IR (KBr): 2856 cm^{-1}(C-H, aliphatic), 3329 cm^{-1} and 3200 cm^{-1}(NH_2), 3385 cm^{-1}(OH). ^{1}H-NMR (DMSO-d6): δ 9.11 (s, OH, 1H), 6.9-6.4 (m, PhH, 12H), 5.04 (s, CH, 1H), 4.83 (s, NH2, 4H).

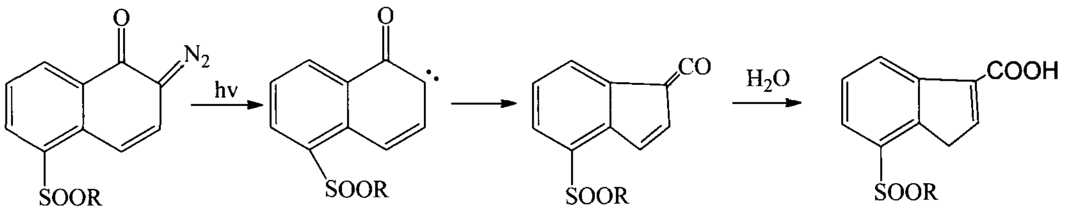
Synthesis of BHTDA. 16 g of benzophenonetetracarboxylic dianhydride (50 mmol) was dissolved in 20% NaOH aqueous solutions (40mL) and 2g sodium borohydride powder was added to the system at 25 °C by several times. The solution was stirred at 25 °C for 1.5 h and was made acidic by the addition of HCl. A series of purification and separation were carried out and 12g of benzhydroltetracarboxylic acid were obtained. It was then stirred at 25°C with 800 mL of acetic anhydride for 5 days. When acetic anhydride was removed under reduced pressure, crude BHTDA was isolated by filtration and lyophilized in dioxane, washed by pentane and dried under vacuum for 12 h at 50 °C, to give 7 g of white product. IR (KBr): 3400cm^{-1} (O-H), 1850 (asym C=O) and 1780cm^{-1} (sym C=O). ^{1}H-NMR (DMSO-*d6*): δ8.0-8.2 (m, 6H, ArH), 6.8 (s, 1H, OH), 6.2 (s, 1H, -CH-).

Preparation of PIs. To synthesize the PI with hydroxyl group (**PHI**), 6FDA and BHTDA with different molar ratio and DHTM were charged and reacted. A typical procedure proceeded as follows. Into a three-necked flask were placed 0.581g (2mmol) of DHTM, 0.1g of isoquinoline and 20ml m-cresol. To the solution were added 0.324g (1mmol) BHTDA and 0.444g (1mmol) 6FDA at 60℃ under nitrogen. The solution was cooled in ice-water bath with stirring for 0.5h and then heated at 180℃ for 5h. The viscous clear polymer solution was poured into a large amount of methanol. The precipitate was collected by filtration, washed with methanol and dried at 50 °C under vacuum. IR (KBr): 3400 (O-H), 1783 (asym C=O), 1723(sym C=O), and 1376 cm-1 (C-N).

Synthesis of PI-DNQ. 0.5g of PHI was dissolved in 15ml diglyme and reacted with various concentrations of DNQ in the presence of equimolar triethylamine at room temperature for 24h under a nitrogen flow. The polyimides with varying amounts of DNQ in the side chain were precipitated from the solution with methyl alcohol and dried at 40°C under vacuum. IR (KBr): 2115cm^{-1}(N=N).

Results and Discussion

Synthesis of co-Poly(hydroxyimide) (co-PHI). For enhancing the optical transparency to UV rays and the solubility of PIs, to introduce trifluoromethyl group into the main chain is considered to be a more versatile technique. [1] However, the high hydrophobicity of –CF$_3$ go against the photochemical reaction of DNQ (Scheme 1). Thus, for harmonizing the contradiction, a second dianhydride (BHTDA) which can increase the solubility was employed. The hydroxyl group of BHTDA effectively improves the hydrophilicity and meanwhile maintains good solubility. The polymer was confirmed by infrared spectroscopy. The IR spectrum exhibited characteristic absorptions at 3400, 1783 and 1723cm^{-1} due to the hydroxyl group and the imide carbonyl (Fig 1).



