**Dieses Dokument ist eine Zweitveröffentlichung (Verlagsversion) /
This is a self-archiving document (published version):**

Robert Pöttsch, Brian C. Stahl, Hartmut Komber, Craig J. Hawker, Brigitte I. Voit

High refractive index polyvinylsulfide materials prepared by selective radical mono-addition thiol-yne chemistry

Erstveröffentlichung in / First published in:

Polymer Chemistry. 2014, 5(8), S. 2911–2921 [Zugriff am: 04.11.2019]. Royal Society of Chemistry. ISSN 1759-9962.

DOI: <https://doi.org/10.1039/c3py01740k>

Diese Version ist verfügbar / This version is available on:

<https://nbn-resolving.org/urn:nbn:de:bsz:14-qucosa2-364225>

„Dieser Beitrag ist mit Zustimmung des Rechteinhabers aufgrund einer (DFGgeförderten) Allianz- bzw. Nationallizenz frei zugänglich.“

This publication is openly accessible with the permission of the copyright owner. The permission is granted within a nationwide license, supported by the German Research Foundation (abbr. in German DFG).

www.nationallizenzen.de/

High refractive index polyvinylsulfide materials prepared by selective radical mono-addition thiol–yne chemistry†

Cite this: *Polym. Chem.*, 2014, 5, 2911

Robert Pötzsch,^{ab} Brian C. Stahl,^c Hartmut Komber,^a Craig J. Hawker^c and Brigitte I. Voit^{*ab}

We report on a new framework for preparing high-refractive index polymeric materials which combines the selective thiol radical mono-addition to phenyl-acetylene derivatives with hyperbranched architectures. Using this strategy we have synthesized a series of linear and hyperbranched polyvinyl sulfide (PVS) materials, employing different dithiol (A_2 and A'_2) and di- and trialkyne (B_2 and B_3) monomers. The process requires only a simple radical initiator, such as AIBN, *in lieu* of expensive or toxic catalysts and this chemistry produces polymers in high yield (up to 96%) and high molecular weight (up to 123 000 g mol^{−1}). The polymers are optically transparent, thermally stable (up to 420 °C) and readily form high-quality films. The end group composition of the hyperbranched materials can be easily adjusted by changing the A_2/B_3 feed ratio. The sulfur incorporation and conjugation resulting from thiol–yne coupling with selective mono-addition results in materials with high refractive indices in the visible and IR region ($n_D = 1.68$ – 1.75) and optical dispersions as low as 0.004. Moreover, we demonstrate that the hyperbranched architecture produces materials with better performance in terms of light reflection and chromatic dispersion compared to linear structures.

Received 18th December 2013
Accepted 28th January 2014

DOI: 10.1039/c3py01740k

www.rsc.org/polymers

Introduction

High-refractive index materials play an important role in many advanced optical and optoelectronic technologies, including antireflective coatings,¹ waveguides and light-emitting diodes.² Inorganic materials have historically been used as high-refractive index optical components (*e.g.* MgF₂ anti-reflective coatings), however with the advent of advanced optics and optoelectronics a need for high-refractive index polymers (HRIPs) has arisen for applications such as polymer waveguides,³ organic lasers,⁴ and encapsulants for traditional² and organic light-emitting diodes.⁵ Two leading strategies have emerged to develop HRIPs – filling a polymer matrix with high-refractive index inorganic nanoparticles, and altering the chemical structure of the polymer to increase its intrinsic refractive index. Nanoparticle-filled polymer composites have

shown promise but suffer from poor storage stability, processing challenges and high optical losses. An effective strategy for increasing the intrinsic refractive index of polymers is to increase the incorporation of high-molar refraction groups, such as sulfur atoms and aromatic structures.⁶ As a result, sulfur-containing polymers have received significant, recent attention and are a technologically important class of polymers, finding applications in rubber technologies,⁷ biomedicine,⁸ and organic electronics.⁹ One particular class of sulfur-containing polymers, polyvinylsulfides (PVSs), shows remarkable potential for optical applications due to its high concentration of sulfur and C=C bonds; however, this material has received relatively little attention until recently in part because the preparation of PVS-based materials is not straightforward. The Tang group recently presented an approach yielding PVSs with up to 100% *E* configuration.¹⁰ Although this approach allowed access to PVS polymers with a high degree of structural control, the synthesis required expensive rhodium catalysts making this method less attractive for industrial applications. In subsequent studies, the same group also developed an organic base-mediated polymerization method yielding PVSs with good stereoselectivity and high refractive indices, although this chemistry seemed to be restricted to monomers with a strong electron-withdrawing carboxyl group adjacent to the alkyne moiety.¹¹ A more convenient route towards PVS consists of the radical-mediated addition of a thiol and an alkyne. This type of reaction, also known as a “Thiol–Yne” (TY) reaction, is often thought to result in

^aLeibniz-Institut für Polymerforschung Dresden e.V., Hohe Straße 6, 01069 Dresden, Germany. E-mail: voit@ipfdd.de

^bTechnische Universität Dresden, Center for Advancing Electronics Dresden (cfaed) and Chair of Organic Chemistry of Polymers, 01062 Dresden, Germany

^cMaterials Research Laboratory, Materials Department, and Department of Chemistry and Biochemistry, University of California, Santa Barbara, CA, USA

† Electronic supplementary information (ESI) available: Synthesis and NMR analysis of model compounds, ¹H and ¹³C NMR spectra of **hb-P8**, **hb-P9**, **hb-P10** and **lin-P4**, IR and UV-vis spectra of selected polymers, thermal analysis (TGA and DSC traces) of the polymers, as well as AFM analysis of selected polymer films. See DOI: 10.1039/c3py01740k

predominant formation of bis-adducts formed by the addition of a second thiol onto the formed vinyl sulfide.^{12,13} In this vein, radical-initiated polyaddition of dialkynes and dithiols to prepare PVS polymers was investigated by the groups of Nuyken^{14,15} and Kobayashi,^{16,17} however bis-adduct formation was again shown to occur. To preferentially form the desired monoaddition product, the group of Hudson made the interesting observation that selective formation of vinyl sulfides occurs upon thiol addition to phenylacetylene (PA)-based small molecules.¹⁸ This feature could not only be useful in new material synthesis but also unlocks potential for application in orthogonal “click” functionalization.¹⁹ With this regard, we have recently reevaluated the thiol-yne reaction (TYR) with a focus on PA-based substrates and demonstrated the preparation of a hyperbranched polymer.²⁰ The development of hyperbranched structures has shown tremendous progress over the last two decades and these materials often constitute with their improved properties suitable alternatives among modern electro-optical and biological applications.^{21–26} In this paper, we present a new framework for the preparation of intrinsic HRIPs using simple radical chemistry to synthesize linear and hyperbranched (hb) PVSs using $A_2 + B_2$ and $A_2 + B_3$ approaches starting from commercially available dithiols (A_2 and A'_2) and di- or trialkyne (B_2 and B_3) monomers.

Results and discussion

Monomer and polymer synthesis

We have recently demonstrated that a thiol can be added selectively to the diphenylacetylene group, forming a vinyl sulfide and avoiding thiol bis-addition, if an equimolar ratio of thiol to alkyne groups is used.²⁰ The alkyne-bearing monomers 1,3,5-tris(phenylethynyl)benzene (B_3) and 1,4-bis(phenylethynyl)benzene (B_2) (Scheme 1) were synthesized according to the literature by Sonogashira coupling of the brominated precursors and phenylacetylene.²⁷ Hexanedithiol (A_2) and benzene-1,4-dithiol (A'_2) were purchased from Sigma Aldrich and used as received. The alkyne groups within the

phenylacetylene monomers used in this approach can therefore be treated as mono-functional groups, in contrast to other examples from the literature involving bis-addition TYR for polymer preparation.^{28–32} The mechanism of TYR with 1,2-diphenyl-substituted alkynes is depicted in Scheme 2. The thiyl radicals formed upon thermal initiation by AIBN quickly add to the alkyne group (left circle). The intermediate vinyl sulfide radical then forms the vinyl sulfide (with an *E/Z* ratio of approximately 2 : 3) upon H-abstraction from a thiol. As we have shown, the second addition of a thiyl radical resulting from H-abstraction in the corresponding 1,2-disulfide (right circle) is possible, however this reaction is sterically and electronically hampered and only occurs if the reaction is carried out with a large excess of thiol and allowed to proceed for long reaction times.²⁰

In the investigation of polymer synthesis, hexanedithiol was used as the thiol-containing A_2 monomer and mixed with

Scheme 2 Basic mechanism of the thiol-yne reaction on diphenylacetylene.

