A New UV-curable Resist with Liquid Volume-Expanding Monomers

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Nanoimprint lithography (NIL) has been regarded as one of the most promising nanofabrication techniques due to its ability to fabricate nanoscale structures with low cost and high throughput. However, UV-curing NIL still faces the issue of resist volume shrinkage during curing, which not only affects the pattern fidelity but also induces pattern defects during mold releasing [1]. Although many methods have been employed to reduce the shrinkage, including inorganic additives and choosing polymers with bulky side groups or low overall concentration of double bonds, success has been very limited. However, our previous work confirmed that we could achieve low shrinkage and even volume expansion by mixing the epoxy mononers with spiro-orthocarbonate monomers.

Spiro-orthocarbonate is a monomer that undergoes volume expansion upon cationic ring-opening polymerization. In our previous work, 1,5,7,11- tetraoxaspiro [5,5] undecane was chosen as the volume expansion monomer. However, it is a solid at room temperature with a poor solubility in epoxy monomers. This makes it necessary to use solvent in the resist formulation. It also causes phase separation during spin-coating. Also, when the viscosity of the mixture was taken into the consideration, the amount of the expanding monomers in the resist formulation was very limited. In this work, 3,9-diethyl-3,9-bis(allyloxymethyl)-1,5,7,11-tetraoxastetraoxaspiro [5.5] undecane (DB-TOSU) (shown in Fig. 1) is introduced into the resist formula for the purpose of reducing the volume shrinkage caused by the curing of commonly used epoxy compound. Because DB-TOSU is a liquid at room temperature, we can solve the miscibility and viscosity problem very easily. DB-TOSU was synthesized through the reaction of trimethylolpropane allyl ether with TEOC[2], and the reaction profile is shown in Fig. 1. The synthesized product was characterized by ^{1}H-NMR spectrum, which is shown in Fig. 2. The ^{1}HNMR spectrum shows the desired DB-TOSU compound is successfully obtained.

DB-TOSU polymerizes at room temperature under UV light and at the presence of photo-generated acids. The relationship between the resist shrinkage after curing and the amount of DB-TOSU in resist formulation will be further studied in detail, and an optimized formulation with zero volume shrinkage will be reported. We expect that zero volume shrinkage will yield imprinted structures without residual stress, which consequently reduce pattern defects in UV NIL by significantly lowering demolding forces.

References

[1] X. Cheng, L. J. Guo, and P. F. Fu, Adv. Mater., 17, 1419-1424, 2005.
[2] C. C. Chappelow, C. S. Pinzino, S.-S. Chen, L. Jeang, J. D. Eick, J. Appl. Poly., 103, 336-344, 2006

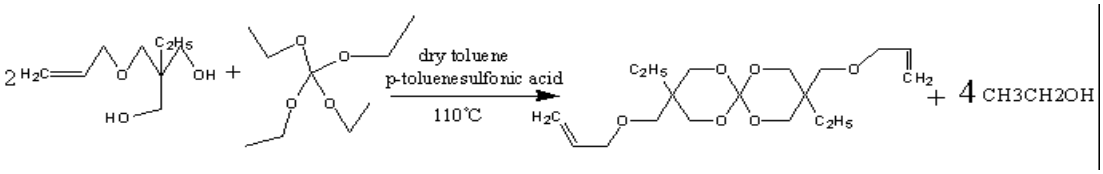

Fig. 1. The reaction profile of synthesizing DB-TOSU

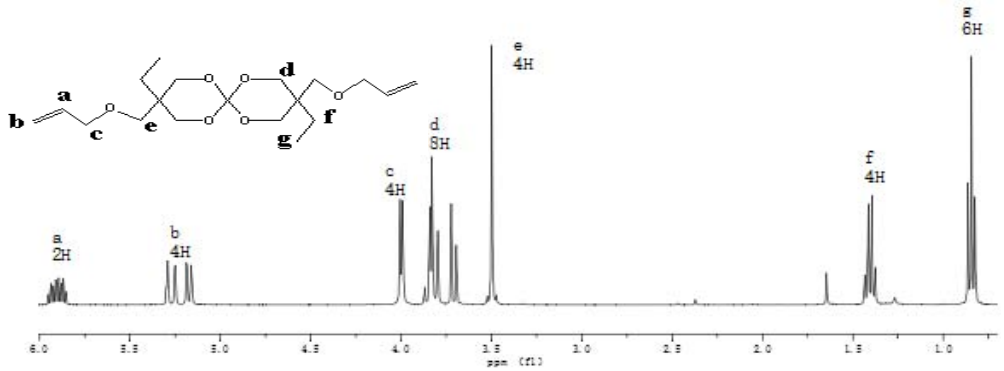

Fig. 2. [1]HNMR spectrum of the synthesized compound. The peaks are labelled corresponding to the hydrogens in the molecular structure.