# Solution-processable conjugated polymers containing alternating 1-alkyl-1,2,4-triazole and N=S=N links†

Mingfeng Wang and Fred Wudl\*

Received 2nd February 2010, Accepted 5th May 2010 First published as an Advance Article on the web 4th June 2010 DOI: 10.1039/c0jm00254b

Poly(sulfur nitride),  $[SN]_x$ , is an infinite  $\pi$ -bonded system and only known polymeric superconductor composed of nonmetallic elements. The appealing electronic properties of  $[SN]_x$ , along with the safety issue involved in the synthesis, have motivated research on  $[SN]_x$  analogues, for example, conjugated polymers consisting of sulfur–nitrogen moieties separated by heterocyclic groups. In this paper, we report an exploration for a new N=S=N-linked polymer, with a major objective to improve its solubility for low-cost, large-area fabrication of molecular devices based on a solution process. Specifically, we present the synthesis and characterization of a conjugated polymer based on alternating 1-alkyl-1,2,4-triazole and sulfur–nitrogen. We found that 4-dimethylamino pyridine is an effective catalyst for the polymerization of bis-*N*-sulfinyl-3,5-diamino-1-dodecyl-1,2,4-triazole, resulting in polymers that show a broad absorption band in the range of 400 to 600 nm. Moreover, this polymer exhibits high solubility in a variety of non-polar solvents, including tetrahydrofuran, chloroform, dichloromethane, and chlorobenzene.

### 1. Introduction

Poly(sulfur nitride),  $[SN]_x$ , was the first example of a polymeric metal and superconductor.1 Thanks to its two-dimensional character with a large degree of anisotropy; the electronic conductivity of  $[SN]_x$  is largest along the backbone direction, where the overlapping of  $\pi$ -orbitals on sulfur and nitrogen leads to the formation of a conduction band. Besides the electronic conductivity,  $[SN]_x$ shows high electronegativity, even greater than that of gold. Despite these appealing properties,<sup>2</sup> the exploitation of  $[SN]_{x}$  in electronic devices has been compromised by the explosive nature of the S<sub>4</sub>N<sub>4</sub> starting material and intermediate S<sub>2</sub>N<sub>2</sub> molecule that are key precursors in the synthesis of  $[SN]_x$ . This safety issue has prompted researches to investigate other synthetic strategies to  $[SN]_x$  or its analogues. To this end, polymers containing alternating sulfur-nitrogen moieties separated by heterocyclic groups have been synthesized.3 However, these polymers, to date, were insoluble in common solvents, raising a significant challenge for characterizing and processing these materials.

To meet the need of low-cost, large-area fabrication of molecular devices based on a solution process, it is important to explore new sulfur-nitrogen-based polymers that show both desired solubility and optoelectronic properties. Herein we report the synthesis and characterization of a conjugated polymer based on alternating 1-alkyl-1,2,4-triazole and sulfurnitrogen. Our initial objective of incorporating triazole units into the backbone of polymer chains relies on the intrinsic high electron affinity of triazoles and the established electron-injection/transport properties in devices such as organic light emitting diodes.<sup>4</sup> The combination of triazole with N=S=N links can lead to new n-type polymers with high electron affinity. The primary focus of this paper is to describe effective synthetic methodologies for highly soluble polymers containing N=S=N links in the backbone.

We have found that dimethylamino pyridine is a good polymerization catalyst for bis-*N*-sulfinyl-3,5-diamino-1-decyl-1,2,4-triazole, which was synthesized from the diamine with *N*-sulfinyl-*p*-toluenesulfonamide. These polymers, showing a broad absorption band in the range of 400 to 600 nm, are easily soluble in a variety of non-polar solvents such as tetrahydro-furan, chloroform, dichloromethane, and chlorobenzene.

### 2. Experimental section

### 2.1 Materials and instruments

Chemicals were purchased from Sigma-Aldrich or Across Organics and used as received without further purification. All dry solvents were freshly distilled under argon over an appropriate drying agent prior to use. <sup>1</sup>H and <sup>13</sup>C NMR spectra were obtained on a Varian Unity Inova 500 MHz spectrometer and referenced to the solvent peak. Mass spectrometry was performed by UC Santa Barbara Mass Spectrometry Laboratory. UV-vis spectra were recorded on an Agilent 8453 spectrophotometer using a THF solution in 1 cm quartz cuvettes or a drop-cast film on a quartz-slide at room temperature.