Scheme 1 Synthesis of linear and hyperbranched PVS materials prepared from $A_2 + B_2$ and $A_2 + B_3$ monomers, respectively.

alkyne-substituted **B**₂ or **B**₃ monomers to prepare linear or hyperbranched PVSs, respectively (Scheme 1). An alternative thiol-containing monomer, benzene-1,4-dithiol (**A'**₂), was employed since its addition to di-substituted alkynes proceeds in a similar efficient and selective manner as shown for aliphatic thiols (Scheme 3), while the aromatic structure of this monomer would produce a polymer with a higher aromatic content and hence a higher refractive index.²⁰ In all experiments, toluene was used as the solvent and the reactions were thermally initiated by 2,2'-azobis(2-methylpropionitrile) (AIBN). For most cases, the reactants were diluted with toluene to a concentration of one molar with respect to the alkyne groups, and 5 mol% AIBN was added per alkyne group. The reaction time varied between 2 and 20 hours, and all reactions were performed at 90 °C. The results of the polymerizations with hyperbranched (**B**₃) and linear (**B**₂) monomers are summarized in Tables 1 and 2, respectively. The polymers were usually obtained in yields around 80–90%. In the case of hb-PVS, different thiol-to-alkyne functionality ratios were used in the feed ratio which largely affected the polymers' molecular weight and functional group composition. Significantly, all the

polymers obtained were easily soluble in common organic solvents such as chloroform, toluene or THF.

A modular gel permeation chromatography (GPC) system equipped with both a multi angle light scattering (MALS) detector and a refractive index (RI) detector was employed for molecular weight and dispersity M_w/M_n ($\bar{D}$) determination. Especially in the case of hyperbranched polymers, light scattering (LS) detectors usually provide a more reliable estimation of the weight-average molecular weight (M_w) compared to RI detectors with PS calibration due to the significant difference in hydrodynamic radii between linear and hyperbranched polymers of the same molecular weight. However, we had the experience that dispersity analyzed from RI detection is more realistic than that from the LS detectors. Accordingly, the $\bar{D}$ values presented in this work were obtained from the RI detector and are reported together with the respective RI M_w data. As expected, in the case of hb polymers, M_w values by LS are systematically significantly higher than those by RI detection whereas for linear polymers both values agree reasonably well. The hb-PVS materials displayed a trend towards higher M_w and increasing $\bar{D}$ when the thiol-to-alkyne (T/A) ratio was

Scheme 3 Synthesis of linear and hyperbranched fully aromatic polyvinylsulfides prepared from **A'**₂ and **B**₂ or **B**₃, respectively.

Table 1 Reaction conditions and polymer characteristics of hyperbranched PVS **hb-P1**–**hb-P10**

Entry	A ₂ / B ₃ ratio	T/A ratio	Reaction time	[c] _{alkyne}	Yield	M_w^b [g mol ^{−1}] (RI)	$\bar{D}^b$	M_w^c [g mol ^{−1}] (MALS)
hb-P1	1 : 1	2 : 3	2 h	1 M	57%	4700	2.5	6000
hb-P2	1 : 1	2 : 3	6 h	1 M	83%	3700	2.3	6800
hb-P3	1 : 1 ^d	2 : 3	20 h	1 M	90%	3900	3.9	8400
hb-P4	5 : 4 ^d	5 : 6	2 h	1 M	85%	10 300	5.7	22 300
hb-P5	3 : 2	1 : 1	2 h	1 M	78%	15 700	4.3	41 600
hb-P6	3 : 2	1 : 1	6 h	1 M	90%	15 900	4.6	43 400
hb-P7	3 : 2 ^d	1 : 1	20 h	1 M	96%	41 600	17.3	123 300
hb-P8	2 : 1	4 : 3	2 h	1 M	76%	26 500	12.0	113 000
hb-P9 ^a	1 : 1	2 : 3	2 h	0.5 M	80%	3600	2.1	4200
hb-P10 ^a	3 : 2	1 : 1	2 h	0.5 M	74%	17 400	5.2	66 000

^a Prepared from **A'**₂. ^b Determined by GPC with a RI detector and PS calibration. ^c Determined by GPC with a MALS detector. ^d Experimental **A**₂/**B**₃ ratios determined by ¹H NMR spectroscopy: 1.11 for **hb-P3**, 1.34 for **hb-P4** and 1.6 for **hb-P7**, respectively.

Table 2 Reaction conditions and polymer characteristics of linear PVS lin-P1–lin-P4

Entry	Reaction time	[c] _{alkyne}	Yield	M_w^b [g mol ⁻¹] (RI)	$\bar{D}^b$	M_w^c [g mol ⁻¹] (MALS)
lin-P1	5 h	0.5 M	74%	6600	2.5	6000
lin-P2	6 h	1 M	77%	7600	2.0	7000
lin-P3	20 h	1 M	80%	3200	2.7	5500
lin-P4 ^a	2 h	1 M	69%	2200	1.7	4200

^a Prepared from A'₂. ^b Determined by GPC with a RI detector and PS calibration. ^c Determined by GPC with a MALS detector.

increased towards unity, each reaching their highest respective values for an equimolar T/A ratio with $M_w = 123\,000\text{ g mol}^{-1}$ and $\bar{D} = 17.3$ (**hb-P7**, Table 1). The reaction time appears to influence the molecular weight only when thiol and alkyne groups are present in an equimolar ratio, *i.e.* **hb-P7** shows a significant increase in molecular weight whereas **hb-P3** does not. Despite the long reaction time, no evidence for gelation was found in **hb-P7**. In all the other cases, the final M_w seems to be limited by the T/A feed ratio and the M_w reaches a plateau within the first two hours. In contrast to molecular weight, the isolated reaction yields do appear to increase with reaction time as shown in Table 1. The GPC traces, recorded separately by MALS and RI detectors, of **hb-P3**, **hb-P4** and **hb-P7** are shown in Fig. 1 and indicate a shift towards higher M_w values upon increasing the T/A feed ratio. The broadening of the peaks obtained from the RI detector also indicates increasing $\bar{D}$ as expected for systems approaching gelation. For the linear PVS polymers (**lin-P1**, **lin-P2** and **lin-P3**) the molecular weight did not exceed 7000 g mol^{-1} corresponding to a degree of polymerization (DP) of ~ 30 with extended reaction times showing little influence on the molecular weight. The hb-PVS polymers prepared with the alternative A'₂ monomer displayed similar trends in M_w and $\bar{D}$ (Table 1). Two hyperbranched samples **hb-P9** and **hb-P10** were prepared using T/A ratios of 2 : 3 and 1 : 1, respectively. An equimolar T/A feed ratio dramatically increased the M_w from 4200 to $66\,000\text{ g mol}^{-1}$ after two hours of reaction time; $\bar{D}$ also increased from 2.1 to 5.2.

