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Alicyclic Polyimides Based on Bicyclo[2.2.1]Heptane-Tetracarboxylic Dianhydride

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Alicyclic polyimides have attracted much attention in recent years because of their potential applications including use as liquid crystal orientation layers, solar cell substrates, or high-temperature low dielectric materials. In the present study, the alicyclic polyimide synthesis based on a bicyclo[2.2.1]heptane dianhydride and the properties will be described.

Bicyclo[2.2.1]heptane-2*exo*,3*exo*,5*exo*,6*exo*-tetracarboxylic 2,3:5,6-dianhydride (**BHDAxx**) was prepared from nadic anhydride according to the previous paper¹⁾. Polycondensations of **BHDAxx** with aromatic and cycloaliphatic diamines were carried out in hexamethylphosphoric triamide at room temperature^{2,4)}. The structures and their abbreviations of monomers are illustrated in **Fig. 1**. The poly(amic acid) solutions possessed lower η_{inh} 's ranging 0.13-0.38, however, they afforded alicyclic polyimides as flexible and colorless films after being cast and cured.

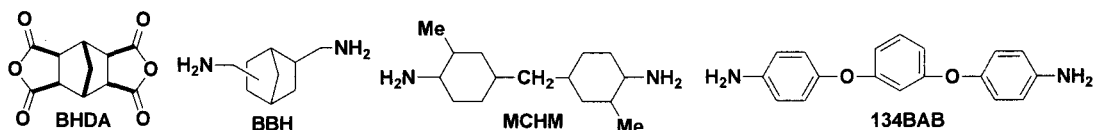


Fig. 1 Structures and abbreviations of monomers for alicyclic polyimides.

The results are listed in **Table 1**. The films were colorless with a cutoff at wavelength shorter than 280 nm for semiaromatic and 224 nm for fully aliphatic polyimides. The average refractive indices of the polyimide films were 1.521-1.598, and optical anisotropies were nearly zero. The dielectric constants that were estimated from the refractive indices according to the modified Maxwell's equation were 2.55-2.59. The polyimides have good thermal stability with the decomposition temperatures over 450°C and with Tg's over 200°C.

Table 1 Properties of BHDA-based alicyclic polyimide films.

Polyimides	η^a (dL/g)	T5 ^b (°C)	Td ^c (°C)	Tg ^d (°C)	$\lambda_{cut-off}$ (nm)	n_{av}^e	Δn^f	ϵ^g
PI(BHDA-MCHM)	0.23	395	448	219	224	1.5212	10^{-4}	2.55
PI(BHDA-134BAB)	0.38	454	494	197	280	1.5981	10^{-4}	2.78
PI(BHDA-BBH)	0.13	426	465	212	224	1.5349	10^{-4}	2.59

^a Poly(amic acid) in HMPA, 0.5g/dL, 30°C. ^b 5% Weight-loss and ^c decomposition temperatures in N₂.

^d by TMA. ^e Averaged refractive index at 589 nm. ^f Birefringence by ellipsometry. ^g $\epsilon=1.1n_{av}^2$.

1. Yamada, M.; Kusama, M.; Matsumoto, T.; Kurosaki, T. *J. Org. Chem.* **57**, 6075(1992).
2. Yamada, M.; Kusama, M.; Matsumoto, T.; Kurosaki, T. *Macromolecules* **26**, 4961(1993).
3. Matsumoto, T.; Kurosaki, T. *Macromolecules* **28**, 5684(1995).
4. Matsumoto, T. *Macromolecules* **32**, 4933(1999).