### 2.2 Synthesis of 3,5-diamino-1-decyl-1,2,4-triazole (DDTA)

The synthesis of 3,5-diamino-1-decyl-1,2,4-triazole followed a literature procedure.<sup>5</sup> To a 250 mL 3-neck round-bottom flask, 3,5-diamino-1,2,4-triazole (5.0 g, 0.05 mol) and methanol

Department of Chemistry and Biochemistry, Center for Polymers and Organic Solids, Mitsubishi Chemical Center for Advanced Materials and Materials Research Laboratory, University of California, Santa Barbara, CA, 93106-6105, USA. E-mail: wudl@chem.ucsb.edu

<sup>&</sup>lt;sup>†</sup> Electronic supplementary information (ESI) available: <sup>1</sup>H and <sup>13</sup>C NMR spectra of DDTA, UV-vis absorption spectra of PBSDDT-1 in THF in air, FTIR spectra of PBSDDT-1 purified twice, <sup>1</sup>H NMR and FTIR spectra of PBSDDT-2. See DOI: 10.1039/c0jm00254b

(80 mL) were added. The flask was equipped with a condenser, a N<sub>2</sub> inlet and an addition funnel. Metallic sodium (1.2 g, 0.05 mol) was added piece by piece to the mixture under stirring, resulting in a clear dark red solution. (Note: 3,5-diamino-1,2,4triazole itself is not soluble in methanol at room temperature.) The mixture was then heated to 80-85 °C for 1 h, followed by dropwise addition of 1-bromododecane (13.0 g, 0.052 mol) over 3 h. The mixture turned from dark red to bright vellow with the progress of the reaction. After 24 h of refluxing, the reaction was stopped by cooling down to room temperature. The solvent was removed under vacuum and the solid residue was re-dissolved in a mixture of 2-propanol (70 mL) and distilled water (30 mL) and was poured into 500 mL of distilled water. A pale yellow solid was collected by filtration, followed by drying at 50 °C for 3 days. Yield: 7.66 g (57%). <sup>1</sup>H NMR (DMSO-d<sub>6</sub>, 500 MHz): δ (ppm) 5.8 (s, 2H), 4.7 (s, 2H), 3.6 (t, 2H), 1.6 (t, 2H), 1.2-1.3 (m, 18H), 0.8-0.9 (t, 3H). <sup>13</sup>C NMR (DMSO-d<sub>6</sub>, 500 MHz): δ (ppm) 160, 154, 45, 32, 29, 28, 26, 22, 14. +ESI-TOF MS:  $M_{\rm w} = 267.41$  (calculated), m/z 268.27 (measured). Elemental analysis: calculated for C14H29N5: C 62.3, H 9.6, N 25.1%. Found: C 62.9, H 10.8, N 26.2%.

#### 2.3 Synthesis of N-sulfinyl-p-toluenesulfonamide

The synthesis of *N*-sulfinyl-*p*-toluenesulfonamide followed a procedure reported by Kresze.<sup>6</sup> *p*-Toluene sulfonamide (5.0 g, 0.029 mol), SOCl<sub>2</sub> (21 mL, 0.29 mol, freshly distilled) and 30 mL of anhydrous benzene were mixed in a 100 mL Schlenk flask. The mixture was kept at 85–95 °C for 3 days. The excess SOCl<sub>2</sub> and benzene were removed under vacuum, resulting in dark yellow viscous liquid, which solidified upon cooling to *ca.* -5 °C. (Note: this product was quickly hydrolyzed into *p*-toluene sulfonamide upon exposure to air.)

# 2.4 Synthesis of bis-*N*-sulfinyl-3,5-diamino-1-decyl-1,2,4-triazole (BSDDT-1) using *N*-sulfinyl-*p*-toluenesulfonamide

*N*-Sulfinyl-*p*-toluenesulfonamide (6.0 g, 0.028 mol) was dissolved in 25 mL of anhydrous benzene in a 100 mL Schlenk flask treated with 3,5-diamino-1-decyl-1,2,4-triazole (3.8 g, 0.014 mol) under a N<sub>2</sub> atmosphere, resulting in a dark red mixture. The mixture was stirred at room temperature in the dark for 5 days. A white solid that formed during the reaction was removed by filtration under N<sub>2</sub> atmosphere. The filtrate was dried under vacuum, resulting in a dark red gum. Yield: 2.1 g (48%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta$  (ppm) 4.2–4.4 (t, 2H), 1.7–2.0 (t, 2H), 1.1–1.4 (m, 18H), 0.7–0.9 (t, 3H).