Structural characterization

The ¹H and ¹³C NMR spectra of linear and hb-PVS polymers are quite complex due to the different structural and regiochemical isomers formed by the attack of the thiyl radical on the

respective C-atom of the triple bond coupled with the resulting *E/Z* isomers for both products. This is illustrated in Scheme 4. In particular for the central 1,4- and 1,3,5-substituted benzene rings a multitude of different isomers must be considered. As a result, a large number of NMR signals with similar chemical shifts results in minimal differentiation of the overlapping ¹H and ¹³C NMR signals.

Therefore to further understand the course of these addition reactions, model experiments were carried out by reacting the B₃ monomer with either 1 or 3 equivalents of monofunctional hexanethiol. Despite the simple structure of the reactants, the ¹H and ¹³C NMR spectra of these products exhibit a large variety of signals due to the large number of aforementioned isomers, clearly illustrating the need for model studies (Fig. S1 and S2†). The model compound **b₃** is of particular interest since its ¹³C NMR spectrum (Fig. S2†) exhibits no signals in the chemical shift range between 85 and 95 ppm indicating that all three phenylethynyl groups have undergone reaction and demonstrates that steric hindrance in the formation of dendritic units

Scheme 4 Schematic representation of the thiyl attack on the alkyne group of the B₂ or B₃ monomer leading to four different isomers for the resulting vinyl sulfide derivatives.

Fig. 1 GPC traces of hb-PVS using different A₂/B₃ feed ratios. (a) MALS detector signal and (b) RI detector signal.

from **B**₃ monomers should be insignificant and that hyperbranched-PVS polymers with a high degree of branching (DB) can be obtained. Fig. 2 depicts the ¹H NMR spectra of **hb-P3**, **hb-P4** and **hb-P7** in CD₂Cl₂ showing the effect of different T/A feed ratios including 2 : 3, 5 : 6 and 1 : 1. All three spectra are characterized by signals in regions related to aromatic and vinylic protons (6.3–8.3 ppm), the protons of the methylene groups adjacent to the sulfur atom (SCH₂) (1.9–2.7 ppm) and the protons of the four remaining methylene groups originating from the **A**₂ monomer segment (0.8–1.7 ppm). While the spectral changes are small, the signal intensity from the aliphatic methylene protons increases relative to the aromatic and olefinic protons with the increasing T/A feed ratio, confirming a higher incorporation of **A**₂ repeat units in the structure.

Moreover, the absence of any signals in the range of 3.7 to 4.4 ppm indicates that the **A**₂ and **B**₃ monomers undergo nearly exclusive monoaddition to give the desired vinyl sulfide units and that bis-addition did not occur, as the signal from the methine groups on the 1,2-dithioether linkage resulting from bis-addition is expected in this region.²⁰ Bis-addition only occurs when the T/A feed ratio is increased above 1 : 1, as in the case of **hb-P8**, as evidenced by a broad signal between 3.7 and 4.4 ppm (Fig. S3†). Additional structural information was obtained from quantitative ¹³C NMR spectra of **hb-P3**, **hb-P4** and **hb-P7**, shown in Fig. 3. Three distinctive broad signal regions are typically found in the spectra and originate from the aliphatic CH₂ carbons (24.5–39.5 ppm), ethynyl carbons (87.5–92.0 ppm) and aromatic and olefinic C and CH carbons (122.5–142.5 ppm). The intensity of the signals in the region for the ethynyl carbons originating from linear **b**₂**B** units and terminal **bb**₂ units decreases with the increasing T/A ratio (~0.6 and 0.25 equivalents of ethynyl groups per **A**₂ monomer for **hb-P3** and **hb-P4**, respectively) and the signals are absent in the spectrum of **hb-P7**. The same holds true for the signal of the aromatic carbons adjacent to the ethynyl group between 122.5 and 125

Fig. 3 ¹³C NMR spectra of **hb-P3** (a), **hb-P4** (b) and **hb-P7** (c) (solvent: CD₂Cl₂).

ppm and the signal of the aromatic CH carbons *ortho* to the adjacent phenyl ring (131.9 ppm). Signals originating from thiol end groups appear at 24.7 ppm (HS–CH₂–) and at 34.1 ppm (HS–CH₂–CH₂–) in the spectra of **hb-P4** and **hb-P7**. Minor traces of disulfide linkages due to thiyl homo-coupling (less than one percent with respect to the overall SCH₂ intensity) were detected by the signal of their adjacent CH₂ groups at 39.1 ppm as demonstrated with model compounds (Fig. S4†). The complete absence of ethynyl groups present in linear and terminal **B**₃ units, together with the minor content of thiol end groups for the polymers obtained using a 1 : 1 T/A ratio, suggests that the degree of branching is relatively high. However, the overlapping signals make differentiating the linear, dendritic and terminal units impossible and preclude direct calculation of the degree of branching. In the case of **hb-P8**, in addition to the broad signal of the CH carbons of the 1,2-dithioether linkage at 54.0–57.5 ppm resulting from bis-addition, a large concentration of thiol end groups (signals at 24.7 and 34.1 ppm) is found suggesting a macromolecule with unreacted thiol functional groups (Fig. S3†).

In contrast to the ¹H and ¹³C NMR spectra of **hb-PVS** polymers, spectra of the linear polymer analogues, e.g. **lin-P3**, show increased resolution (Fig. 4) due to a decreased number of possible isomeric structures with the ¹H NMR spectrum of **lin-P3** again displaying three distinct broad signal regions (*c.f.* hyperbranched analogues). The absence of signals in the range of 3.7 to 4.4 ppm indicating bis-addition demonstrates that, like the hyperbranched materials, the **A**₂ and **B**₂ monomers are exclusively linked together through vinyl sulfide linkages. Similarly, the ¹³C NMR signal assignments of the **lin-PVS**

Fig. 2 ¹H NMR spectra of **hb-P3** (a), **hb-P4** (b) and **hb-P7** (c) (solvent: CD₂Cl₂; magnifications refer to the region of 3.5–4.5 ppm).

Fig. 4 ^1H (top) and ^{13}C NMR spectra (bottom) of **lin-P3** (solvent: CD_2Cl_2).

materials correspond to those of the **hb-PVS** with both thiol and alkyne end groups being observed in a *ca.* 1 : 1 ratio. The *E/Z* ratio is in good agreement with the results of the model reaction reported previously.²⁰ Assuming a statistical distribution of the end groups over all polymer chains, a M_n of about 2400 g mol^{-1} and a $\text{DP} \sim 11$ can be calculated by end group analysis from the ^{13}C NMR spectrum (ethynyl group and HS-CH_2), which is in good agreement with the M_n value reported by GPC.

The ^1H and ^{13}C NMR spectra of the fully aromatic PVS materials prepared with the aromatic thiol monomer benzene-1,4-dithiol (**hb-P9**, **hb-P10** and **lin-P4**) show even more pronounced signal broadening when compared to the materials prepared with linear hexanedithiol. The ^1H NMR spectra of **hb-P9** and **hb-P10** exhibit only one broad signal from the aromatic and olefinic protons in the range of 6.3 to 8.0 ppm (Fig. S5 and S6†) and only in the case of **lin-P4** the signal from thiol end groups at 3.4 ppm can be detected (Fig. S7†). In addition to the signals from aromatic and olefinic C and CH carbons in the range of 120–142 ppm, the ^{13}C NMR spectra of **hb-P9** (T/A ratio = 2 : 3) show a broad set of signals around 90 ppm from the phenylethynyl end groups which is expected based on the excess of the alkyne-bearing monomer in the feed ratio (Fig. S5†). Further proof of the proposed structure was provided by infrared (IR) spectroscopy; the IR spectra of **lin-P3**, **hb-P3** and **hb-P7** are shown in Fig. 5. All three spectra exhibit C–H bands of the aliphatic segments at 2850 and 2924 cm^{-1} and of the aromatic segments around 3030 cm^{-1} . The spectra are also characterized by strong vibration peaks at 690 and 753 cm^{-1} originating from the aromatic ring C–H bending, whereas the band at 728 cm^{-1} in the hyperbranched sample is due to the substitution pattern of the central benzene ring in the **B**₂ and **B**₃ monomers and differentiates the linear and hyperbranched materials.

