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RESEARCH ARTICLE

Synthesis and characterization of poly(1,2,3-triazole)s with inherent high sulfur content for optical applications

Kajari Mazumder[1,2] | Hartmut Komber[2] | Eva Bittrich[2] | Brigitte Voit[2,3] |
Susanta Banerjee[1]

[1]Materials Science Centre, Indian Institute of Technology Kharagpur, Kharagpur, India

[2]Leibniz-Institut für Polymerforschung Dresden e.V., Institute of Macromolecular Chemistry, Dresden, Germany

[3]Chair Organic Chemistry of Polymers, Technische Universität Dresden, Dresden, Germany

Correspondence
Brigitte Voit, Leibniz-Institut für Polymerforschung Dresden e.V., Hohe Strasse 6, Dresden 01069, Germany.
Email: voit@ipfdd.de

Susanta Banerjee, Materials Science Centre, Indian Institute of Technology Kharagpur, Kharagpur 721302, India.
Email: susanta@matsc.iitkgp.ac.in

Abstract

The synthesis of solution-processable sulfur-containing polytriazoles for optoelectronic applications is a relatively less explored domain in polymer research. The synthesis of novel bifunctional (DA) and trifunctional (TA) azido-monomers with inherent high sulfur content and of organo-soluble high refractive index poly(1,2,3-triazole)s using the azido-monomers via Cu(I) assisted click polymerization reactions are reported in this work. The azido-monomers were synthesized by the conversion of previously reported amine-functionalized compounds to azides using azidotrimethylsilane in a polar aprotic solvent. Dialkyne monomers were also synthesized and reacted with the azides to prepare a series of five linear and two hyperbranched poly(1,2,3-triazole)s. Fourier transform infrared spectroscopy, nuclear magnetic resonance spectroscopy, differential scanning calorimetry and thermogravimetric analysis were used to characterize the synthesized polymers. It was also demonstrated that the use of the trifunctional azide in optimized conditions resulted in increased solubility of an otherwise insoluble linear poly(1,2,3-triazole). The optical characterization of the polymers was carried out on thin polymer films with thickness in the nanometer range, which were successfully prepared by spin-coating on silicon wafers. It was found that the increase in the sulfur and aromatic content in the polymer backbone successfully increased the refractive index of the polymers up to 1.743 at 589 nm.

KEYWORDS
birefringence, click polymerization, high refractive index, optical properties of poly (1,2,3-triazole)s, sulfur containing poly(1,2,3-triazole)s

1 | INTRODUCTION

The past few decades have seen remarkable advances in the field of optoelectronics, and the need to develop highly functional materials is of utmost relevance.[1,2] Polymeric materials having an inherent high refractive index (RI) are of great significance due to the enormous diversity of applications they provide in optical devices, which include display devices, lenses, waveguides, prisms, and so forth. Polymeric materials are superior to inorganic glasses in terms of their light weight, ease of solution processing, impact resistance, and dying ability.[3,4] Another reason to prefer polymer-based materials as outcoupling layers for electronic devices instead of small molecules is the ease of their deposition technique. On the one hand, polymers can be efficiently deposited on a substrate using low-temperature techniques like drop casting, spin coating or dip coating. Whereas, the deposition of small molecules, for example, Alq$_3$, involves rather complex procedures such as neutral cluster beam deposition, thermal evaporation or ionized cluster beam deposition.

The incorporation of sulfur in a polymer chain has been well studied due to the wide range of applications the class of sulfur-containing polymers provides, for example, as cathode materials in lithium-ion batteries,[5] memory devices,[6] conducting polymers[7] and as optical materials.[8] The introduction of sulfur to the polymer backbone or as a pendant moiety resulted in an increased refractive index (RI) by many folds. Several groups have been motivated to prepare novel polymers containing sulfur to optimize the refractive index of the final polymer.[9–12] One of the approaches of preparing polymers with high sulfur content includes the use of elemental sulfur. Polysulfides, with a similar structure to polymeric sulfur, can be directly derived from S$_8$ in mainly three polymerization techniques, like, condensation,[13] free-radical,[14,15] and ionic polymerization.[16,17] Other strategies involve the use of sulfur containing monomers to prepare polymers with high sulfur content using condensation polymerizations. This has led to the preparation of sulfur containing poly(arylene ether)s,[18,19] polyimides,[20–22] polyvinylsulfides,[23–25] and polyamides.[26] Methodologies that result in a hybrid system by the combination of an organic polymer matrix and inorganic nanoparticles have also been explored to achieve materials with enhanced properties in terms of mechanical, thermal as well as optoelectronic.[27–29]

Polytriazoles fall in the category of high-performance polymers by virtue of their excellent thermal and thermal oxidative stability and chemical resistance. Several poly(1,2,3-triazole)s have been reported in the past for proton-exchange membrane applications by our group.[30–36] Furthermore, polytriazoles also find potential use in optical applications.[37] A considerable number of scientific groups have also been dedicated to preparing poly(1,2,3-triazole)s resins with advanced functions in materials science.[38] Functional linear and branched poly(1,2,3-triazole)s can be efficiently prepared using the Cu(I) catalyzed azide-alkyne cycloaddition reactions (CuAAC).[39] The uniqueness and wide applicability of CuAAC reaction lies in its atom efficiency and selectivity in the synthesis of 1,4-disubstituted poly(1,2,3-triazole)s.[40] This is a powerful tool in the field of organic synthesis and has been explored by several groups for multiple application, for example, in the field of biology[41–44] as well as materials science.[45–49] Furthermore, step growth polymerizations following CuAAC mechanism is well known to synthesize polymers with high T$_g$ owing to the presence of the rigid 1,2,3-triazole unit.[50–53] Additionally, fluorine-containing polymers are known for their ease of solubility without compromising their thermal stability. The presence of bulky –CF$_3$ moiety helps to increase the solubility of the polymer, decreasing the intramolecular chain interactions.[54]

This study focuses on the preparation of a sulfur-containing diazide monomer, 2,5-bis(4-((4-azidophenyl)thio)-3-(trifluoromethyl)phenyl)thiophene (DA) and its click reactions with the dialkyne monomers, 4,4′-(propane-2,2-diyl)bis((prop-2-yn-1-yloxy)benzene) (BPADAL), 4,4′-sulfonylbis((prop-2-yn-1-yloxy)benzene) (BPSDAL), 1,3-diethynylbenzene (DEB), 1,4-bis(prop-2-yn-1-yloxy)benzene (HQDAL) and 4,4′-bis(prop-2-yn-1-yloxy)-1,1′-biphenyl (HPDAL), to synthesize a series of high refractive index linear poly(1,2,3-triazole)s (PTz 1–5) (Table 1). This study also reports the preparation of a sulfur-containing triazide monomer, 1,3,5-tris(4-((2-(trifluoromethyl)phenyl)thio)azido)benzene (TA) and its utilization for the synthesis of soluble hyperbranched poly(1,2,3-triazole)s (hb-DEB), containing DEB as the dialkyne monomer under mild reaction conditions.

