12.Synthesis of A Novel Multiblock Copolyimide Incorporated with Triamine-terminated Three-arm Star-branched Polyisobutylene

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Abstract: Recently, the demand for interlayer dielectric films for high-frequency applications, such as 5G/6G communication devices, has increased. However, conventional wholly aromatic polyimides (PIs), which are typical super-engineering plastics with excellent mechanical properties and high thermal/chemical resistance, do not satisfy the required dielectric constant (D_k < 3) for use as insulating materials in such devices. Therefore, the development of low-D_k PIs is necessary. In addition, a low dielectric loss tangent (D_f) is also required to minimize high-frequency signal loss.

In this study, a three-arm star-branched polyisobutylene (PIB) bearing a chloroallyl moiety at each chain end (tri-PIB-Cl) was synthesized *via* living cationic polymerization using 1,3,5-tris(1-chloro-1-methylethyl)benzene/$TiCl_4$ as the initiating system and isobutylene as the monomer, followed by functional group transformation to afford a novel triamine-terminated PIB (tri-PIB-NH_2). A novel multiblock copolyimide incorporating three-arm star-branched PIB segments (tri-PIB-PI) was successfully synthesized by copolymerization of a mixture of 2,2′-bis(trifluoromethyl)benzidine (TFMB) and tri-PIB-NH_2 with pyromellitic dianhydride (PMDA), followed by post-imidization.

The obtained copolymer exhibited excellent dielectric properties at 10 GHz, with a D_k value of 2.90 and a D_f value of 0.00474, while maintaining high thermal stability (5% weight loss temperature, $T_{d5\%}$ = 506 °C). These findings suggest that incorporating three-arm PIB segments into PIs is a promising molecular design strategy for reducing D_f while maintaining low D_k and high thermal stability.

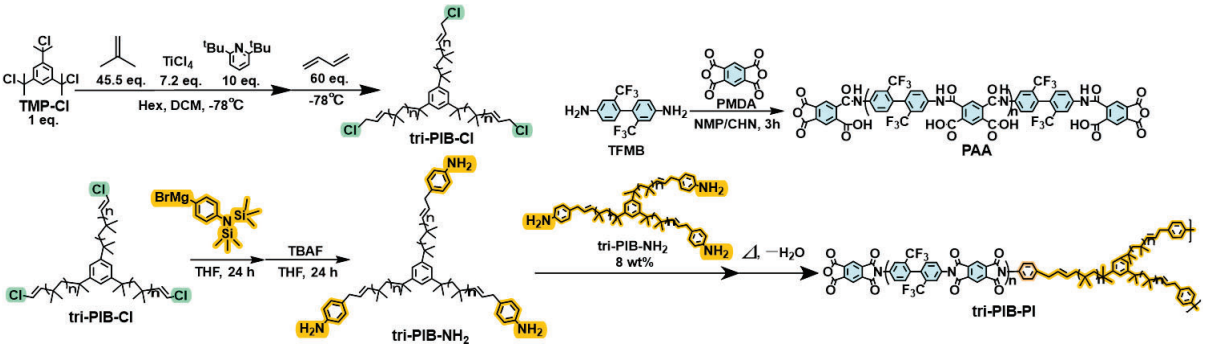

Figure 1. Synthetic routes of tri-PIB-Cl, tri-PIB-NH2, and tri-PIB-PI.

Key words: polyimide, polyisobutene, low-dielectric polyimide, multiblock copolymer

[1] Higashihara, T. et al. Japan Patent 2022-169849.
[2] Ojiha, U. et al. Macromolecules 2008, 41, 3832–3841.