

Development of High Refractive Index and Low Birefringence Novel Triazine-based Poly(phenylene sulfide)s

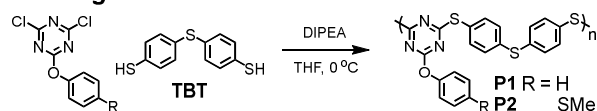
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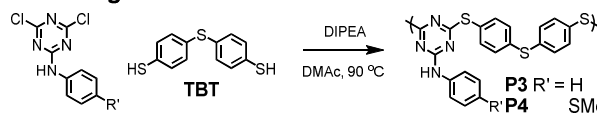
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High-refractive-index (high- n) polymers (HRIPs) with a high optical transparency and low birefringence (low Δn) are highly needed in the applications of advanced optoelectronic devices due to the significant improvement in the device's performance. However, the types of high- n polymers with the balancing of all the desired optical properties are still limited. Previously, Oishi and coworkers reported that the hyperbranched poly(guanamine)s which were prepared from cyanuric chloride and aromatic diamines showed high- n values ($n_D > 1.70$).¹ In our previous work, the linear poly(phenylene sulfide)s (PPSs) were synthesized by triazine derivatives and aromatic dithiols, also exhibiting high- n values ($n_{633\text{nm}}$: 1.64-1.75).² Based on these results, the polymers with triazine unit showed the promising high- n values and high transparency in visible region. To study the structure-property relationship in detail, four different triazine monomers (T1-T4) were prepared from cyanuric chloride and aniline or phenol derivatives by the substitution reactions in acetone in good yields (> 90%). The triazine monomers could be divided into two series of *O-linkage* and *NH-linkage*, (T1, T2 and T3, T4, respectively), and these monomers were further polymerized with aromatic dithiol, 4,4'-thiobisbenzenethiol (TBT) through the solution polycondensation, affording P1 - P4 (Figure 1). This series of PPSs

O-linkage



NH-linkage



Scheme 1. Synthesis of triazine-base PPSs (P1-P4)

showed high- n values ($n_{633\text{nm}}$: 1.6902-1.7169), high transmittance in visible region ($T\%_{400\text{nm}} \sim 90\%$) and low birefringence (Δn : 0.0015-0.0042). It is worthy to note that, P3 and P4 with *NH-linkages*, exhibited 20°C higher of T_g than P1 and P2 with *O-linkages*, which is probably due to the contribution of H-bonding; such an H-bonding effect also led to the higher n values of P3 and P4 (1.7112 and 1.7169, respectively) than P1 and P2 (1.6902 and 1.7082, respectively). In summary, four new triazine monomers and their corresponding PPSs were successfully synthesized in good yields, exhibiting excellent optical and thermal properties. The results of this work not only show the high potential in the applications to optical materials but also suggest a new design concept for high- n value and low birefringence polymers.

Refs: ¹N. Nishimura et al, *J. Photopolym. Sci. Technol.* **25**, 355, 2012. ²M.-C. Fu et al, *J. Polym. Sci. Part A, Polym. Chem.* **56**, 724, 2018.

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