TABLE 1 Structures of dialkynes used to prepare the poly(1,2,3-triazole)s.

Entry	Structure
BPADAL	
BPSDAL	
DEB	
HQDAL	
HPDAL	

2 | EXPERIMENTAL

2.1 | Instruments

The nuclear magnetic resonance (NMR) measurements were carried out on an Avance III 500 spectrometer (Bruker) at 500.13 MHz (^{1}H), 125.76 MHz (^{13}C), and 470.59 MHz (^{19}F). The spectra were referenced to the solvent signal (DMSO-d$_6$: δ (^{1}H) = 2.50 ppm; δ (^{13}C) = 39.6 ppm; CDCl$_3$: δ (^{1}H) = 7.26 ppm; DMF-d$_7$ [C(O)H signal]: δ (^{1}H) = 8.05 ppm; δ (^{13}C) = 162.5 ppm). The ^{19}F NMR spectra were referenced on external C$_6$F$_6$. The signal assignments were confirmed by ^{1}H-^{1}H and ^{1}H-^{13}C correlated spectra. Vertex 80v (Bruker) instrument was used to measure Fourier-transform infrared (FTIR) spectra for the polymers with a Golden Gate Diamant ATR (attenuated total reflection) unit. Inherent viscosity (η_{inh}) measurements for the polymers were made with an Ubbelohde viscometer at 0.5 dL/g concentration in NMP at 22°C. Thermogravimetric analysis (TGA) of the polymers was carried out using Thermobalance Q5000 (TA Instruments). A heating rate of 10 K/min was followed, and all the experiments were performed under N$_2$ atmosphere at 60 mL/min with a mass flow of 50 mL/min. Differential scanning analysis (DSC) for the polymers was carried out using the dynamic differential calorimeter Discovery DSC 2500 (TA Instruments). The heating rate was 10 K/min, and the experiments were performed under a nitrogen environment.

Size exclusion chromatography (SEC) measurements were performed using HPLC-Pump 1200 of Agilent Technologies with dimethylacetamide (DMAc) as the eluent for the polymers at a flow rate of 1.0 mL/min at 150°C. Light scattering (LS) – Detector MiniDAWN TREOS II (Wyatt Technology) and refractive index (RI) – Detector K-2301 (KNAUER) were used. The refractive index increment (dn/dc) was determined from RI curves averaging three measurements for each sample. Weight average molar mass ($\overline{M}_w$) and number average molar mass ($\overline{M}_n$) were calculated from the average value of three injections per sample and are reported in kilodaltons (kDa). Dispersity (Đ) values were calculated as $\overline{M}_w/\overline{M}_n$. The polystyrene samples used for calibration were PS-Standard PS2-A (377,400, 96,000, 20,650, 5460, 1300 g/mol) and PS-Standard PS1-B (2.581e6, 281,700, 74,800, 10,110, 580 g/mol). Elemental carbon, hydrogen and sulfur of the compounds were analyzed by the pyrolysis method using the Vario MICRO cube (Elementar). The UV–visible absorption spectra for polymer solutions were measured with a PerkinElmar Lambda 365 absorption spectrophotometer. For the preparation of polymers films on interference-enhanced Si substrates (IES) (1000 nm SiO$_2$ on Si, IHM TU Dresden),[55] a Polos wafer spinner was used with the parameters: 3000 rotations for 1 min at an acceleration of 1000 rotations/min^2, for each sample, until homogenous films were developed. Ellipsometry data of spin-coated polymer films were recorded using a rotating compensator multi-wavelength ellipsometer M2000-UI (J.A. Woollam Co. Inc.) with a spectral range of 245–1690 nm at incidence angles of 65°, 70°, and 75°. For optical modeling, a box model of silicon, SiO$_2$, and polymer film with sharp interfaces was applied, using optical dispersions from the database for silicon and SiO$_2$ (CompleteEase, J. A. Woollam Co. Inc.). The optical dispersion of the polymer films was modeled by 1 Tauc-Lorentz and 1–2 Gaussian oscillators with an isotropic model.

2.2 | Materials

Tert-butyl nitrite (*t*-BuONO), azidotrimethylsilane (TMSN$_3$), acetonitrile (CH$_3$CN), propargyl bromide, tetrabutylammonium bromide (TBAB), NaOH pallets and copper(I) iodide were bought from Aldrich, Germany, and used as obtained. Dimethyl sulfoxide was stirred with NaOH and then distilled from P$_2$O$_5$ at low pressure before use. The dihydroxy compounds 4,4′-(propane-2,2-diyl)diphenol (BPA) and hydroquinone (HQ) were recrystallized with ethanol and water, respectively. 4,4′-sulfonyldiphenol (BPS), 4,4′-dihydroxybiphenyl (HP) and 1,3-diethynylbenzene (DEB) were used as received. The diamine and triamine compounds, 4,4′-((thiophene-2,5-diylbis(2-(trifluoromethyl)-4,1-phenylene))bis(sulfanediyl))dianiline and 1,3,5-tris (4-((2-(trifluoromethyl)phenyl)thio)-aniline)benzene were prepared previously by our group, using the procedures given in the literature.[56]
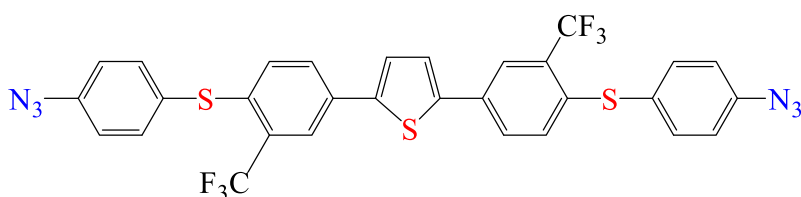
2.3 | Synthesis of monomers

2.3.1 | 2,5-bis(4-((4-azidophenyl)thio)-3-(trifluoromethyl)phenyl)thiophene, DA (Scheme 1)

1.85 g (0.003 moles) 4,4′-((thiophene-2,5-diylbis(2-(trifluoromethyl)-4,1-phenylene))bis(sulfanediyl))dianiline and 10 mL CH$_3$CN were taken in a 50 mL three-necked round bottom flask fitted with a reflux condenser and constant nitrogen flow. The temperature of the reaction mixture was brought to 0°C using an ice bath. 0.93 g (0.009 moles) *t*-BuONO was added to the reaction mixture, followed by the dropwise addition of 0.85 g (0.007 moles) TMSN$_3$. The reaction mixture was continued to stir for 2 h, after which the diazide product was obtained by removing CH$_3$CN using a vacuum evaporator and subsequent hexane wash. This crude product was purified by recrystallization in