# 2.5 Synthesis of poly(bis-*N*-sulfinyl-3,5-diamino-1-decyl-1,2,4-triazole) (PBSDDT-1) *via* 4-dimethylaminopyridine

Bis-*N*-sulfinyl-3,5-diamino-1-decyl-1,2,4-triazole (1.45 g, 4.7 mmol) was charged in a 50 mL Schlenk flask and 4-dimethylaminopyridine (DMAP) (0.571 g, 4.7 mmol) dissolved in 6 mL of freshly distilled  $CH_2Cl_2$  was added to the flask with a syringe. The mixture was allowed to stand under  $N_2$  atmosphere at room temperature in the dark for 2 days and treated with 40 mL of dry  $CH_3CN$ . The mixture was filtered under  $N_2$  atmosphere and the solid was washed with dry  $CH_3CN$  twice (30 mL each portion), followed by drying under vacuum at room temperature overnight. Yield: 0.9 g (78%), dark brown solid. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta$  (ppm) 4.2–3.6 (m, 2H), 1.9–1.7 (m, 2H), 1.4–1.1 (m, 18 H), 0.9–0.8 (t, 3H).

# 2.6 Synthesis of poly(bis-*N*-sulfinyl-3,5-diamino-1-decyl-1,2,4-triazole) (PBSDDT-2) *via* AlCl<sub>3</sub>

BSDDT-1 (0.51 g, 1.6 mmol), see above, AlCl<sub>3</sub> (4.5 g, 33.8 mmol) and freshly distilled toluene (10 mL) were mixed in a 50 mL Schlenk flask. The mixture was allowed to stand in the dark at room temperature for 2 days. The mixture was filtered under  $N_2$  atmosphere, followed by passing through diatomaceous earth to remove excess AlCl<sub>3</sub>. Drying of the filtrate under vacuum led to a dark brown solid. The <sup>1</sup>H NMR (Fig. S5†) and FTIR (Fig. S6†) spectra of this product are presented in the ESI†.

### 3. Results and discussion

Mainly two kinds of methods have been used so far to synthesize analogues of poly(sulfur nitride). The first one involves reactions of bis(trimethylsilyl)sulfur diimide with mono-<sup>7</sup> or di-functional arylsulfenyl chlorides.<sup>3b</sup> However, sulfur dichloride is no longer commercially available from reliable sources. The second method starts from the preparation of *N*-sulfinylamines that can be converted to sulfodiimides using a catalyst such as pyridine,<sup>3</sup> AlCl<sub>3</sub>,<sup>8</sup> and Na metal.<sup>6b</sup> Despite the success of these synthetic methods in making small molecules, very few conjugated polymers containing -N=S=N- units have been synthesized so far.<sup>3</sup>

Herein we report the synthesis and characterization of a conjugated polymer based on alternating 1-alkyl-1,2,4-triazole and sulfur-nitrogen. The synthetic route is shown in Scheme 1. In the exploration of soluble triazole molecules that are amenable for further functionalization, we started by using 3,5-diamino-1,2,4-triazole which is commercially available and low-cost. 3,5-Diamino-1,2,4-triazole itself is readily soluble in polar solvents such as water, DMF and DMSO but insoluble in either alcohols or non-polar solvents. To enhance the solubility of this molecule in organic solvents, it is necessary to introduce an alkyl chain. As a consequence, we started by refluxing 3,5diamino-1,2,4-triazole with either 1-bromohexane or 1-bromododecane in methanol in the presence of sodium metal, which automatically leads to the connection of the alkyl chains to N-1 position of 1,2,4-triazole.<sup>5</sup> In this paper, we mainly target efficient synthetic methodologies towards polymerization of monomers derived from 1-dodecyl-1,2,4-triazole. We expect that similar synthetic approaches could be applicable to more interesting triazole-based molecules such as 4-alkyl-1,2,4-triazoles.

#### 3.1 Monomer synthesis and characterization

We found that a hexyl group made 3,5-diamino-1,2,4-triazole soluble only in water or methanol, but not in less polar solvents such as 2-propanol and THF. Thus we synthesized 3,5-diamino-1-dodecyl-1,2,4-triazole (DDTA). The dodecyl hydrocarbon chain connected to the N-1 position of the triazole unit rendered this molecule soluble in a range of solvents, including dimethyl sulfoxide (DMSO), methanol, 2-propanol, acetone, tetrahydro-furan (THF), pyridine and dichloromethane. DDTA was insoluble in hexane, toluene, ethyl ether, acetonitrile or ethyl acetate, presumably due to the two polar –NH<sub>2</sub> groups.



Scheme 1 Synthetic approach to a conjugated polymer based on alternating 1-dodecyl-1,2,4-triazole and sulfur-nitrogen.