The IR spectra of the PVS polymers **lin-P4**, **hb-P9** and **hb-P10** based on the alternative phenyl-based **A'**₂ monomer are shown in Fig. S8.† These spectra exhibit the typical bands for aromatic

Fig. 5 IR spectra of (a) **lin-P3**, (b) **hb-P3** and (c) **hb-P7**.

compounds around 3030 cm^{-1} (C–H stretching) as well as 690 and 752 cm^{-1} (C–H bending), while the typical bands for aliphatic segments around 2900 cm^{-1} are absent due to the replacement of the aliphatic **A**₂ monomer by the aromatic **A'**₂. A new band unique to materials prepared with **A'**₂ is observed at 811 cm^{-1} which originates from the aromatic ring in this monomer. As before, the band at 728 cm^{-1} (not present in **lin-P4**) is characteristic of the substitution pattern of the central benzene ring in the **B**₃ monomer and can be used to differentiate between the linear and hyperbranched materials. The PVS polymers were also investigated by UV-vis spectroscopy (Fig. S9†). Apart from **lin-P4** which absorbs light in the visible region below 430 nm , all the other materials do not show any absorption above 400 nm . Both linear polymers show clear bathochromic shifts in their absorption maxima of 26 nm for the aromatic–aliphatic **lin-P3** and 57 nm for the fully aromatic **lin-P4**, respectively, indicating that the structure of these materials are more strongly conjugated than the hyperbranched materials. The bathochromic absorption shift exhibited by **hb-P8** compared to other hyperbranched samples incorporating the same monomers is explained by the presence of 1,2-dithioether linkages from the excess of **A**₂ monomer used in the reaction. Importantly, the minimal optical absorbance observed for these materials enables them to be used in advanced photonic applications.

Thermal properties

The thermal properties of the PVS materials were determined by TGA and DSC and are summarized in Table 3. All materials investigated displayed good thermal stability as shown by the decomposition curves obtained by thermogravimetric analysis (TGA) in a nitrogen atmosphere (Fig. S10†). The decomposition temperature corresponding to a 5% mass loss ($T_{d5\%}$), generally occurring between 320 and $350\text{ }^\circ\text{C}$, was unaffected by the molecular weight of the polymers as evidenced by the comparison of **hb-P5** ($41\,600\text{ g mol}^{-1}$) and **hb-P7** ($123\,300\text{ g mol}^{-1}$). However, substantial differences are apparent in samples prepared with different monomer feed ratios; materials prepared with an excess of alkyne end groups (*e.g.* **hb-P2**)

Table 3 Thermal properties of linear and hyperbranched PVS materials

Polymer	Composition	$T_{d5\%}$ [°C]	Residual mass at 800 °C in N ₂ (%)	T_g^b [°C]
hb-P1	A ₂ + B ₃ (1 : 1)	349	32	75
hb-P2	A ₂ + B ₃ (1 : 1)	356	44	82
hb-P3	A ₂ + B ₃ (1 : 1)	351	21	68
hb-P4	A ₂ + B ₃ (5 : 4)	340	26	72
hb-P5	A ₂ + B ₃ (3 : 2)	327	22	68
hb-P6	A ₂ + B ₃ (3 : 2)	324	25	66
hb-P7	A ₂ + B ₃ (3 : 2)	327	12	67
hb-P8	A ₂ + B ₃ (2 : 1)	312	17	43
hb-P9 ^a	A' ₂ + B ₃ (1 : 1)	420	68	149
hb-P10 ^a	A' ₂ + B ₃ (3 : 2)	401	60	190
lin-P1	A ₂ + B ₂	314	15	32
lin-P2	A ₂ + B ₂	322	18	23
lin-P3	A ₂ + B ₂	320	13	31
lin-P4 ^a	A' ₂ + B ₂	374	52	102

^a A'₂ = benzene-1,4-dithiol. ^b Determined by DSC.

displayed decomposition temperatures up to 40 °C higher than the sample prepared with an excess of thiol end groups (**hb-P8**). This phenomenon could be explained by secondary, thermal crosslinking of the residual alkyne units. In this context, the PVS materials with fully aromatic structures (**hb-P9** and **hb-P10**) show an increased thermal stability with $T_{d5\%}$ values of 400 °C and higher. The mass of the material remaining at 800 °C, also known as the char yield, of the aliphatic–aromatic materials is between 10% and 44% and is highest for materials having the lowest aliphatic chain incorporation (**hb-P2**), which is to be expected considering that aliphatic compounds undergo thermal decomposition more readily than aromatic compounds. Accordingly, the fully aromatic materials **hb-P9** and **hb-P10** had substantially higher char yields (68% and 60%, respectively) than other materials. Their high char yield also makes these fully aromatic materials interesting as precursors to carbonaceous porous materials.^{33,34} Differential scanning calorimetry (DSC) analysis, shown in Fig. S11,†, revealed substantial differences in the thermal properties of the compounds. The aliphatic–aromatic hb-PVS materials generally exhibited glass transition temperatures (T_g) around 70 °C with the exception of **hb-P8** which, due to its higher incorporation of aliphatic hexanedithiol segments, exhibited a T_g of 43 °C while the fully aromatic polymers **hb-P9** and **hb-P10** had significantly higher T_g values (149 °C and 190 °C, respectively). The aliphatic–aromatic linear materials **lin-P1** and **lin-P3** exhibited T_g s around 30 °C whereas the fully aromatic linear material **lin-P4** exhibited a T_g of 102 °C.

Thin film preparation and optical properties

As previously mentioned, incorporating sulfur and conjugated or aromatic groups generally increases the refractive index (RI) of polymeric materials as these structural components possess a high molar refraction and a high refractive index (among other characteristics).⁶ To demonstrate their potential for optical applications, we investigated the UV-vis absorption and

RI of the linear and hyperbranched PVS materials. As mentioned previously, all the materials reported herein, with the exception of **lin-P4**, show no absorption at wavelengths longer than 400 nm (Fig. S9†), making them well-suited to optical applications. To study the RI over a wide wavelength range, thin films of PVS materials of 60–80 nm thickness were prepared by spin-coating onto clean Si wafers and investigated by variable-angle spectroscopic ellipsometry. All the polymers formed high-quality thin films with smooth surfaces (*cf.* Fig. S12†) and surface roughness values (R_a) around 0.2 nm. The RI vs. wavelength curves obtained from ellipsometry are presented in Fig. 6 and show high RI values ranging from $n = 1.6$ at longer wavelengths increasing to slightly above $n = 2.0$ around 400 nm. These materials display RI values significantly higher than commercially important polymers such as poly(methyl methacrylate) ($n_D = 1.49$) and poly(ethylene terephthalate) ($n_D = 1.59$), where n_D is the refractive index at the Fraunhofer D line.³⁵ RI values at the Fraunhofer D, F and C spectral lines (589.3, 486.1 and 656.3 nm, respectively) and at specific infrared wavelengths relevant to applications such as lasers and telecommunication (1064, 1319 and 1550 nm) are summarized in Table 4. The aliphatic–aromatic hyperbranched polymers **hb-P1** and **hb-P6** exhibit RI values as high as 1.67 at 1064 nm and 1.74 at 486.1 nm, while the highest RI values over a wide wavelength range are obtained for the fully aromatic material **hb-P10** with 1.72 at 1064 nm and 1.81 at 486.1 nm. This increase in RI can be explained by the replacement of aliphatic structural components with aromatic components (*i.e.* replacing the A₂ monomer with A'₂), which are known to exhibit a higher molar refraction.⁶ The RI of the linear polymers **lin-P1** and **lin-P4** is slightly lower than their hyperbranched analogues in the visible-IR wavelength range, however these linear materials display a sharp increase in the RI at short wavelengths; this phenomenon could be attributed to the absorption these materials display at wavelengths around 400 nm. The basic difference in RI between the linear and hyperbranched materials observed in the IR and visible regions could be explained by differences in the molecular packing of linear and hyperbranched molecules.