SCHEME 1 Synthesis scheme of 2,5-bis(4-((4-azidophenyl)thio)-3-(trifluoromethyl)phenyl)thiophene, DA.
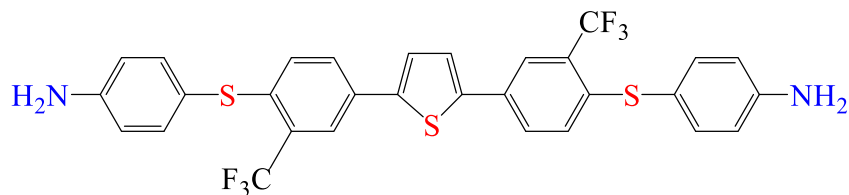
4,4'-((thiophene-2,5-diylbis(2-(trifluoromethyl)-4,1-phenylene))bis(sulfanediyl))dianiline

i) t-BuONO
ii) TMSN$_3$
iii) CH$_3$CN
0 °C ⟶ RT

2,5-bis(4-((4-azidophenyl)thio)-3-(trifluoromethyl)phenyl)thiophene, **DA**

SCHEME 2 Synthesis scheme of 1,3,5-tris(4-((2-(trifluoromethyl)phenyl)thio)azido)benzene, TA.
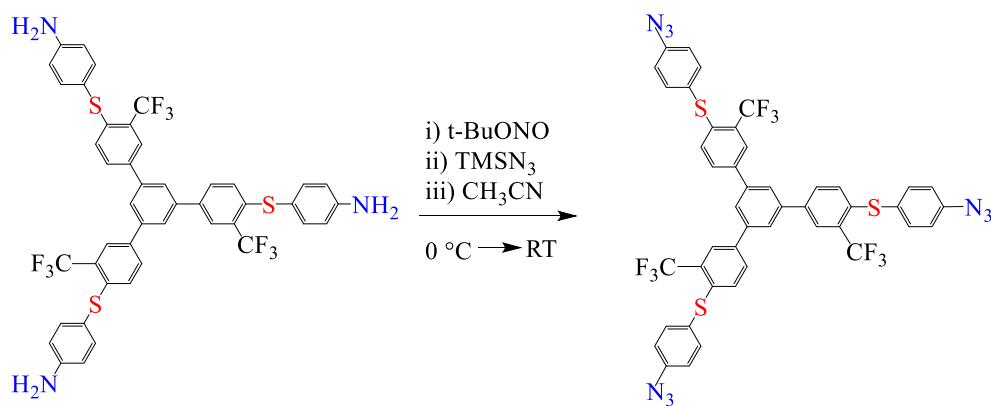
1,3,5-tris(4-((2-(trifluoromethyl)-phenyl)thio)aniline)benzene

1,3,5-tris(4-((2-(trifluoromethyl)-phenyl)thio)azido)benzene, **TA**

acetone. Yield: 1.85 g (~93%). Further analytical data are reported in the ESI.

2.3.2 | 1,3,5-Tris(4-((2-(trifluoromethyl)phenyl)thio)azido)benzene, TA (Scheme 2)

The reaction set-up for the preparation of the triazide compound was similar to that of the diazide compound.

1.84 g (0.002 moles) triamine compound was added to 10 mL CH$_3$CN in a 50 mL three-necked round bottom flask fitted with a reflux condenser under constant nitrogen flow. Initially, the temperature of the reaction mixture was maintained at 0°C using an ice-bath. To this, 1.07 g (0.010 moles) t-BuONO and 1.01 g (0.008 moles) TMSN$_3$ were dropwise added and the reaction mixture was continued to stir for 2 h. The trifunctional azide compound was obtained by removing CH$_3$CN using a

vacuum evaporator and subsequent hexane wash. This crude product was purified by recrystallization in acetone. Yield: 1.90 g (∼95%). Further analytical data are reported in the ESI.

2.3.3 | Dialkyne monomers (BPADAL, BPSDAL, DEB, HQDAL and HPDAL)

The dialkyne monomers, BPADAL, BPSDAL, HQDAL and HPDAL were synthesized using the procedure given in literature[33] while DEB was commercially available. The detailed synthesis procedure and the ^1H NMR data of the prepared dialkynes are provided in the Supplement Information. Table 1 contains the structures of the dialkynes used in this study.

2.3.4 | Synthesis of linear polytriazoles (PTz 1–5) and hyperbranched polytriazoles (hb-$DEB_{(n:m)}$)

All the poly(1,2,3-triazole)s were synthesized using Cu(I) iodide-catalyzed click-chemistry polymerization. The procedure for synthesizing the linear polymers involved taking the diazide monomer, DA and the dialkyne monomers in stoichiometric ratio, along with 5 mol% of CuI in the presence of DMSO as solvent under a continuous nitrogen flow. The reaction was maintained for 12 h at 80°C until the viscosity of the reaction mixture was increased significantly. The weight percent of the solid content was adjusted to 10% (w/v). Finally, the work-up of the polymer involved precipitating the polymer into isopropanol when the fibrous polymer was obtained. It was then filtered and washed continuously with an excess of deionized water and 20% NH$_4$OH. For the preparation of PTz 3, commercially available 1,3-diethynylbenzene was used as the dialkyne. The preparation of the hyperbranched polymers involved

the addition of a mixture of the azido monomers into the reaction mixture dropwise. For example, the preparation of hb-$DEB_{(0.70:0.20)}$ involved initially taking the required amount of 1,3-diethynylbenzene in a round bottom flask along with DMSO under an inert atmosphere. The reaction temperature was raised to 60°C, and then a mixture of DA and TA was added dropwise to the reaction mixture over 1 h. The reaction mixture was continued to stir until there was a visible increase in the viscosity of the reaction mixture. The polymer was obtained after precipitation in isopropanol and washing the fibrous portions with a copious amount of deionized water and NH$_4$OH.

PTz 1. 0.687 g (0.001 moles) DA, 0.312 g (0.001 moles) BPADAL, 0.009 g (5 mol%) CuI, 10 mL DMSO.

PTz 1
IR (KBr): ν (cm^{-1}) = 1777, 1717, 1596, 1472, 1362, 1327, 1235, 1125, 743 cm^{-1}.
  ^1H NMR (DMF-d$_7$): δ (ppm) 9.04 (14), 8.19 (4), 8.09 (12), 8.01 (8), 7.88 (1), 7.70 (11), 7.56 (7), 7.21 (19), 7.04 (18), 5.30 (16), 1.65 (22). ^{13}C NMR (DMF-d$_7$): δ (ppm) 156.8 (17), 145.3 (15), 143.9 (20), 142.2 (2), 137.1 (13), 135.3 (7), 134.9 (10), 133.9 (6), 133.8 (3), 133.6 (11), 130.5 (q, $^2J_{CF}$ = 30 Hz; 5), 130.2 (8), 128.1 (19), 127.6 (1), 124.2 (q, $^1J_{CF}$ = 274 Hz; 9), 124.0 (4), 123.0 (14), 121.8 (12), 114.6 (18), 61.7 (16), 41.9 (21), 30.9 (22). ^{19}F NMR (DMF-d$_7$): δ (ppm) -61.7.