The treatment of DDTA with *N*-sulfinyl-*p*-toluenesulfonamide in benzene led to the formation of bis-*N*-sulfinyl-3,5-diamino-1-dodecyl-1,2,4-triazole (BSDDT-1) under mild conditions, accompanied by the formation of a white precipitate of *p*-toluenesulfonamide. The 'H NMR spectrum (Fig. 1A) of BSDDT-1 showed a triplet at 4.2 ppm that corresponds to the first methylene group next to the triazole. In addition, some *p*-toluenesulfonamide contaminated the BSDDT-1 after filtration, despite its marginal solubility in benzene. Further purification of BSDDT-1 proved to be difficult due to its sensitivity to atmospheric moisture.

In contrast to DDTA, BSDDT-1 was soluble in most of the nonpolar solvents such as pentane, hexane, toluene, THF, chloroform and dichloromethane. The product, a dark red solid that was stable under inert atmosphere, was sensitive to moisture, hydrolyzing immediately upon exposure to air with concomitant bleaching.



Fig. 1 <sup>1</sup>H NMR (CDCl<sub>3</sub>) of BSDDT-1 and PBSDDT-1. The BSDDT-1 monomer presented here was synthesized using *N*-sulfinyl-*p*-toluenesulfonamide as the sulfinylating agent.

#### 3.2 Polymer synthesis and characterization

We investigated two kinds of catalysts for the polymerization of BSDDT-1. The first was 4-dimethylaminopyridine (DMAP). There was no obvious change for the mixture of BSDDT-1 and 10 mol% DMAP in CH<sub>2</sub>Cl<sub>2</sub>, even over 24 h. In contrast, when the amount of DMAP was increased to 1 equivalent (relative to BSDDT), some black solid formed overnight, accompanied by a color change from dark red to dark brown. The material obtained in this way was insoluble in CH<sub>3</sub>CN. Considering the good solubility of both DMAP and *p*-toluenesulfonamide in CH<sub>3</sub>CN, we purified the final product by adding excess dry CH<sub>3</sub>CN to a concentrated solution of the reaction mixture in CH<sub>2</sub>Cl<sub>2</sub>, followed by filtration under N<sub>2</sub> atmosphere and a washing with CH<sub>3</sub>CN.

The final product, which appeared as a dark brown powder, was soluble in most non-polar solvents such as THF, CHCl<sub>3</sub>, CH<sub>2</sub>Cl<sub>2</sub>, chlorobenzene and toluene. The trace amount (*ca.* 2%) of impurities could be further removed by repeated precipitation of a CH<sub>2</sub>Cl<sub>2</sub> solution with CH<sub>3</sub>CN. However, over-purification resulted in a color change of the solid product from dark brown to orange, indicating partial hydrolysis during handling. The details of this hydrolysis will be discussed later in this section.

The <sup>1</sup>H NMR spectrum of the solid dissolved in CDCl<sub>3</sub> (Fig. 1B) shows that most of the impurities were removed from the final product after precipitation with CH<sub>3</sub>CN. Compared to the <sup>1</sup>H NMR spectrum of BSDDT (Fig. 1A), interestingly, the  $-CH_{2}$ - resonance connected to the triazole N-1 position in the polymer (denoted as PBSDDT) splits into four peaks at 4.2–3.6 ppm. The two peaks at 4.2 and 4.0 ppm, respectively, are multiplets. The one at 3.9 ppm with relatively high intensity appeared single and broad, while the one at 3.6–3.7 ppm was triplet. In addition, there are two broad peaks at 5.3 and 4.5 ppm, respectively, that correspond to the  $-NH_2$  group at the chain end of PBSDDT. The integration ratio of the peak at 4.5 ppm over that at 0.8–0.9 ppm (corresponding to  $-CH_3$ ) gives an average value of 11 for the number of repeating units.

Fig. 2 shows the FTIR spectra of PBSDDT-1 and DDTA. One can see two small peaks at 1215 and 1182 cm<sup>-1</sup>, respectively, in the sample of PBSDDT. Both peaks are assigned to the



Fig. 2 FTIR spectra of DDTA and PBSDDT-1. This polymer was synthesized from the polymerization of BSDDT that was prepared by using *N*-sulfinyl-*p*-toluenesulfonamide as the sulfinylating agent. DMAP was used as the catalyst for the polymerization. The inset shows the spectra in the window of  $1800-4000 \text{ cm}^{-1}$ .

asymmetric vibrations of -N=S=N- plus another strong peak at 1039 cm<sup>-1</sup> that may correspond to N–S bonds. In addition, the two peaks in the range of 3000–3600 cm<sup>-1</sup> corresponding to  $-NH_2-$  in PBSDDT decreased in intensity, compared to those of DDTA.

