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Synthesis of Photosensitive and Thermosetting Poly(phenylene ether) Containing Butenyl Groups

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1. Introduction

Photopatternable insulating polymers with low dielectric constant (ε), low dissipation factor (tan δ), low moisture uptake, and good thermal stability are required for protective chip over coatings for mega-bit memories and logic components, and planarizing low ε interlayer dielectrics in complex multi-layer electronic devices to achieve high switching speeds in thin-film multi-chip modules [1]. For these purposes, photosensitive poly(imide)s and poly(benzoxazole)s with fluoro substituents are investigated so far [2]. Poly(2,6-dimethyl-1,4-phenylene ether) (PPE) prepared by oxidative coupling polymerization of 2,6-dimethyl phenol (**2**) by copper-amine catalyst, which is an atom economical polymerization [3], shows a low ε (2.5), a low tan δ (0.0007), and low moisture uptake (<0.05). However its glass transition temperature (T_g) is about 210 °C, inadequate for solder resistance. The thermosetting PPE having allyl groups has been developed, in which the high T_g of 250 °C are realized in addition to low dielectric properties [4]. However, the synthetic route involving lithiation of PPE, followed by allylation with allyl halide is troublesome, and the structure of resulting polymer is not clear due to the possibility of plural allylation in a unit of PPE. Therefore, it is interesting to develop a simpler procedure for the development of photosensitive and thermosetting PPEs.

This article describes the successful synthesis and properties of novel thermosetting PPEs having allyl groups by oxidative coupling copolymerization of 2,6-di(3-methyl-2-butenyl)phenol (**1**) with **2**, and development of a negative-tone and chemically amplified photosensitive polymer based on the PPE and a photoacid generator (5-propylsulfonyloxyimino-5H-thiophen-2-ylidene)-(2-methylphenyl)-acetonitrile (PTMA).

2. Experimental

2.1 Materials

The monomer (**1**) was prepared according to the reported procedure [5]. Other reagents and solvents were purified by ordinal way before use.

2.2 Polymerization

Homopolymers of **2** and copolymers of **1** with **2** were prepared by a conventional oxidative coupling polymerization using a copper (I) chloride-pyridine catalyst under oxygen at 25 °C. White fibrous polymers were collected after precipitation in methanol containing concentrated HCl, and dried at 80 °C for 12 h under vacuum.

2.3 Measurements

Infrared spectra were recorded on a Horiba FT-720 spectrometer. NMR spectra were recorded on a BRUKER DPX300 (^{1}H; 300 MHz) spectrometer. UV-visible spectra were recorded on a Jasco V-560 spectrophotometer. Thermal properties were measured with a Seiko TG/DTA 6300, TMA/SS 6100, and DMS 6100 under nitrogen. Molecular weights were estimated by GPC on a Jasco GULLIVER 1500 system eluted with $CHCl_3$ at 40 °C using polystyrene standards. Refractive indices of polymer films on quartz substrates were measured at a wavelength of 1.320

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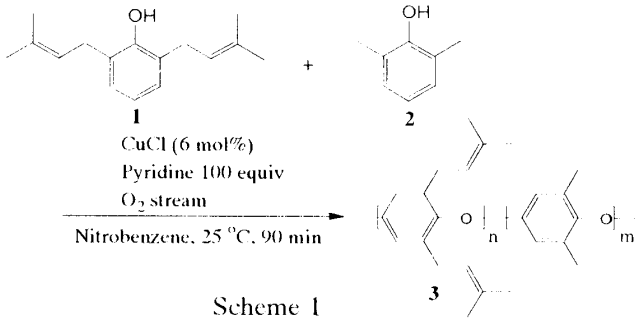
μm at 20 °C with a Metricon model PC-2000 prism coupler.

3. Results and discussion

3.1 Polymerization

Copolymers (**3a-3c**) were prepared by the oxidative coupling polymerization of **1** with **2** in the presence of copper (I) chloride and pyridine in nitrobenzene (Scheme 1). [5]. Considering the amount of crosslinking sites, the feed monomer molar ratios of **1** and **2** were set at 7 / 93 (for **3a**), 14 / 86 (for **3b**), and 20 / 80 (for **3c**). The compositions of copolymers were estimated by the integration ratio between signals at 6.47 and 5.17 ppm in ^{1}H NMR spectra of copolymers.



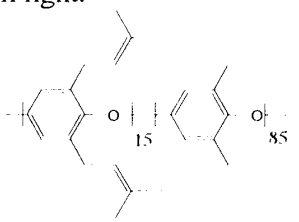
Scheme 1

3.2. Cross-linking reaction

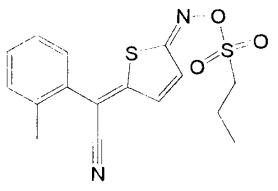
Cross-linking reactions of copolymers **3** were carried out by thermal treatment at 300 °C for 1 h, giving cross-linked copolymers with high T_g of 238 (**3a**), 256 (**3b**), and 300 °C (**3c**). The refractive index of cured copolymer **3c** is 1.5452 estimated by a prism coupler method that can be translated in ε of 2.6 at 1 MHz.

3.3 Lithographic Evaluation

A photosensitive polymer consisting of copolymer **3c** (85 wt%) and PTMA (15 wt%) was formulated. The sensitivity curve is shown in Figure 1. This resist showed a high sensitivity ($D_{0.5}$ = 35 mJ cm^{-2}) and a contrast ($\gamma_{0.5}$ = 1.6) with 436 nm light.



Copolymer **3c**



PTMA

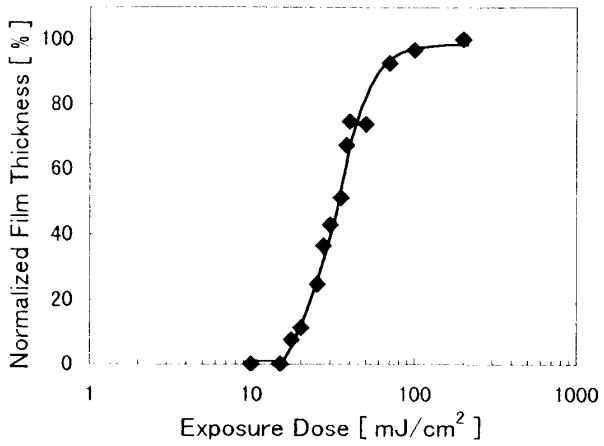


Fig. 1. Exposure characteristic curve of the system of **3c** (85 wt%) and PTMA (15 wt%) using toluene as a developer

4. Conclusion

A novel chemically amplified photosensitive and thermosetting polymer based on PPE having allyl group with a photoacid generator PTMA has been developed. Copolymers **3** prepared by oxidative coupling polymerization of **1** with **2** showed high thermal stability (T_g = 300 °C after curing), solvent resistance, and low ε value (2.6). Therefore, these materials would be of useful in high-speed and high frequency printed circuit board application.

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