PTz 2. 0.672 g (0.001 moles) DA, 0.327 g (0.001 moles) BPSDAL, 0.009 g (5 mol%) CuI, 10 mL DMSO.

PTz 2
IR (KBr): ν (cm^{-1}) = 1777, 1717, 1596, 1472, 1362, 1327, 1235, 1125, 743 cm^{-1}.

^{1}H NMR (DMF-d$_7$): δ (ppm) 9.07 (14), 8.19 (4), 8.06 (12), 7.97 (8, 19), 7.88 (1), 7.69 (11), 7.57 (7), 7.34 (18), 5.46 (16). ^{13}C NMR (DMF-d$_7$): δ (ppm) 162.5 (17), 144.4 (15), 142.2 (2), 137.0 (13), 135.4 (7), 135.0 (10, 20), 133.8 (3, 6), 133.5 (11), 130.6 (q, $^2J_{CF}$ = 30.5 Hz; 5), 130.2 (8), 130.0 (19), 127.6 (1), 124.2 (q, $^1J_{CF}$ = 274 Hz; 9), 124.0 (4), 123.4 (14), 121.8 (12), 116.1 (18), 62.2 (16). ^{19}F NMR (DMF-d$_7$): δ (ppm) -61.7.

PTz 3. 0.841 g (0.001 moles) DA, 0.158 g (0.001 moles) DEB, 0.011 g (5 mol%) CuI, 10 mL DMSO.

PTz 4

IR (KBr): ν (cm^{-1}) = 1777, 1717, 1596, 1472, 1362, 1327, 1235, 1125, 743 cm^{-1}.

^{1}H NMR (DMF-d$_7$): δ (ppm) 9.04 (14), 8.21 (4), 8.11 (12), 8.02 (8), 7.91 (1), 7.72 (11), 7.58 (7), 7.11 (18), 5.30 (16). ^{13}C NMR (DMF-d$_7$): δ (ppm) 153.4 (17), 145.4 (15), 142.3 (2), 137.2 (13), 135.4 (7), 134.9 (10), 133.9 (6), 133.8 (3), 133.6 (11), 130.5 (q, $^2J_{CF}$ = 30 Hz; 5), 130.2 (8), 127.6 (1), 124.3 (q, $^1J_{CF}$ = 275 Hz; 9), 124.0 (4), 123.0 (14), 121.8 (12), 116.4 (18), 62.4 (16). ^{19}F NMR (DMF-d$_7$): δ (ppm) -61.9.
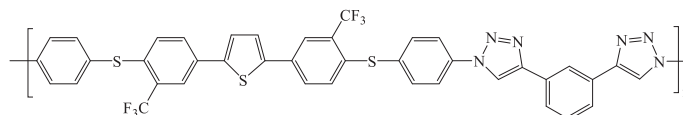
PTz 3

IR (KBr): ν (cm^{-1}) = 1777, 1717, 1596, 1472, 1362, 1327, 1235, 1125, 743 cm^{-1}.

No NMR characterization because the sample is not soluble in common NMR solvents.

PTz 4. 0.782 g (0.001 moles) DA, 0.217 g (0.001 moles) HQDAL, 0.011 g (5 mol%) CuI, 10 mL DMSO.

PTz 5. 0.718 g (0.001 moles) DA, 0.281 g (0.001 moles) HPDAL, 0.010 g (5 mol%) CuI, 10 mL DMSO.

PTz 5

IR (KBr): ν (cm^{-1}) = 1777, 1717, 1596, 1472, 1362, 1327, 1235, 1125, 743 cm^{-1}. No NMR characterization is given because only very low molecular weight fraction is soluble under the NMR conditions.
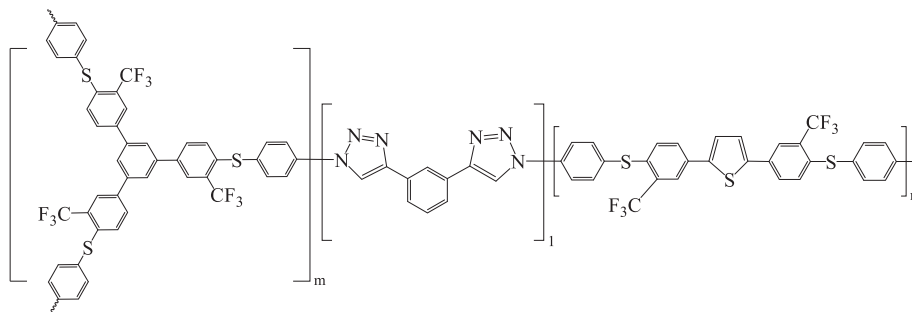
hb-DEB(n:m)

hb-DEB$_{(0.70:0.20)}$ (n = 0.70, m = 0.20). 0.160 g (0.0012 moles) DEB, 0.596 g (0.0008 moles) DA and 0.243 g (0.0002 moles) TA, 10 mL DMSO.

IR (KBr): ν (cm^{-1}) = 1777, 1717, 1596, 1472, 1362, 1327, 1235, 1125, 743 cm^{-1}.

No NMR characterization is given because only very low molecular weight fraction is soluble under the NMR conditions.

hb-DEB$_{(0.60:0.27)}$ (n = 0.60, m = 0.27). 0.160 g (0.0012 moles) DEB, 0.513 g (0.0008 moles) DA and 0.326 g (0.0002 moles) TA, 10 mL DMSO.

IR (KBr): ν (cm^{-1}) = 1777, 1717, 1596, 1472, 1362, 1327, 1235, 1125, 743 cm^{-1}.

No NMR characterization is given because only very low molecular weight fraction is soluble under the NMR conditions.

2.3.5 | Polymer film preparation

To prepare thin films with thickness in the range of ~40 nm, the polymer samples were dissolved in hot DMAc (20 mg in 1 mL). Then the solutions were filtered through PTFE membranes and spin-coated on IES wafers using a Polos wafer spinner at 3000 rpm with an acceleration of 1000 rotations/min^2 for 1 min and then annealed at 150°C for half an hour.