Fig. 6 Refractive index vs. wavelength for linear and hb polymer samples.

Table 4 Refractive indices (n), Abbe numbers (ν) and chromatic dispersions of PVS polymers

Polymer	n_F^a	n_D^a	n_C^a	ν	D	n_{1064}	n_{1319}	n_{1550}	ν'	D'
hb-P1	1.7447	1.7055	1.6938	13.9	0.0719	1.6751	1.6732	1.6727	280.5	0.0036
hb-P6	1.7350	1.6970	1.6861	14.3	0.0699	1.6681	1.6664	1.6658	289.7	0.0035
lin-P1	1.7470	1.6824	1.6630	8.1	0.1234	1.6321	1.6291	1.6280	153.4	0.0065
hb-P9 ^b	1.7938	1.7422	1.7267	11.0	0.0909	1.7019	1.6995	1.6987	218.6	0.0046
hb-P10 ^b	1.8072	1.7558	1.7404	11.3	0.0885	1.7158	1.7134	1.7125	216.2	0.0046
lin-P4 ^b	1.7900	1.6885	1.6580	5.2	0.1923	1.6094	1.6047	1.6030	94.5	0.0106

^a Fraunhofer D, F and C lines corresponding to the wavelengths 589.3, 486.1 and 656.3 nm, respectively. ^b Fully aromatic material.

In addition to the refractive index, the Abbe number (ν) is also an important characteristic of optical materials. The Abbe number is a measure of the optical dispersion, or how strongly the refractive index varies with wavelength; a small Abbe number indicates a large optical dispersion and *vice versa*. The Abbe number can be calculated according to eqn (1) where n_D , n_F and n_C are the RI values at the corresponding Fraunhofer D, F and C lines.

$$\nu = \frac{n_D - 1}{n_F - n_C} \quad (1)$$

The general trend for polymers is that materials with higher RI values tend to have smaller Abbe numbers; polymers with a refractive index of 1.70 or higher typically have Abbe numbers of 20 or less. In contrast, polymers with a moderate RI tend to have larger Abbe numbers in the range of 30–50. PMMA, for example, has a RI of $n_D = 1.49$ and an Abbe number of $\nu = 55$.³⁵ The hyperbranched PVS materials reported herein have significantly higher Abbe numbers than their linear counterparts in addition to larger RI; ν ranges from 11.0 to 14.3 for the hb-PVS, while the linear PVS materials display ν values ranging from 5.2 to 8.1. This difference in ν can be attributed to their hyperbranched architecture and suggests that incorporating hyperbranching may be a route to obtaining simultaneously higher RI and higher Abbe numbers for future generations of high-refractive index polymers. An alternative Abbe number (ν') was proposed by Yang *et al.* and later slightly modified by Jim *et al.* for the evaluation of optical dispersion in the IR wavelength region.^{36,37} It can be calculated by eqn (2) where n_{1064} , n_{1319} and n_{1550} are the RI values at 1064, 1319 and 1550 nm wavelengths, respectively. Furthermore, the optical dispersions D and D' can be obtained by eqn (3) and (4) by forming the reciprocals of the Abbe numbers.

$$\nu' = \frac{n_{1319} - 1}{n_{1064} - n_{1550}} \quad (2)$$

$$D = \frac{1}{\nu} \quad (3)$$

$$D' = \frac{1}{\nu'} \quad (4)$$

The IR-region Abbe numbers of these materials are again high with $\nu' = 290$ for the hyperbranched aliphatic–aromatic materials and $\nu' = 218$ for the hyperbranched purely aromatic structures. These values are significantly higher than values

reported by Liu *et al.* and Jim *et al.* for PVS polymers synthesized by other methods.^{10,11} The optical dispersions D and D' are as low as 0.07 and 0.0035, respectively, for the hyperbranched aliphatic–aromatic samples. Significantly, the materials reported herein have high refractive indices, moderate Abbe numbers and negligible absorption in the visible range, making them ideally suited for advanced optical applications. Moreover, the hyperbranched architecture is advantageous and provides better performance in terms of improved light reflection over a broad wavelength range and appreciably lower chromatic dispersion compared to the linear structure. The use of thiol–yne coupling chemistry combined with a hyperbranched architecture reported herein constitutes a new platform for developing high-refractive index materials. The resulting PVS materials could be highly impactful in applications requiring high refractive index layers and facile solution processing, such as in antireflective coatings,¹ displays,³⁸ optical waveguides,^{3,39} organic lasers^{4,40} and light emitting diodes (LEDs).^{5,41}

Conclusion

We have developed a new framework for preparing high-refractive index materials utilizing facile and inexpensive thiol–yne coupling chemistry and incorporating hyperbranched architectures. This strategy allows a variety of linear and hyperbranched polyvinylsulfides (PVS) employing aliphatic (**A**₂) and aromatic (**A'**₂) dithiol and aromatic di- and trialkyne (**B**₂ and **B**₃) monomers to be prepared. Key to the success of this approach is the recently demonstrated radical thiol–yne variant which allows the selective mono-addition of a thiol to an aromatic alkyne resulting in a vinyl sulfide.²⁰ The synthesis yielded hyperbranched PVS materials with high molecular weights and in high yields. Materials with different end group functionalities were prepared by adjusting the **A**₂ to **B**₃ monomer feed ratio. Significantly, all the materials are readily soluble in common organic solvents, show excellent thermal stability, form high-quality films and are transparent in the visible wavelength range. Most importantly, the high sulfur and aromatic content of materials prepared using this framework results in high refractive indices at visible and IR wavelengths which can be tuned by varying the architecture and monomers used. These easily processed materials could find use in modern photonic/optical applications such as lasers, waveguides or light emitting diodes, and application testing is currently underway.

Experimental part

Measurements

NMR spectra were recorded on a Bruker Avance III 500 NMR spectrometer operating at 500.13 MHz for ^1H and 125.75 MHz for ^{13}C using CD_2Cl_2 and CDCl_3 as solvents. The spectra were referenced on the solvent signal ($\delta(^1\text{H}) = 7.26$ ppm; $\delta(^{13}\text{C}) = 77.0$ ppm for CDCl_3 and $\delta(^1\text{H}) = 5.31$ ppm; $\delta(^{13}\text{C}) = 53.7$ ppm for CD_2Cl_2). The signal assignments were determined from the combination of 1D and 2D NMR spectra. Quantitative ^{13}C NMR spectra were obtained using inverse gated decoupling, $\pi/2$ ^{13}C pulses and a pulse delay of 12 s.

Gel permeation chromatography (GPC) with a Waters Alliance HPLC System, 2695 Separation Module with a column type MZ-Gel SD plus 100 Ang (300×8.00 mm) and a combination of a MALS and RI detector (Wyatt DAWN HELEOS-II) with a laser operating at 663.1 nm and Wyatt Optilab rEX (RI) was used for determination of absolute M_w values. A Waters Alliance HPLC System with a MIXED-D column (300×7.5 mm) and a Waters 2410 Differential Refractometer (RI) was used to determine dispersity indices. Chloroform with 0.25% of TEA was used as the eluent in both cases and the flow rate was set to 1 ml min^{-1} .

DSC Q 1000 and TGA Q 5000 (from TA-Instruments) at a heating rate of $10^\circ\text{C min}^{-1}$ under a nitrogen atmosphere were used to determine T_g and $T_{d5\%}$.

