

Volume-expansion polymerization for UV-curable nanoimprint

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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 after 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 low concentration of functional groups, success has been very limited. In this work, we formulate a nanoimprint resist that utilizes volume-expansion polymerization.

Spiro-orthocarbonate is a monomer that undergoes volume expansion upon cationic ring-opening polymerization. It is an effective method to reduce the resist shrinkage through the copolymerization of spiro-orthocarbonate and epoxy compound. In this study, 1,5,7,11-tetraoxaspiro[5,5] undecane (shown in Fig. 1) has been introduced to the resist formula to compensate the volume shrinkage caused by the curing of commonly used epoxy compound. 1,5,7,11-tetraoxaspiro[5,5] undecane was synthesized through the reaction of tetramethyl orthocarbonate with 1,3-Propanediol^[2], and the reaction profile is shown in Fig.1. The synthesized product was characterized by IR and ¹H-NMR spectra, which are shown in Fig.3 and Fig. 4, respectively. In the ¹H-NMR spectrum (Fig. 3), the two peaks at 1.805 ppm and 4.059 ppm are attributed to the methylenes protons (CH₂) and the methylenes protons adjacent to the ether oxygens (CH₂O), and the area of the former peak is two times of the latter one's, which is consistent with the structure of 1,5,7,11-tetraoxaspiro[5,5] undecane. In the IR spectrum (Fig. 4), the absorption peak at 1210 cm⁻¹ corresponds to the spiro structure of 1,5,7,11-tetraoxaspiro[5,5] undecane. The IR and ¹H-NMR data demonstrate the desired 1,5,7,11-tetraoxaspiro[5,5] undecane is obtained.

1,5,7,11-tetraoxaspiro[5,5] undecane can be polymerized at 30 °C with 10% volume expansion. The effect of the amount of 1,5,7,11-tetraoxaspiro[5,5] undecane added to the resist system on the volume change after resist curing will be further studied in detail, and an optimized formulation with zero volume shrinkage after curing will be reported. Since the shrinkage of this new resist before demolding is zero, there will be not residual stress left in the cured resist structures. It is also expected that zero volume change of resist after curing will lower the separation energy required during demolding. Thus the nanoimprint pattern defects caused by residual stress and high demolding energy are expected to be reduced.

[1] X. Cheng, L. J. Guo, and P. F. Fu, *Adv. Mater.*, 17, 1419-1424, 2005.

[2] T. Toshikazu, A. Toshiro, and E. Takeshi, *Macromolecules*, 25, 3829-3833, 1992.

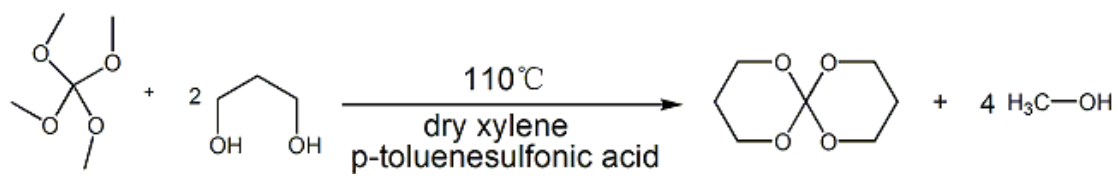


Fig. 1. Reaction profile of synthesizing 1,5,7,11-tetraoxaspiro[5,5] undecane

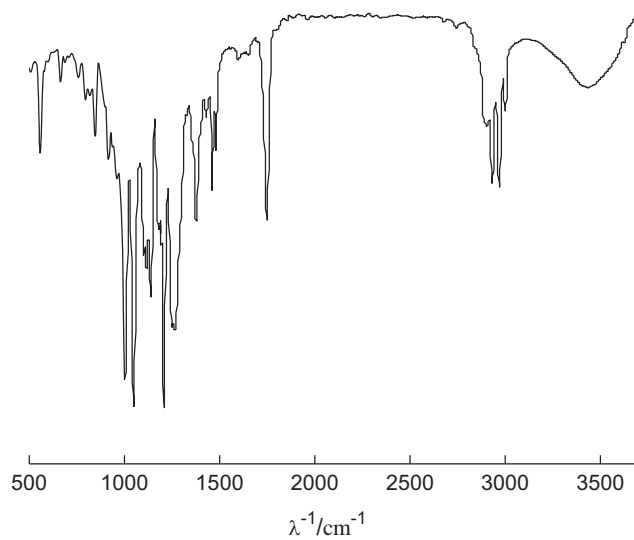


Fig. 2. Infrared spectrum of the synthesized product.

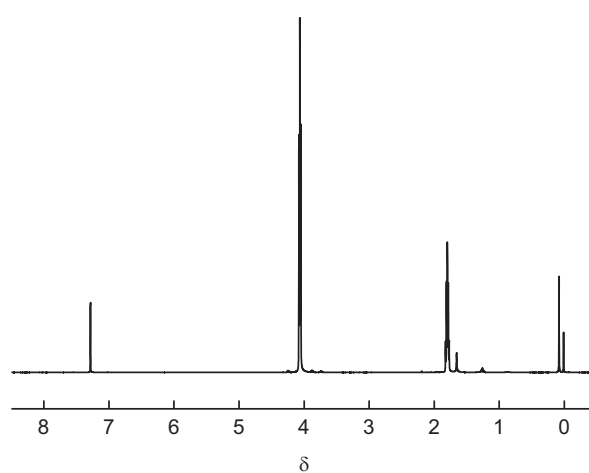


Fig. 3. ¹H NMR spectrum of the synthesized product.