3 | RESULTS AND DISCUSSIONS

3.1 | Synthesis of the diazide, triazide and dialkyne monomers

We designed novel azido monomers with inherent high sulfur content to have a high refractive index of the final polymer material. The preparation of the azide containing bifunctional and trifunctional monomers, DA and

TA, respectively, was performed using an efficient procedure involving mild reaction conditions with *t*-BuONO and azidotrimethylsilane which used aromatic amines as starting materials via the formation of the corresponding diazonium intermediate.[57] This method resulted in high yields of the desired azido product. At the same time, it was possible to convert aromatic amine to aromatic azide via the preparation of non-explosive intermediates in a non-hazardous environment. Schemes 1 and 2 show the route for synthesizing the azido monomers. NMR spectroscopy demonstrated successful preparation of the azido monomers (Figure S1). The preparation of the dialkyne monomers followed a facile conversion of commercially available dihydroxy compounds using propargyl bromide in the presence of a phase transfer catalyst. The reaction progressed in mild conditions and resulted in high yields of the desired dialkyne monomers. The structure of the dialkyne monomers was confirmed via ^{1}H NMR spectroscopy.

3.2 | Synthesis of the linear and hyperbranched polymers

Two different series of poly(1,2,3-triazole)s were prepared in this work. The polymerization reactions followed a Cu(I) initiated click chemistry pathway in the presence of DMSO as solvent. The employment of the click polymerization resulted in a high yield of polymers with high molar masses. The stoichiometric ratio of diazide and dialkyne monomers resulted in linear polymers, PTz 1–5. The use of 1,3-diethynylbenzene to prepare PTz 3 resulted in the formation of a completely insoluble polymer, in which the presence of the triazole unit was confirmed only via FTIR spectroscopy. Since this particular polymer was insoluble in common solvents, probably due to a very rigid moiety containing triazole-*m*-phenylene-triazole unit which restricted chain movement, its characterization via NMR spectroscopy could not be

performed. Scheme 3 shows the reaction scheme for the preparation of PTz 1–5. Furthermore, we wanted to investigate the effect of introducing a branching unit in the polymer backbone on the solubility of the polymer material, so we prepared another series of polytriazoles having branching in their structure.

Thus, the polymers of the hb-DEB$_{(n:m)}$ series were prepared using click polymerization using a trifunctional azido monomer, TA, in addition to DA and DEB according to Scheme 4. The molar masses of the poly(1,-2,3-triazole)s prepared are reported in Table 2. Two different ratios of the bifunctional and trifunctional monomers were studied, which resulted in the enhancement of the solubility of the polymers containing triazole-m-phenylene-triazole moiety, hb-DEB$_{(0.70:0.20)}$

and hb-DEB$_{(0.60:0.27)}$. In both the hyperbranched poly(1,-2,3-triazole)s, the monomer feed ratio was so maintained that the ratio of the functional groups, that is, [N$_3$]:[C ≡ C] was 1:1. The solutions of the azido monomers were slowly added to the reaction mixture in order to avoid gel-formation and to produce a high yield of soluble polymers. For the branched polymers, a much faster reaction time was observed reaching very high molar mass samples. Due to the presence of the branched units in the reaction mixture, a higher yield was obtained faster than in the case of the linear polymers, however, there is a need to monitor the reaction conditions to circumvent gelation. On introduction of TA, we observed that the branching unit helped in increasing the solubility of the branched polymers (hb-DEB) in high boiling
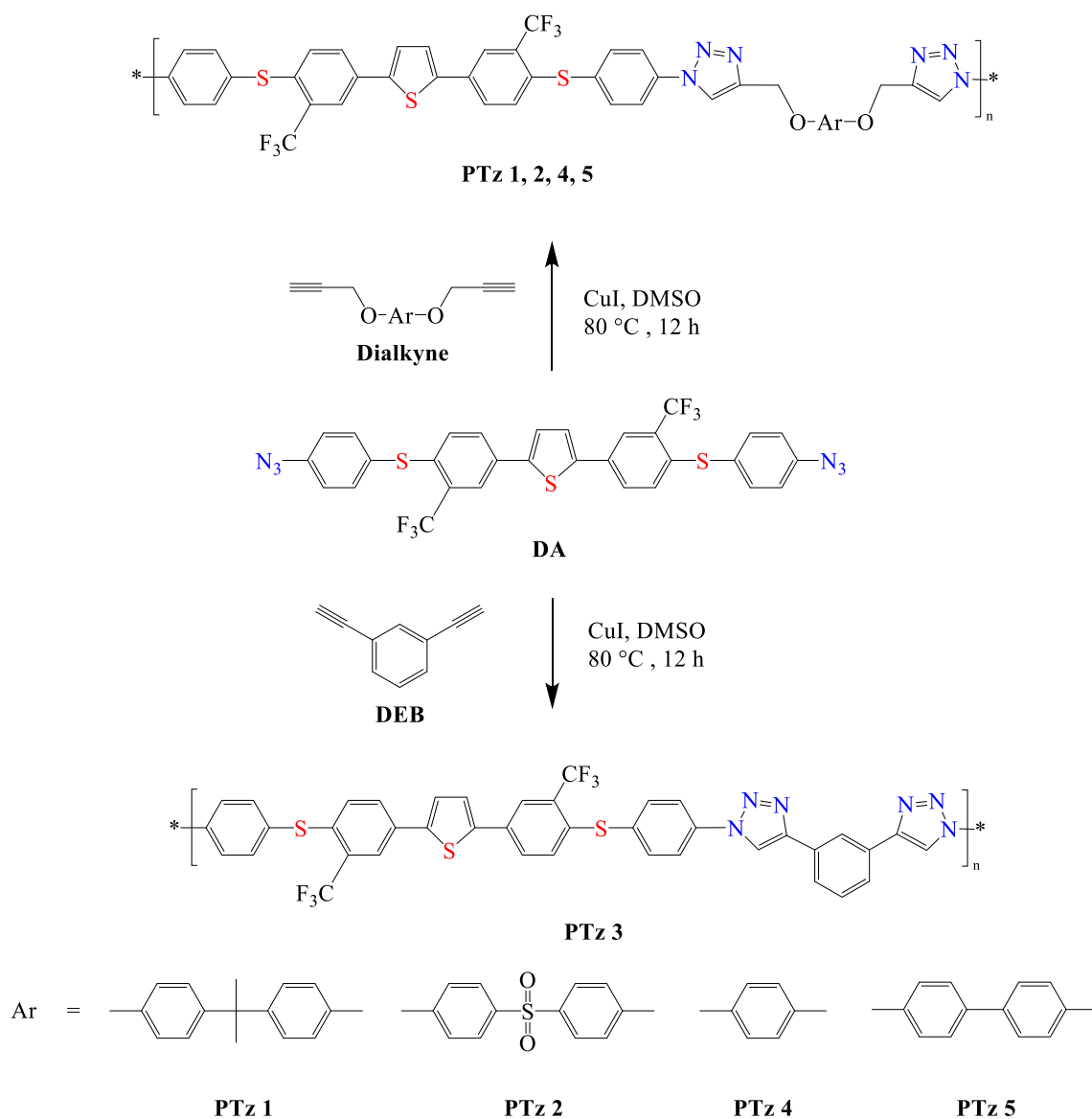
SCHEME 3 Synthesis scheme and structures of linear polytriazoles, PTz 1–5.

