



# High refractive index hyperbranched polymers with different naphthalene contents prepared through thiol-yne click reaction using di-substituted asymmetric bulky alkynes



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## ABSTRACT

In the present study, different aromatic moieties, naphthalene and benzene, were introduced into alkynes to constitute 1,3,5-tris(naphthylethynyl)benzene as B<sub>3</sub> monomer. This monomer could be reacted with different ratios of hexane-1,6-dithiol (A<sub>2</sub> monomer) via mono-selective Thiol-Yne reaction (TYR) to form hyperbranched polymers **PI**. TYR yielded in both, model reactions and polymerizations, mono-adducts with high regioselectivity and proved the absence of any bis-adducts. Polymers of very high molecular weights of up to 625,000 g/mol could be achieved without any sign of gel formation. All the polymers exhibit high transparency in the visible wavelength range and also show high refractive indices of up to 1.745 at 589.7 nm due to the high incorporation of naphthalene and phenyl groups. Besides, all polymers prove excellent solubility and processability together with excellent thermal properties.

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## 1. Introduction

The thiol-yne reaction (TYR), often referred to as a type of “click reactions” [1–3], is the reaction between alkyne groups and thiol groups and can in principle lead to alkenyl sulfides (mono-adducts) or 1,2-dithioethers (bis-adducts). The interest into the TYR was mainly driven after the successful application of thiol-ene chemistry [4–7]. The TYR can be catalyzed by photo [8–10], thermo [11–13], amine [14], and transitional metal catalysts [15,16]. In the last few years, the TYR has been employed in many areas [3,17,18], such as the construction of organic compounds [19], monomers [20] and polymers [21], but also in the modification of polymers [22,23], biomaterials [24,25], and surfaces [26], since the TYR is characterized by advantages such as mild reaction conditions, high atomic economy, functional group tolerance and excellent conversion [3,17].

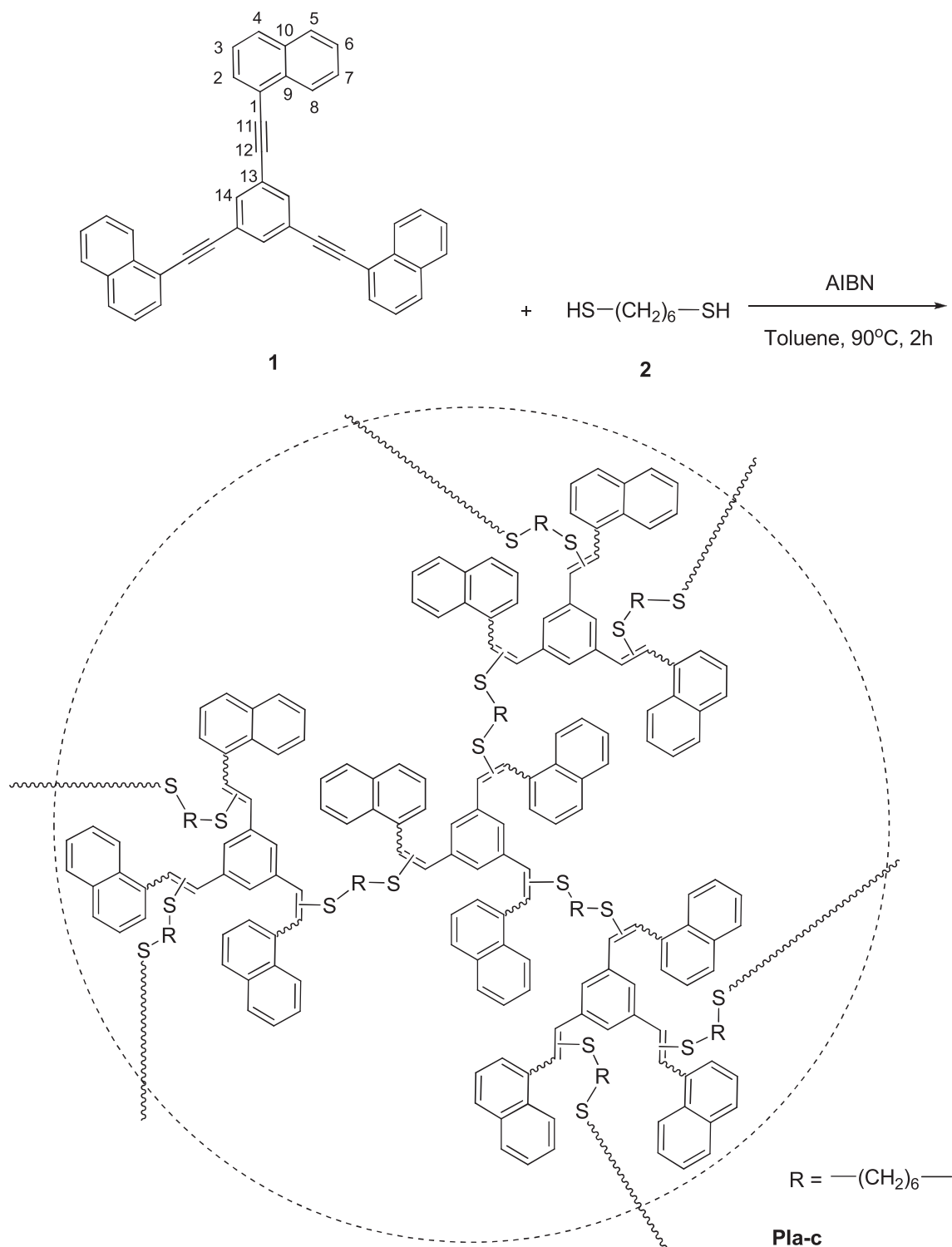
On the other hand, nowadays, increasing attention has been paid to high refractive index (HRI) polymers [27], with broad applications in diverse modern technologies, such as polymer