UV-Vis spectra were recorded on a Shimadzu UV3600 UV-NIR spectrometer.

Thin film samples were prepared by dissolving the PVS materials in HPLC-grade toluene (Fisher Scientific) at 4 wt% concentration, filtering through $0.45 \mu\text{m}$ PTFE-membrane syringe filters, and spin-coating onto piranha-cleaned silicon wafers (Silicon Quest Int'l) at 3000 rpm for 30 seconds. Film thicknesses were approximately 60 to 80 nm as measured by ellipsometry (J.A. Woolam Company model M2000DI VASE). Ellipsometry was also used to measure the refractive index of the material. Ellipsometry measurements were made at three angles (55° , 65° and 75°) and over a wavelength range of 400–1700 nm using a model consisting of a single-layer Cauchy film on Si.

AFM measurements were performed on a Dimension 3100 Nanoscope IV from Digital Instruments Inc. in tapping mode.

Chemicals

1,3,5-Tribromobenzene, 1,4-diiodobenzene, phenylacetylene, hexane-1,6-dithiol, and 1,4-benzenedithiol were purchased from Sigma-Aldrich and used as received. AIBN (Sigma-Aldrich) was recrystallized from methanol prior to use. 1,3,5-Tris(phenylethynyl)benzene and 1,4-bis(phenylethynyl)benzene were synthesized as described previously.²⁷

Synthesis of polymers

Synthesis of aromatic–aliphatic hyperbranched polyvinylsulfides hb-P1–hb-P8. 1,3,5-Tris(phenylethynyl)benzene (378 mg, 1 mmol), hexane-1,6-dithiol (151 mg, 1 mmol for **hb-P1–hb-P3**; 188 mg, 1.25 mmol for **hb-P4**; 226 mg, 1.5 mmol for **hb-P5–hb-P7**; 301 mg, 2.0 mmol for **hb-P8**), AIBN (24.6 mg, 0.15 mmol) and dry toluene (3 ml) were mixed together, stirred

and purged with argon for 10 min. The reaction mixture was heated at 90°C for the indicated time. The polymer was then precipitated in 300 ml of methanol, dissolved in a small amount of dichloromethane and precipitated again in 300 ml of methanol. The final polymers were obtained as yellowish powders after drying in a vacuum oven overnight at 35°C .

Characteristics of hb-P1–hb-P3. ^1H NMR (CD_2Cl_2): δ (ppm) = 0.8–1.7 ($\text{SCH}_2\text{CH}_2\text{CH}_2-$), 1.9–2.7 (SCH_2), 6.3–8.3 (aromatic and olefinic protons).

^{13}C NMR (CD_2Cl_2): δ (ppm) = 25–31 ($\text{SCH}_2\text{CH}_2\text{CH}_2$), 31–34 (SCH_2), 87.8–91.5 ($-\text{C}\equiv\text{C}-$), 122.5–125.0 (C_{quart} adjacent to the ethynyl group), 125–135 (aromatic and olefinic CH), 136–143 (aromatic and olefinic C).

FT-IR: ν (cm^{-1}) = 3078 (w), 3053 (w), 3019 (w), 2995 (w), 2925 (m), 2852 (m), 1596 (m), 1578 (m), 1489 (m), 1457 (w), 1443 (m), 1418 (m), 1366 (w), 1347 (w), 1285 (w), 1261 (m), 1222 (w), 1177 (w), 1155 (m), 1100 (w), 1072 (m), 1028 (m), 1000 (w), 964 (w), 937 (w), 913 (w), 883 (w), 863 (w), 753 (s), 729 (w), 689 (s).

Characteristics of hb-P4. ^1H NMR (CD_2Cl_2): δ (ppm) = 0.8–1.7 ($\text{SCH}_2\text{CH}_2\text{CH}_2$), 1.9–2.7 (SCH_2), 6.3–8.3 (aromatic and olefinic protons).

^{13}C NMR (CD_2Cl_2): δ (ppm) = 24.7 (CH_2SH), 25–31 ($\text{SCH}_2\text{CH}_2\text{CH}_2$), 31–34 (SCH_2), 34.1 ($\text{CH}_2\text{CH}_2\text{SH}$), 87.8–91.0 ($-\text{C}\equiv\text{C}-$), 122.5–125.0 (C_{quart} adjacent to the ethynyl group), 125–135 (aromatic and olefinic CH), 136–143 (aromatic and olefinic C_{quart}).

FT-IR: ν (cm^{-1}) = 3645 (w), 3400 (w), 3149 (w), 3052 (m), 3020 (m), 2922 (s), 2850 (s), 2658 (w), 2599 (w), 2516 (w), 2455 (w), 1981 (m), 1949 (m), 1885 (m), 1803 (m), 1755 (m), 1676 (m), 1595 (s), 1578 (s), 1488 (s), 1443 (s), 1417 (s), 1389 (m), 1365 (m), 1347 (m), 1285 (m), 1258 (m), 1223 (m), 1178 (m), 1156 (m), 1108 (w), 1074 (m), 1029 (m), 1000 (m), 967 (w), 937 (m), 909 (m), 860 (m), 752 (s), 690 (s), 633 (w), 620 (w).

Characteristics of hb-P5–hb-P7. ^1H NMR (CD_2Cl_2): δ (ppm) = 0.8–1.7 ($\text{SCH}_2\text{CH}_2\text{CH}_2$), 1.9–2.7 (SCH_2), 6.3–8.3 (aromatic and olefinic protons).

^{13}C NMR (CD_2Cl_2): δ (ppm) = 24.7 (CH_2SH), 25–31 ($\text{SCH}_2\text{CH}_2\text{CH}_2$), 31–34 (SCH_2), 34.1 ($\text{CH}_2\text{CH}_2\text{SH}$), 39.2 (CH_2SSCH_2), 125–135 (aromatic and olefinic CH), 136–143 (aromatic and olefinic C_{quart}).

FT-IR: ν (cm^{-1}) = 3078 (w), 3052 (m), 3020 (m), 2994 (w), 2926 (m), 2852 (s), 2318 (w), 2228 (w), 2194 (w), 2161 (w), 1941 (m), 1881 (w), 1807 (w), 1675 (w), 1595 (m), 1578 (m), 1488 (m), 1447 (w), 1443 (m), 1418 (m), 1367 (w), 1348 (w), 1287 (m), 1261 (m), 1223 (m), 1178 (m), 1156 (m), 1107 (w), 1074 (m), 1029 (m), 999 (w), 967 (w), 937 (m), 912 (m), 863 (m), 819 (w), 752 (s), 729 (m), 691 (s).

Characteristics of hb-P8. ^1H NMR (CD_2Cl_2): δ (ppm) = 0.8–1.7 ($\text{SCH}_2\text{CH}_2\text{CH}_2$), 1.9–2.7 (SCH_2), 3.7–4.4 ($\text{CH}(\text{Ph})\text{S}$), 6.3–8.3 (aromatic and olefinic protons).

^{13}C NMR (CD_2Cl_2): δ (ppm) = 24.7 (CH_2SH), 25–31 ($\text{SCH}_2\text{CH}_2\text{CH}_2$), 31–34 (SCH_2), 34.1 ($\text{CH}_2\text{CH}_2\text{SH}$), 39.1 (CH_2SSCH_2), 54.0–57.5 ($\text{CH}(\text{Ph})\text{S}$), 125–135 (aromatic and olefinic CH), 136–143 (aromatic and olefinic C_{quart}).

FT-IR: ν (cm^{-1}) = 3339 (w), 3052 (m), 3020 (m), 2923 (s), 2850 (s), 2658 (w), 1945 (w), 1880 (w), 1801 (w), 1741 (w), 1679 (w), 1579 (m), 1488 (m), 1443 (m), 1417 (m), 1365 (w), 1346 (w), 1286

(w), 1260 (m), 1222 (m), 1177 (m), 1155 (m), 1075 (m), 1029 (m), 1000 (w), 967 (w), 937 (m), 910 (m), 859 (m), 751 (s), 728 (m), 692 (s).