SCHEME 4 Synthesis scheme and structures of hyperbranched polytriazoles, hb-DEB$_{(n:m)}$.
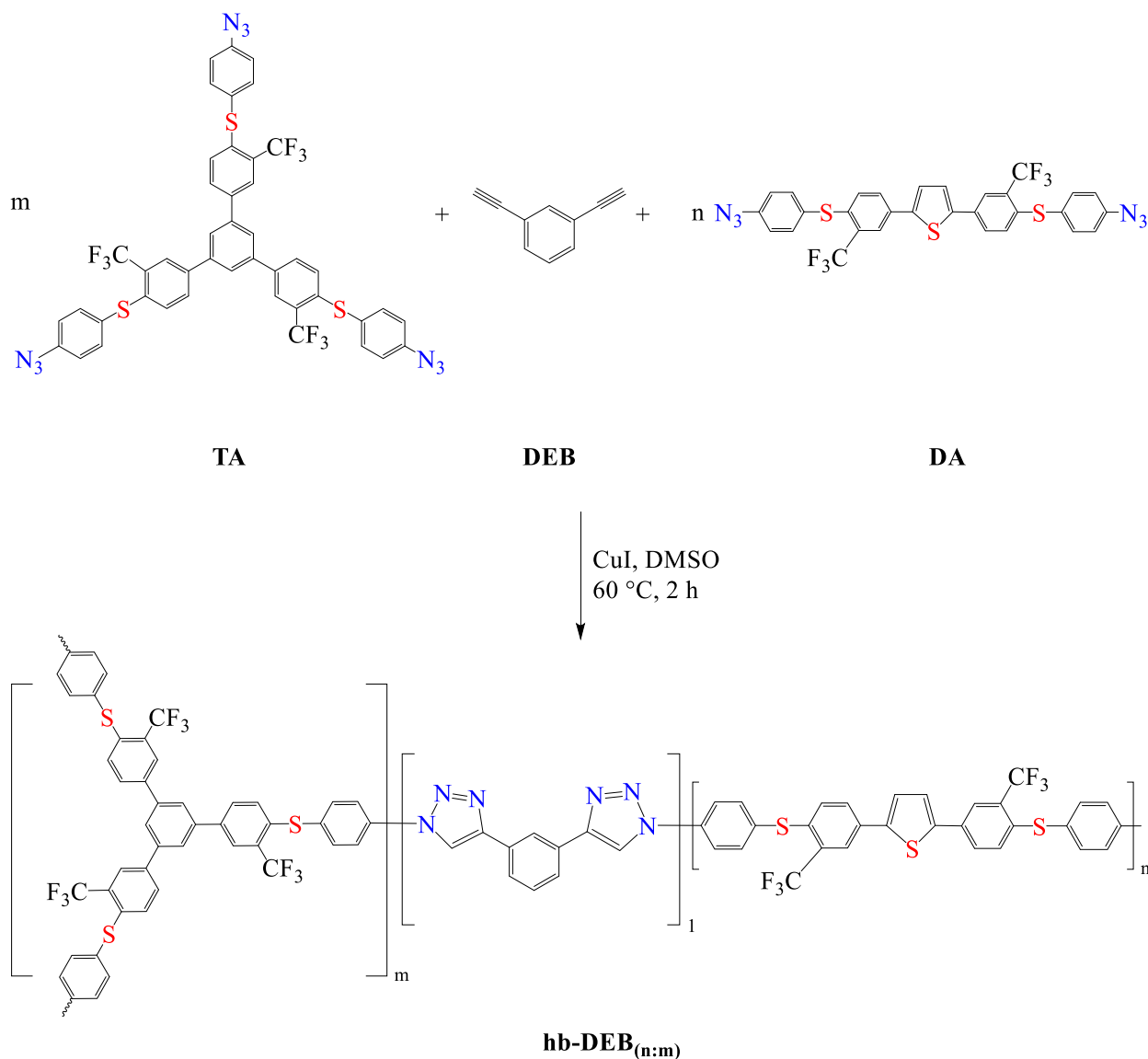
Entry	n	m
hb-DEB$_{(0.70:0.20)}$	0.7	0.2
hb-DEB$_{(0.60:0.27)}$	0.6	0.27

$$m = 2(1-n)/3$$

solvents, however, the branched unit may also result in crosslinking at the critical conversion of the azido groups. Thus, the synthesis protocol of the branched polytriazoles was carefully adjusted so as to have a balance between solubility and gel-formation. The detailed solubility data of the polymers are summarized in Table S1. Table 3 contains the monomer feed ratio of the three different monomers for the preparation of the hyperbranched polymers.

3.3 | Spectroscopic characterizations

As outlined in Table S1, the polymers are insoluble or only partially soluble in common NMR solvents like chloroform, dichloromethane, THF or DMSO. Therefore, DMF-d$_7$ was selected, which is a good solvent for PTz 1, PTz 2 and PTz 4. PTz 3 could not be studied by NMR spectroscopy due to insolubility in all NMR solvents.

TABLE 2 Molar masses ($\overline{M}_n$, $\overline{M}_w$), dispersities (Đ) and inherent viscosities (η_{inh}) of polytriazoles.

Polymer	$\overline{M}_n$ (kDa)	$\overline{M}_w$ (kDa)	Đ	η_{inh} (dL/g)
PTz 1[a]	35	69	1.97	0.65
PTz 2[a]	34	51	1.50	0.69
PTz 3	—	—	—	—
PTz 4[a]	75	120	1.60	1.02
PTz 5[b]	56	100	1.79	0.86
hb-DEB(0.70:0.20)[b,c]	61	100	1.64	1.31
hb-DEB(0.60:0.27)[b,c]	68	110	1.62	0.91

[a]SEC in DMAc at 120°C.

[b]SEC in DMAc at 130°C, polystyrene calibration.

[c]Measured on the soluble part.

TABLE 3 Monomer feed ratios and yields of the hyperbranched polymers compared to the linear insoluble polymer.

Entry	$B_2/A_2/B_3$ (molar ratio)	$[N_3]:[C \equiv C]$	Overall yield[a] (%)	Soluble part[b] (%)
PTz 3	100/100/0	1:1	98	0
hb-DEB(0.70:0.20)	70/100/20	1:1	96	75
hb-DEB(0.60:0.27)	60/100/26.7	1:1	95	80

[a]Including the insoluble part.

[b]Soluble in boiling DMAc; percentage of overall yield; the partial solubility of the branched polymer is caused by starting gelation.

