Wholly Aromatic Polyimides Featuring Linear or Hyperbranched Structures with Stable Optical Nonlinearity Based on Sequential Self-Repetitive Reaction

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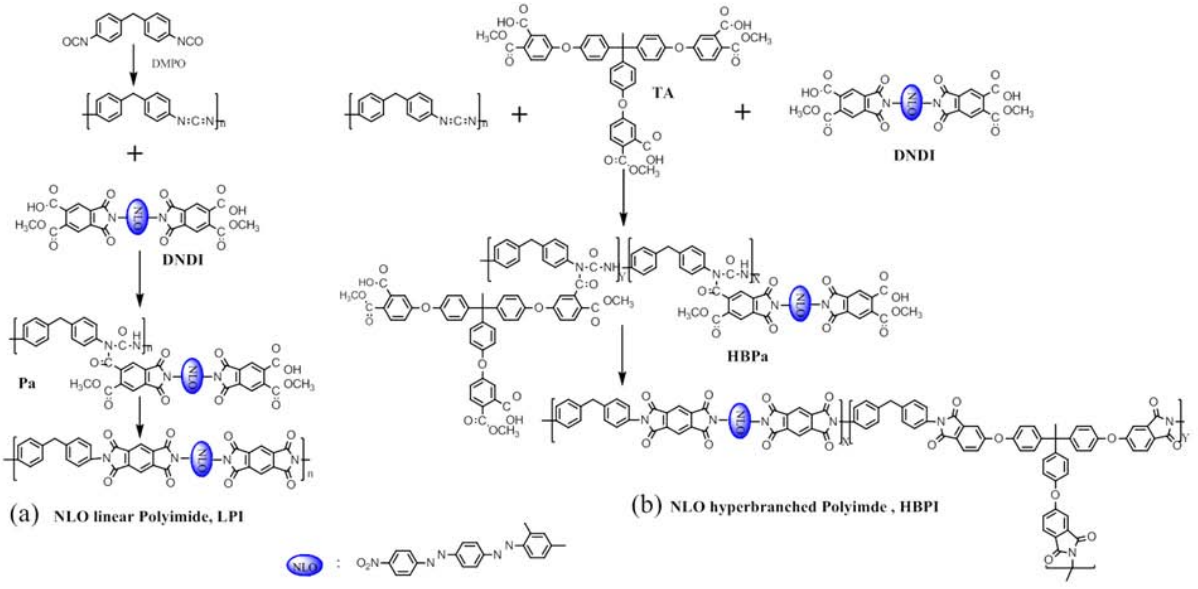
Organic nonlinear optical (NLO) polymeric materials are potentially useful, relative to conventional inorganic crystalline materials, for use in these optical devices because of their advantages such as large optical nonlinearity, solution processable, low cost, ultra-fast response time and superior chemical flexibility.

A sequential self-repetitive reaction (SSRR) [1-3] based on carbodiimide (CDI) chemistry was utilized for preparing a high-yield wholly aromatic nonlinear optical polyimide (Scheme 1 (a)). The polyimide was synthesized with 4,4'-methylenediphenylisocyanate (MDI) and a di(acid-ester) compound, 2,4-diamino-4'-(4-nitrophenyl-diazenyl)-azobenzene derivative containing diimde-di(ester-acid)(DNDI). Poly-CDI was first synthesized from MDI. The DNDI was then reacted with poly-CDI to form poly(N-acylurea) (Pa). After curing process, N-acylurea moiety was converted to di(ester-amide) structure via SSRR and further subjected to a ring-closure reaction to form the wholly aromatic NLO polyimide with a T_g of 208 °C (Table 1). After *in situ* poling and curing processes, the wholly aromatic NLO polyimide was formed with an electro-optical coefficient, r_{33} of 25 pm/V (830 nm). Excellent temporal stability at elevated temperatures (200 °C) and a waveguide optical loss of 2.5 dB cm^{-1} at 1310 nm were also obtained. Base on this approach, we introduce the concept of the three-dimensional spatial separation of the chromophores endowing the polymers with favorable site-isolation effects [4] and further to synthesize the hyperbranched polyimide (Scheme 1(b)) via SSRR. The resulting hyperbranched polymer exhibited excellent organosolubility with a T_g of 168 °C, which enabled the fabrication of high quality optical thin films, and an enhancement of electro-optical coefficient, r_{33} of 35 pm/V (830 nm).

The synthesis of a wholly aromatic polyimide via SSRR has been achieved in this work. Because of better stacking of the rigid imide linkages between the polymer chains via the SSRR process, the thermal stability was clearly enhanced. Hyperbranched NLO-active polymers have been demonstrated to exhibit larger EO coefficients than those of the linear counterparts due to their site isolation effects.



Scheme 1. Synthetic routes for (a) **LPI**, (b) **HBPI**.

Table 1. Characteristics of the polyimides.

code	refractive index	r_{33} (pm/V)	Optical loss (dB/cm)	$T_{d,5\%}$ (^{O}C)	T_g (^{O}C)
LPI	1.78	25	2.5	377	208
HBPI	1.70	35	2.8	262	168

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