Synthesis of fully aromatic hyperbranched polyvinylsulfides hb-P9 and hb-P10. 1,3,5-Tris(phenylethynyl)benzene (378 mg, 1 mmol), 1,4-benzenedithiol (142 mg, 1 mmol for **hb-P9**; 213 mg, 1.5 mmol for **hb-P10**), AIBN (24.6 mg, 0.15 mmol) and dry toluene (6 ml) were mixed together, stirred and purged with argon for 10 min. The reaction mixture was heated at 90 °C for 2 hours. The polymer was then precipitated in 300 ml of methanol, dissolved in a small amount of dichloromethane and reprecipitated in 300 ml of methanol. The final polymer was obtained as a yellowish powder after drying in a vacuum oven overnight at 35 °C.

Characteristics of hb-P9. ^1H NMR (CDCl_3): δ (ppm) = 6.85–7.75 (aromatic and olefinic protons).

^{13}C NMR (CDCl_3): δ (ppm) = 87.6–90.6 ($-\text{C}\equiv\text{C}-$), 122.5–124.1 ($\text{C}_{\text{quart.}}$ adjacent to the ethynyl group), 127.3–138.0 (aromatic and olefinic CH and $\text{C}_{\text{quart.}}$).

FT-IR: ν (cm^{-1}) = 3098 (w), 3078 (w), 3056 (m), 3022 (w), 2997 (w), 2167 (w), 2050 (w), 2012 (w), 1997 (w), 1980 (w), 1963 (w), 1947 (w), 1894 (w), 1881 (w), 1798 (w), 1752 (w), 1677 (w), 1598 (m), 1579 (m), 1490 (m), 1474 (m), 1444 (m), 1421 (m), 1388 (m), 1330 (w), 1308 (w), 1280 (w), 1259 (w), 1218 (w), 1180 (m), 1157 (m), 1099 (m), 1073 (m), 1028 (m), 1012 (m), 1001 (w), 984 (w), 963 (w), 914 (m), 880 (m), 864 (m), 841 (w), 812 (m), 753 (s), 727 (w), 689 (s).

Characteristics of hb-P10. ^1H NMR (CDCl_3): δ (ppm) = 6.3–8.1 (aromatic and olefinic protons).

^{13}C NMR (CDCl_3): δ (ppm) = 127.3–138.0 (aromatic and olefinic CH and $\text{C}_{\text{quart.}}$).

FT-IR: ν (cm^{-1}) = 3078 (w), 3056 (m), 3022 (w), 2997 (w), 2167 (w), 2050 (w), 2012 (w), 1997 (w), 1980 (w), 1963 (w), 1947 (w), 1894 (w), 1881 (w), 1798 (w), 1752 (w), 1677 (w), 1598 (m), 1579 (m), 1490 (m), 1474 (m), 1444 (m), 1421 (m), 1388 (m), 1330 (w), 1308 (w), 1280 (w), 1259 (w), 1218 (w), 1180 (m), 1157 (m), 1099 (m), 1073 (m), 1028 (m), 1012 (m), 1001 (w), 984 (w), 963 (w), 933 (m), 914 (m), 866 (m), 843 (w), 812 (m), 753 (s), 727 (w), 689 (s).

Synthesis of linear polyvinylsulfides lin-P1, lin-P2 and lin-P3. 1,4-Bis(phenylethynyl)benzene (278 mg, 1 mmol), hexanedithiol (151 mg, 1 mmol), AIBN (16.4 mg, 0.1 mmol) and dry toluene (4 ml) were mixed together, stirred and purged with argon for 10 min. The reaction mixture was heated at 90 °C for the indicated time. The polymer was then precipitated in 300 ml of methanol, dissolved in a small amount of dichloromethane and reprecipitated in 300 ml of methanol. The final polymers were obtained as yellowish powders after drying in a vacuum oven overnight at 35 °C.

^1H NMR (CD_2Cl_2): δ (ppm) = 0.8–1.7 ($\text{SCH}_2\text{CH}_2\text{CH}_2$), 2.2–2.7 (SCH_2), 6.5–7.9 (aromatic and olefinic protons).

^{13}C NMR (CD_2Cl_2): δ (ppm) = 24.7 (CH_2SH), 27.5–30.5 ($\text{SCH}_2\text{CH}_2\text{CH}_2$), 32.1 and 33.0 (SCH_2 ; *E* and *Z*), 34.1 ($\text{CH}_2\text{CH}_2\text{SH}$), 39.1 (CH_2SSCH_2), 89.1–90.8 ($-\text{C}\equiv\text{C}-$), 121–124 ($\text{C}_{\text{quart.}}$ adjacent to the ethynyl group), 125–133 (aromatic and olefinic CH), 135.5–142.0 (aromatic and olefinic $\text{C}_{\text{quart.}}$).

FT-IR: ν (cm^{-1}) = 3074 (w), 3055 (w), 3019 (w), 2997 (w), 2924 (m), 2852 (m), 2162 (w), 2050 (w), 1979 (w), 1980 (w), 1950 (w),

1677 (m), 1593 (m), 1572 (w), 1547 (w), 1500 (m), 1488 (m), 1457 (w), 1443 (m), 1414 (m), 1366 (w), 1347 (w), 1307 (w), 1285 (w), 1264 (m), 1226 (w), 1214 (w), 1191 (w), 1176 (m), 1156 (w), 1110 (m), 1073 (m), 1028 (m), 1018 (w), 1000 (w), 955 (w), 935 (m), 911 (m), 871 (m), 842 (m), 816 (m), 753 (s), 733 (m), 719 (m), 693 (s).

Synthesis of linear polyvinyl sulfide lin-P4. 1,4-Bis(phenylethynyl)benzene (278 mg, 1 mmol), 1,4-benzenedithiol (142 mg, 1 mmol), AIBN (16.4 mg, 0.1 mmol) and dry toluene (2 ml) were mixed together, stirred and purged with argon for 10 min. The reaction mixture was heated at 90 °C for 2 hours. The polymer was then precipitated in 300 ml of methanol, dissolved in a small amount of dichloromethane and reprecipitated in 300 ml of methanol. The final polymer was obtained as a yellowish powder after drying in a vacuum oven overnight at 35 °C.

^1H NMR (CDCl_3): δ (ppm) = 3.25–3.48 ($-\text{SH}$), 6.34–7.83 (aromatic and olefinic protons).

^{13}C NMR (CDCl_3): δ (ppm) = 120.8–140.9 (aromatic and olefinic CH and $\text{C}_{\text{quart.}}$).

FT-IR: ν (cm^{-1}) = 3077 (w), 3054 (m), 3021 (w), 2995 (w), 2167 (w), 2050 (w), 2012 (w), 1997 (w), 1980 (w), 1963 (w), 1947 (w), 1894 (w), 1881 (w), 1798 (w), 1752 (w), 1677 (w), 1598 (m), 1579 (m), 1545 (w), 1505 (m), 1489 (m), 1474 (m), 1444 (m), 1406 (m), 1388 (m), 1330 (w), 1309 (w), 1263 (w), 1233 (w), 1179 (m), 1157 (m), 1099 (m), 1075 (m), 1028 (m), 1012 (m), 1000 (w), 984 (w), 964 (w), 934 (m), 912 (m), 878 (m), 838 (w), 812 (m), 754 (s), 718 (w), 692 (s).

