1Pd064

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

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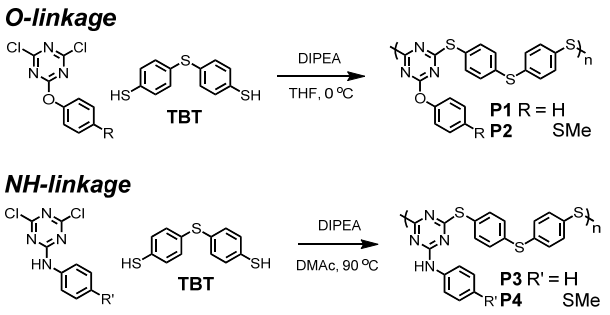
High-refractive-index (high-*n*) polymers (HRIPs) with a high optical transparency and low birefringence (low Δ*n*) are highly needed in the applications of advanced optoelectronic devices due to the significant improvement in the device's performance. However, the types of high-*n* polymers with the 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_{633nm}: 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%). Theses 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 solution polycondensation, affording **P1**-**P4** (Figure 1). This series of **PPS**s showed high-*n* values (n_{633nm}: 1.6902-1.7169), high transmittance in visible region ($T\%_{400nm}$ ~ 90%) and low birefringence (Δ*n*: 0.0042-0.0015). It is worthy to note that, **P3** and **P4** with *NH-linkages*, exhibited higher T_g than **P1** and **P2** with *O-linkages* probably due to the contribution of H-bonding; such a H-bonding effect also leaded to the higher *n* values of **P3** and **P4** (Table 1). In summary, four new triazine monomers and their corresponding **PPS**s 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.



Scheme 1. Synthesis of triazine-base **PPS**s (**P1**-**P4**)

Table 1. The results of synthesis and characterization of **P1**-**P4**

	M_n	$Đ$	Yield (%)	T_{d5} (°C)	T_g (°C)	$n_{av\ 633nm}$	Δ*n*	S (wt%)	$T\%_{400nm}$ (%)
P1	67,000	2.06	80	400	145	1.6902	0.0042	22.93	89
P2	32,000	1.63	75	375	140	1.7082	0.0031	27.54	91
P3	12,000	1.56	70	350	165	1.7112	0.0018	22.98	95
P4	67,000	1.76	85	355	175	1.7169	0.0015	27.60	94

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