Synthesis of highly refractive and transparent poly(arylene sulfide sulfone) based

on 4,6-dichloropyrimidine and 3,6-dichloropyridazine

Gang Zhang¹, Haohao-ren², Dong-sheng Li¹, Sheng-ru Long¹, Jie Yang^{1,3}.

1. Institute of Materials Science & Technology, Analytical & Testing Center, Sichuan University (四川大学), Chengdu 610064, P. R. China

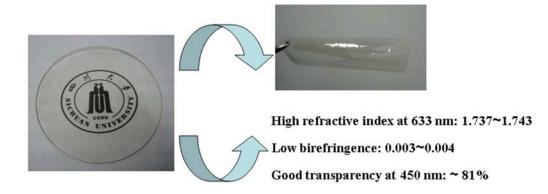
2. College of Physical Science and Technology of Sichuan University, Chengdu, 610065, P. R. China

3. State Key Laboratory of Polymer Materials Engineering (Sichuan University), Chengdu,
610065, P. R. China
E-mail: ppsf@scu.edu.cn
Fax: 86-28-8541-2866

Key words: Synthesis; Optical property; Heterocycle; Molecular design

High refractive index polymeric materials have been rapidly developed and attract significant interest in recent years. They were used in lenses, prisms, components for charge-coupled devices [1] and complementary metal oxide semiconductor image sensors [2] because of their lightweight, impact resistance, processability, and dying ability compared to inorganic glasses. A general approach for increasing the refractive index of polymers is the introduction of substituents with a low molar volume and high molar refraction. The sulfur element is commonly selected because of its high polarizability, stability, and facility to introduce to polymers. Such as aromatic polyamides (PAs) [3,4] and polyimides (PIs) [5,6] containing high content of sulfur elements. Although they exhibit high refractive index in the range of 1.7-1.77, their films have large birefringence and coloration (That is resulted into coloration of aromatic PAs and PIs for its formation charge transfer complexes (CTC) between the electron-donating diamine and the electron-accepting carbonyl group), which are the problems of aromatic PAs and PIs. Thus, in order to enhance the refractive index and optical transparency of polymers, a kind of poly(arylene sulfide sulfone) (PASS) containing pyrimidine (or pyridazine) unit has been developed with the molecular design method in this study. The polymer was prepared by a polycondensation reaction of 4,4'-dimercaptodiphenyl sulfone (DMDPS) and 4,6-dichloropyrimidine (DCPM) (or 3,6-dichloropyridazine (DCPD)). They showed good thermal stabilities such as a relatively high glass transition temperature of 193-202 °C and a 5% weight-loss temperature ($T_{5\%}$) of 370-372 °C. The optical transmittance of the polymer at 450 nm is higher than 81%. The heterocycles unit and plural -S- linkages provides the polymer with a high refractive index of 1.737-1.743 at 633 nm and a low birefringence of 0.003-0.004. Moreover, the synthesis of the DMDPS is more facile and affordable than the other monomers reported for sulfur-containing polymers. Thus, the PASSs can be good candidates as components for advanced optical device applications, such as optical wave guides for CMOS image sensor.

[·] Corresponding author: E-mail: ppsf@scu.edu.cn



References

[1] Geiger F, Stoldt M, Schweizer H, Bauerle P, Umbach E. Adv. Mater., 5, 922-925(1993).

[2] Kunugi Y, Miller L, Maki T, Canavesi A. Chem. Mater., 9, 1061-1062(1997).

[3] Zhang G, Hu JJ, Yang HW, WangXJ, Long SR, Yang J. Polym. Intern., 61, 800-809(2012).

[4] Zhang G, Li DS, Huang GS, WangXJ, Long SR, Yang J. React. Funct. Polym., 71, 775-781(2011).

[5] You NH, Nakamura Y, Suzuki Y, Higashihara T, Ando S, Ueda M. J. Polym. Sci. Part A Polym.

Chem., 47, 4886-4894(2009).

[6] Fukuzaki N, Higashihara T, Ando S, Ueda M. Macromolecules, 43, 1836-1843 (2010).