Under normal NMR conditions at room temperature for the samples PTz 5 and the two hb-DEB(n:m) only the low molecular weight fractions were detected. However, the ^{1}H and ^{13}C NMR spectra of the three fully soluble linear polytriazoles (Figures 1, S2–S5) clearly show that the click reaction was successful and led to the formation of the triazole groups.

bands for the azide functional group around 2118 cm^{-1} confirmed the presence of azide functionality in DA, which was absent in case of the polymers. Absorption bands around the region of 1120–1250 cm^{-1} confirmed the presence of —C—F groups in case of the polytriazoles.[58] Other characteristic bands that were present are around 1600 cm^{-1} (C=C), 1050 cm^{-1}, 1315 cm^{-1} and 1495 cm^{-1} which belonged to
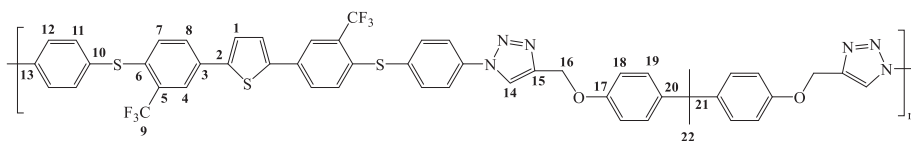
In the ^{1}H NMR spectra, the characteristic triazole proton signal (H$_{14}$) appears downfield as a singlet at ∼9.05 ppm.[35] The triazole units formed result in two ^{13}C NMR signals at ∼145 ppm (C$_{15}$) and ∼ 123 ppm (C$_{14}$), which could be unambiguously assigned and correspond to literature data.[35] Low intensity signals in all spectra indicate end groups. The successful conversion of the azide functionality in DA during the synthesis of the polytriazoles was confirmed using FTIR spectroscopy. The FTIR spectra for the monomer DA and the polymers are shown in Figure 2. The characteristic absorption

the symmetric and asymmetric bands in case of C-O-C (ether) linkages.[59]

3.4 | Thermal studies

The thermal properties of the polytriazoles were evaluated using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) under N$_2$. The degradation temperature, which is often evaluated as 5% weight loss temperature ($T_{d5\%}$) was above 280°C for all
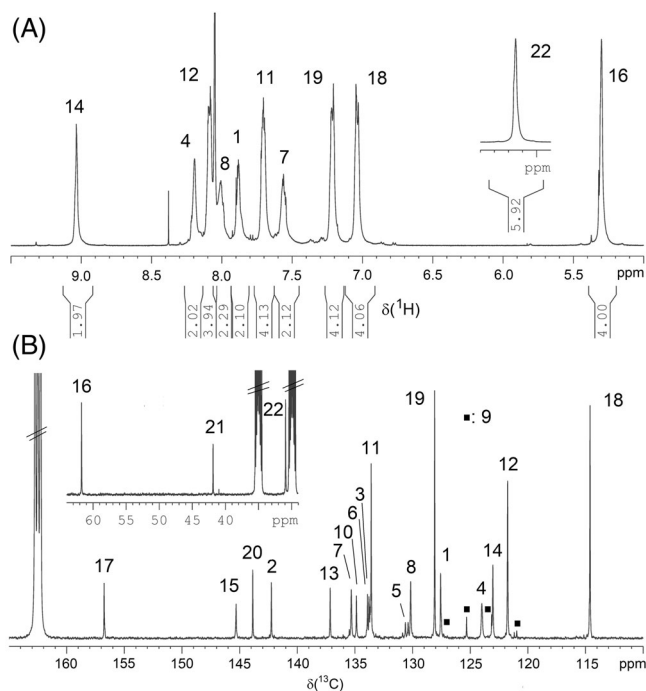
FIGURE 1 ^{1}H (A) and ^{13}C NMR spectrum (B) of PTz 1 (solvent: DMF-d$_7$).
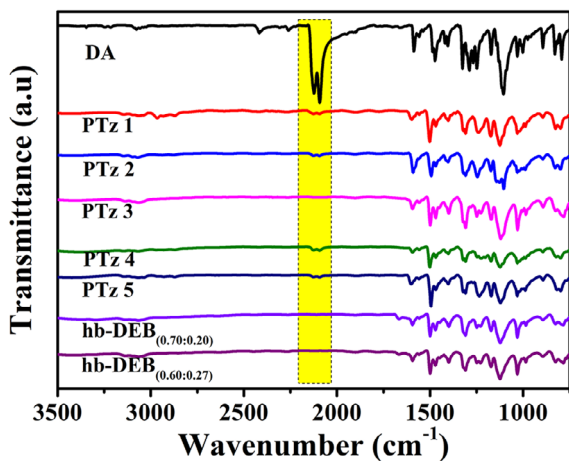

FIGURE 2 FTIR spectra of DA and the polytriazoles.

the polymers prepared in this work, as seen from Figure 3A and listed in Table 4. The high values of $T_{d5\%}$ indicate significant high thermal stability of the polytriazoles. All the polymers were found to exhibit a char yield of more than 50%. Furthermore, the polymers PTz 3 and hb-DEB$_{(n:m)}$ exhibited char yields of more than 60%. This could be attributed to the presence of branching as well as the presence of stiff triazole-*m*-phenylene-triazole units in the polymer frameworks.[60,61]

The glass transition temperatures (T_g) of the polymers were found to be higher than 170°C (Table 4). The polymers

containing triazole-*m*-phenylene-triazole unit in their structures, that is, PTz 3, 5 and hb-DEB$_{(n:m)}$ exhibited no endothermic transition when heated until 300°C, probably due to restrictions in chain mobility. In case of the linear polymers, their T_g value was influenced by the structure of the dialkyne present in the respective polymers. PTz 1 showed the lowest T_g of 170°C, which can be attributed to the presence of a highly flexible isopropylidene moiety. PTz 2 containing an additional —SO$_2$— group showed a higher T_g than PTz 1. Figure 3B shows the DSC plots of PTz 1, 2 and 4. In case of polymers PTz 1 and 2, the difference between their glass transition temperatures and their 5% degradation temperatures is about 150°C, due to which these poly(1,2,3-triazole)s may be thought of to be capable of melt processable. However, further experimental results are required to justify this assumption.

3.5 | Optical characterizations

The polytriazoles prepared in this study were found to exhibit excellent optical transparency as seen from their UV–visible absorption spectra in solution given in Figure 4. All polytriazoles showed a transparency (T$_{589}$ (%)) of more than 80% at 589 nm, which opens the possibility of these polymers to be considered as potential candidates for optical applications. In addition, PTz 2 and PTz 4 exhibited transparencies of more than 95% at 589 nm, which makes these polytriazoles highly explorable for optical applications. All the polymers possess —CF$_3$ moieties in their azide structure, which may contribute to their high optical transparency. The presence of the —CF$_3$ group has been known to increase the optical transparency of synthetic polymers, shifting the maximum absorbance to lower wavelengths.[62] The hb-DEB polymers show a transparency of about 90% at 589 nm.