Acknowledgements

Studienstiftung des deutschen Volkes and Förderverein des Leibniz-Instituts für Polymerforschung are acknowledged for financial support. E. Schierz, K. Arnhold and P. Treppe (IPF Dresden) are acknowledged for conducting GC-MS, TGA, DSC and GPC measurements. This work is partly supported by the German Research Foundation (DFG) within the Cluster of Excellence 'Center for Advancing Electronics Dresden' and by the MRSEC Program of the National Science Foundation (NSF) under Award DMR-1121053 (BCS, CJH).

References

- 1 H. K. Raut, V. A. Ganesh, A. S. Nair and S. Ramakrishna, *Energy Environ. Sci.*, 2011, **4**, 3779–3804.
- 2 D. W. Mosley, K. Auld, D. Conner, J. Gregory, X. Q. Liu, A. Pedicini, D. Thorsen, M. Wills, G. Khanarian and E. Simon, *Proc. SPIE*, 2008, **6910**, 691017.
- 3 H. Ma, A. K. Y. Jen and L. R. Dalton, *Adv. Mater.*, 2002, **14**, 1339–1365.
- 4 M. Stroisch, T. Woggon, C. Teiwe-Morin, S. Klinkhammer, K. Forberich, A. Gombert, M. Gerken and U. Lemmer, *Opt. Express*, 2010, **18**, 5890–5895.
- 5 Z. B. Wang, M. G. Helander, J. Qiu, D. P. Puzzo, M. T. Greiner, Z. M. Hudson, S. Wang, Z. W. Liu and Z. H. Lu, *Nat. Photonics*, 2011, **5**, 753–757.
- 6 J. G. Liu and M. Ueda, *J. Mater. Chem.*, 2009, **19**, 8907–8919.

- 7 P. Ghosh, S. Katare, P. Patkar, J. M. Caruthers, V. Venkatasubramanian and K. A. Walker, *Rubber Chem. Technol.*, 2003, **76**, 592–693.
- 8 S. F. Chong, J. H. Lee, A. N. Zelikin and F. Caruso, *Langmuir*, 2011, **27**, 1724–1730.
- 9 I. Osaka and R. D. McCullough, *Acc. Chem. Res.*, 2008, **41**, 1202–1214.
- 10 J. Z. Liu, J. W. Y. Lam, C. K. W. Jim, J. C. Y. Ng, J. B. Shi, H. M. Su, K. F. Yeung, Y. N. Hong, M. Faisal, Y. Yu, K. S. Wong and B. Z. Tang, *Macromolecules*, 2011, **44**, 68–79.
- 11 C. K. W. Jim, A. Qin, J. W. Y. Lam, F. Mahtab, Y. Yu and B. Z. Tang, *Adv. Funct. Mater.*, 2010, **20**, 1319–1328.
- 12 A. B. Lowe, C. E. Hoyle and C. N. Bowman, *J. Mater. Chem.*, 2010, **20**, 4745–4750.
- 13 R. Hoogenboom, *Angew. Chem., Int. Ed.*, 2010, **49**, 3415–3417.
- 14 O. Nuyken and F. Siebzehnrübl, *Macromol. Chem. Phys.*, 1988, **189**, 541–547.
- 15 O. Nuyken and F. Siebzehnrübl, *Polym. Bull.*, 1988, **19**, 371–375.
- 16 E. Kobayashi, T. Ohashi and J. Furukawa, *Macromol. Chem. Phys.*, 1986, **187**, 2525–2533.
- 17 E. Kobayashi, T. Yoshino, S. Aoshima and J. Furukawa, *J. Polym. Sci., Part A: Polym. Chem.*, 1995, **33**, 2403–2414.
- 18 A. A. Oswald, K. Griesbaum, J. M. Bregman and B. E. Hudson, *J. Am. Chem. Soc.*, 1964, **86**, 2877.
- 19 J. M. Spruell, M. Wolffs, F. A. Leibfarth, B. C. Stahl, J. Heo, L. A. Connal, J. Hu and C. J. Hawker, *J. Am. Chem. Soc.*, 2011, **133**, 16698–16706.
- 20 R. Pötzsch, H. Komber, B. C. Stahl, C. J. Hawker and B. I. Voit, *Macromol. Rapid Commun.*, 2013, **34**, 1772–1778.
- 21 C. J. Hawker, *Macromolecular Architectures*, 1999, 147, pp. 113–160.
- 22 B. I. Voit and A. Lederer, *Chem. Rev.*, 2009, **109**, 5924–5973.
- 23 H. M. Shih, R. C. Wu, P. I. Shih, C. L. Wang and C. S. Hsu, *J. Polym. Sci., Part A: Polym. Chem.*, 2012, **50**, 696–710.
- 24 W. B. Wu, Z. C. Zhu, G. F. Qiu, C. Ye, J. G. Qin and Z. Li, *J. Polym. Sci., Part A: Polym. Chem.*, 2012, **50**, 5124–5133.
- 25 Y. Mori, K. Nakaya, X. Q. Piao, K. Yamamoto, A. Otomo and S. Yokoyama, *J. Polym. Sci., Part A: Polym. Chem.*, 2012, **50**, 1254–1260.
- 26 J. H. Tan, N. A. J. McMillan, E. Payne, C. Alexander, F. Heath, A. K. Whittaker and K. J. Thurecht, *J. Polym. Sci., Part A: Polym. Chem.*, 2012, **50**, 2585–2595.
- 27 K. Stumpe, H. Komber and B. I. Voit, *Macromol. Chem. Phys.*, 2006, **207**, 1825–1833.
- 28 J. Han, B. Zhao, A. J. Tang, Y. Q. Gao and C. Gao, *Polym. Chem.*, 2012, **3**, 1918–1925.
- 29 G. J. Chen, J. Kumar, A. Gregory and M. H. Stenzel, *Chem. Commun.*, 2009, 6291–6293.
- 30 O. Turunc and M. A. R. Meier, *J. Polym. Sci., Part A: Polym. Chem.*, 2012, **50**, 1689–1695.
- 31 D. Konkolewicz, S. Gaillard, A. G. West, Y. Y. Cheng, A. Gray-Weale, T. W. Schmidt, S. P. Nolan and S. Perrier, *Organometallics*, 2011, **30**, 1315–1318.
- 32 D. Konkolewicz, C. K. Poon, A. Gray-Weale and S. Perrier, *Chem. Commun.*, 2011, **47**, 239–241.
- 33 M. B. Vazquez-Santos, A. Martinez-Alonso and J. M. D. Tascon, *J. Anal. Appl. Pyrolysis*, 2012, **95**, 68–74.
- 34 H. Jiang, P. S. Lee and C. Z. Li, *Energy Environ. Sci.*, 2013, **6**, 41–53.
- 35 J. Brandrup, E. H. Immergut and E. A. Grulke, *Polymer Handbook*, Wiley & Sons, New York, 1999.
- 36 C. J. Yang and S. A. Jenekhe, *Chem. Mater.*, 1994, **6**, 196–203.
- 37 C. K. W. Jim, A. J. Qin, J. W. Y. Lam, M. Häußler, J. Z. Liu, M. M. F. Yuen, J. K. Kim, K. M. Ng and B. Z. Tang, *Macromolecules*, 2009, **42**, 4099–4109.
- 38 K. Kitamura, K. Okada, N. Fujita, Y. Nagasaka, M. Ueda, Y. Sekimoto and Y. Kurata, *Jpn. J. Appl. Phys., Part 1*, 2004, **43**, 5840–5844.
- 39 W. F. Ho, M. A. Uddin and H. P. Chan, *Polym. Degrad. Stab.*, 2009, **94**, 158–161.
- 40 N. Tsutsumi and M. Shinobu, *Appl. Phys. B: Lasers Opt.*, 2011, **105**, 839–845.
- 41 J. Y. Cho, K. J. Byeon, H. Park, J. Kim, H. S. Kim and H. Lee, *Nanoscale Res. Lett.*, 2011, **6**, 578.