waveguides [28], organic lasers [29] and OLED wrapping plastic [30,31]. The TYR allowed us previously to synthesize a variety of different linear and branched poly(vinylsulfide) (PVS) materials with HRI [27]. As for the aimed optical applications, the radical-mediated TYR has many advantages over other metal-ion or amine catalyzed methodologies towards PVS [14,32], since it is conveniently done under mild reaction conditions, is metal-free, uses easily available starting materials, and needs no specific purification procedures. Although mono-adduct formation is often accompanied by the formation of bis-adducts in radical-mediated thiol-yne reactions [33–36], which can pose a challenge to the precise control over the polymeric structures, it was found that phenylacetylene-based molecules adopted to react with thiols resulted selectively in vinyl sulfide units through monoaddition [37].

In our previous work [11,38] we have designed 1,3,5-tris(phenylethynyl)benzene to construct hyperbranched polymers by easy radical-mediated TYR, which showed both, high regioselectivity [37] and high refractive index (1.70 at 589 nm). In this paper, in order to obtain polymers with even higher RI values, we synthesized a new B<sub>3</sub> monomer incorporating naphthalene groups instead of phenyl groups (Scheme 1), since according to the Lorentz–Lorenz equation [39], the naphthalene units exhibit higher molar refraction than phenylene [40].

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**Scheme 1.** Polymerization of  $B_3$  (alkyne **1**) and  $A_2$  (thiol **2**) to **Pla-c**.

## 2. Experimental

### 2.1. Materials and instrumentations

Anhydrous tetrahydrofuran (THF), triethylamine (TEA), and toluene sealed over molecular sieves were purchased from Sigma–Aldrich. Triphenylphosphine, copper(I) iodide, bis(triphenylphosphine)palladium(II) dichloride, hexane-1,6-

dithiol, hexanethiol and 1-iodonaphthalene were also supplied by Sigma–Aldrich while 1,3,5-triethynylbenzene was purchased from TCI.

$^1\text{H}$  (500.13 MHz) and  $^{13}\text{C}$  (125.75 MHz) NMR spectra were recorded on an Avance III 500 NMR spectrometer (Bruker Biospin, Germany) using  $\text{CD}_2\text{Cl}_2$  as a solvent, lock, and internal standard ( $\delta(^1\text{H}) = 5.31$  ppm;  $\delta(^{13}\text{C}) = 53.7$  ppm). The signal assignments were determined from the combination of 1D and 2D NMR

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