Scheme 1. Photochemical reaction Scheme of DNQ

Synthesis of PI-DNQ. In the presence of triethylamine, the 2-Diazo-1-naphthol-5-sulfonyl chloride (DNQ) reacts with the hydroxyl group of PHI to form the PI-DNQ. What needs to be noted is that the aliphatic hydroxyl group in the backbone is hard to react with acyl chloride according to the report by M. Berrada, et al.[14] Thus it will be controllable to make the main reaction focus on the phenol hydroxyl by adding dropwise. The PHI based on DHTM/6FDA was prepared and characterized to give the evidence that the reaction was feasible (Fig 1). The phenol hydroxyl was substituted totally. The IR spectrum shows that the characteristic absorptions of hydroxyl group at 3400cm^{-1} vanished and the important peak 2115cm^{-1} representing to N=N appeared.

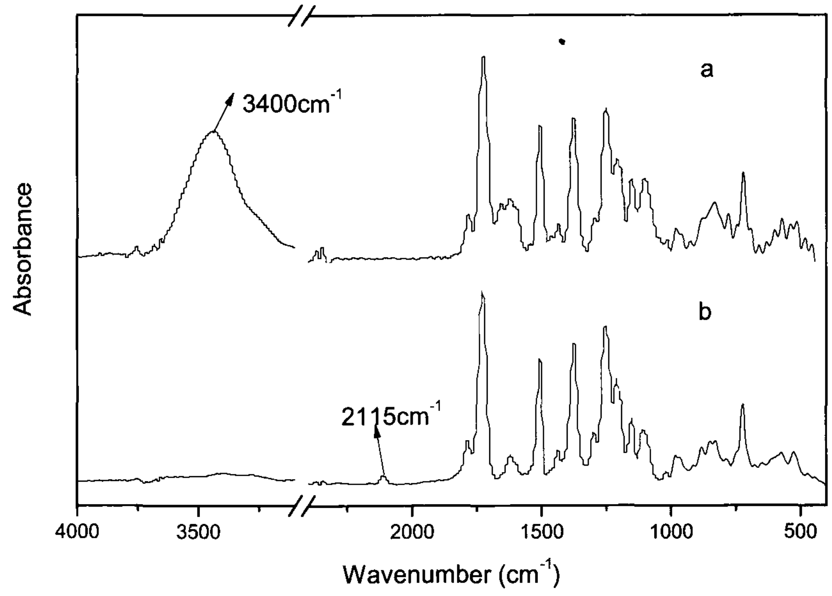
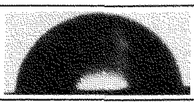
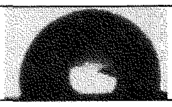
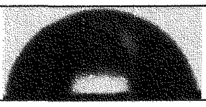


Fig 1 FTIR spectra of (a) PI based on DHTM/6FDA, (b) PI-DNQ

As a typical dissolution inhibitor, the introduction of DNQ in the pendant group directly results in the decrease of solubility of PHI. According to the experiment, the PI-DNQ became insoluble when the aromatic hydroxyl was replaced by DNQ fully. As we mentioned above, the photoreaction of DNQ needs certain moisture. The contact angle (Table 1) was tested to confirm that the introduction of BHTDA indeed is benefit to heighten the hydrophilicity.

Table 1. Water contact angles and images of PHI and PI-DNQ

Films	PHI	(6FDA/DHTM-DNQ)	(6FDA/BHTDA/DHTM-DNQ)
Images of water contact angle			

Water contact angles (°)	89	105	89

The photolithography behaviors were investigated on the basis of diverse conditions. The moisture, atmosphere, concentration of DNQ, baked temperature and so on, all of them can influence the photochemical reaction. Photoreactive polyimides based on DHTM and 6FDA exhibit no lithographic behavior when the -OH was fully substituted by hydrophobic DNQ. The further work need be done to obtain excellent photosensitive material.

Conclusions

As a summary, two kinds of monomers and the photosensitive polyimides based on them and DNQ (6FDA/BHTDA/DHTM)-DNQ have been synthesized in our present work. The structures and properties of the monomers and PIs was tested and confirmed.

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