The refractive indices (RI) of the polymers were determined for polytriazole films with thickness in the range of 30–40 nm using an ellipsometer. The samples were prepared by spin coating polymer solutions in DMAc and consecutive annealing. The sulfur and fluorine content (wt%) of the polymer backbone mainly influence the refractive index of the material. The average refractive index for the polymer thin films at 589 nm (n_{avD}) is reported in Table 5. For linear polymers we expect a rise in RI with increase in sulfur content and decrease in fluorine content, which is reflected in the high RI values for PTz 2 and PTz 4 as compared to PTz 1 and PTz 5. PTz 2 shows lower RI despite having highest sulfur content among the polymers in this series as a result of the presence of electronegative SO$_2$ groups in its repeat unit. From Table 5 it is seen that RI increases with increase in sulfur content with PTz 4 showing the highest RI at
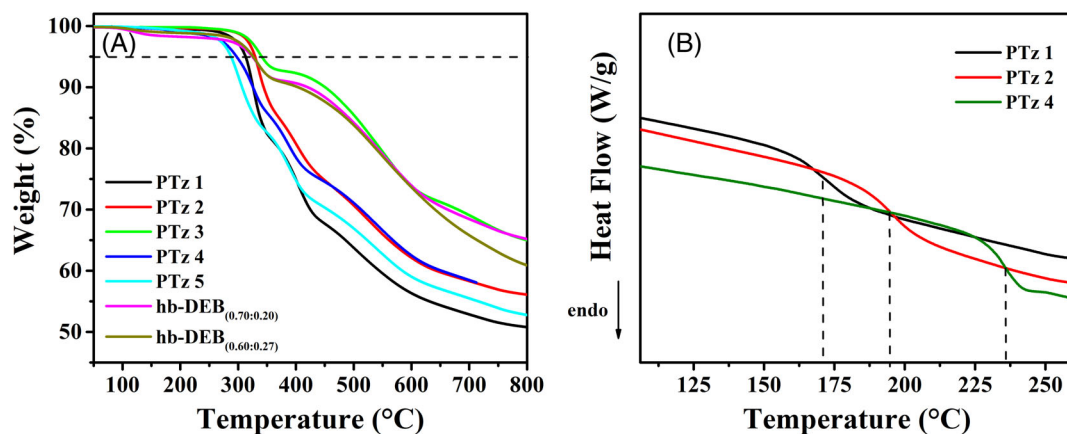
FIGURE 3 (A) TGA plots of linear and branched polytriazoles, (B) DSC plots of PTz 1, 2 and 4.

TABLE 4 Thermal properties of the polytriazoles.

Entry	$T_{d5\%}$	T_g
PTz 1	315	170
PTz 2	330	195
PTz 3	340	—
PTz 4	300	235
PTz 5	290	—
hb-DEB$_{(0.70:0.20)}$	325	—
hb-DEB$_{(0.60:0.27)}$	325	—

TABLE 5 Optical properties of the polytriazoles.

Entry	Sulfur content (wt%)	Fluorine content (wt%)	T_{589}[a] (%)	n_{avD}[b]	n_{calc}[c]	ν_D[d]
PTz 1	10.16	12.04	85	1.694 ± 0.004	1.532	11
PTz 2	13.24	11.76	98	1.704 ± 0.008	1.518	11
PTz 4	11.60	13.75	98	1.743 ± 0.008	1.620	9
PTz 5	7.221	12.83	87	1.700 ± 0.005	1.604	10
hb-DEB$_{(0.70:0.20)}$	11.00	14.48	92	1.676 ± 0.008	—	16
hb-DEB$_{(0.60:0.27)}$	10.64	14.54	91	1.603 ± 0.001	—	17

[a]Transmittance measured for polymer solutions in DMAc.
[b]Average experimental refractive index of thin films at 589 nm.
[c]Calculated refractive index.
[d]Abbe number of thin films.

FIGURE 4 UV–visible absorption spectra of the polytriazoles (10 mg/mL) measured in DMAc solutions.

589 nm, among the thin films of linear polymers. In case of the branched polytriazoles, the fluorine content is enhanced and as a result respective thin films show lower RI and higher transparency.[63–65] Table 5 also reports the calculated RI values (n_{calc}) for the linear polymers. The calculations were done using contributions to the molar refractions of the various functional groups as reported by van Krevelen, which allows a rough estimation and provides trends for RI values.[56,66] To account for the optical dispersion of the polymers, we calculated the Abbe number of the poly(1,2,3-triazole)s from thin film refractive index data as, $\nu_D = (n_D - 1)/(n_F - n_C)$, where, n_C, n_D and n_F are the respective RI of the thin films at 656.3 nm, 589.3 nm, and 486.1 nm (Fraunhofer C, D$_1$ and F spectral lines respectively). The ν_D was found to be between 9 and 17 for the prepared polymer films in this series, with films showing high ν_D with low RI and vice versa, indicating to the general trade-off between RI and ν_D.[67] Notable, films from branched polymers show higher ν_D at a similar RI compared to films from linear polymers.

4 | CONCLUSIONS

The synthesis of two novel azido functional monomers was reported in this work, one difunctional and one trifunctional. Their structures were established using FTIR and NMR spectroscopic studies. Four dialkyne monomers, BPADAL, BPSDAL, HQDAL and HPDAL were also

prepared using established reaction schemes in literature and the formation of the dialkyne monomers was confirmed using ^{1}H NMR spectroscopy. Using the azido and alkyne monomers we were able to synthesize two series of new poly(1,2,3-triazole)s with an inherent high sulfur content via Cu(I) assisted click polymerization reactions. In case of the linear polymers a molar mass as high as 120 kDa was achieved in DMAc as solvent. Furthermore, the introduction of TA as the branching unit was significantly instrumental in improving the solubility of the polymers with stiff triazole-*m*-phenylene-triazole unit arising due to 1,3-diethynylbenzene (DEB) moiety. The synthesis protocol for the branched polymers was balanced so as to prepare soluble polymers, and also to avoid gelation arising from the introduction of trifunctional monomers. Homogeneous thin films were efficiently spin coated on IES wafers. High transparency of more than 80% and high RI in the range of 1.60–1.74 at 589 nm was observed for the polymers in this series. The polytriazole, PTz 4, exhibited the best properties in terms of solubility and thermal stability. Also, PTz 4 showed a very high transparency of more than 95% and a very high RI of 1.743 at 589 nm, arising from its structural attributes, making it very promising for optical applications.

ORCID
Brigitte Voit https://orcid.org/0000-0002-4531-691X
Susanta Banerjee https://orcid.org/0000-0002-0358-3198

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