Fig. 3 shows the UV-vis absorption spectra of PBSDDT-1 (purified once by precipitation with CH<sub>3</sub>CN) and DDTA. The latter shows a narrow absorption band at 216 nm, without absorption in the visible range, whereas PBSDDT-1, dissolved in dry THF under Ar atmosphere, showed a broad absorption band centered at 476 nm with an onset around 630 nm. The absorption of PBSDDT-1 in solid film state showed no obvious shift compared to its absorption in THF. When the same sample was prepared under ambient condition, the absorption peak in the



**Fig. 3** UV-vis absorption spectra of PBSDDT-1 in THF and in solid films as cast on a quartz slide. For comparison, the absorption spectrum of DDTA is also shown. This polymer was synthesized from the polymerization of BSDDT-1 that was prepared by using *N*-sulfinyl-*p*-toluenesulfonamide as the sulfinylating agent. DMAP was used as the catalyst for the polymerization.



**Fig. 4** Evolution of <sup>1</sup>H NMR (CDCl<sub>3</sub>) spectrum of PBSDDT-1 during aging and purification. This polymer was synthesized from the polymerization of BSDDT-1 that was prepared by using *N*-sulfinyl-*p*-toluenesulfonamide as the sulfinylating agent. DMAP was used as the catalyst for the polymerization.

visible range shifted to 460 nm, accompanied by an increase in the absorption at both 285 and 214 nm (Fig. S3<sup>†</sup>).

In order to examine the stability of PBSDDT-1, we checked the <sup>1</sup>H NMR spectrum (Fig. 4B) of the same sample in CDCl<sub>3</sub> after standing in a capped and sealed NMR tube for 24 h. One can see that the intensity of the triplet peak at 3.6–3.7 ppm increased, whilst the intensity of the peak at 4.2 ppm decreased relative to the two peaks at 4.0 and 3.9 ppm, respectively. In addition, the single peak at 1.8 ppm splits into two after 24 h of aging. There is also a slight up-field shift (*ca.* 0.1 ppm) for the peaks at 4.0 ppm and 3.7 ppm.

The instability of PBSDDT-1 toward hydrolysis could be further discerned during the purification of PBSDDT-1 by a second precipitation in CH<sub>3</sub>CN. The <sup>1</sup>H NMR spectrum (Fig. 4C) shows no DMAP or *p*-toluenesulfonamide in the purified product. However, the two peaks at 4.2 and 4.0 ppm, respectively, disappeared, whilst the intensity of the triplet peak at 3.6–3.7 ppm increased. In addition, the two broad peaks at 1.6–1.9 ppm can be seen clearly, with a relative increase in the intensity for the peak at 1.7 ppm.

The <sup>1</sup>H NMR results (Fig. 1 and 4) described above imply several structural characteristics of PBSDDT-1. First, the multiple peaks at 4.2-3.6 ppm are presumably due to the relatively low regioregularity of this polymer. Similar to the case of regiorandom poly(3-alkylthiophene), one can imagine that several coupling modes, including head-to-head (HH), head-totail (HT) and tail-to-tail (TT), may exist during the polymerization of BSDDT-1. Second, the polydispersity of the polymer molecular weights may also contribute to these multiple peaks of the -CH<sub>2</sub> at N-1 position. The results above indicate that the chemical shift of the -CH2 at N-1 position is sensitive to the electron affinity of the groups linked to C-3 and C-5 of the triazole group. The peaks with larger chemical shifts (e.g. 4.2 and 4.0 ppm) presumably correspond to polymer chains with relatively long chain lengths, in which the long conjugation lengths lead to down-field shift of the proton signals for the first and the second -CH<sub>2</sub> groups linked to the triazole moiety.

The hydrolysis of PBSDDT-1 during the second purification was also reflected in the FTIR spectrum (Fig. S4<sup> $\dagger$ </sup>), in which the peak at 1215 cm<sup>-1</sup> disappeared, while the peak at 1183 cm<sup>-1</sup> and the one at 1038 cm<sup>-1</sup> were still present.

The cyclic voltammetry of PBSDDT-1 in dry  $CH_2Cl_2$  (containing 0.1 M tetrabutylammonium hexafluorophosphate, scanning rate: 100 mV s<sup>-1</sup>) showed an irreversible reduction peak at -0.94 V, and an irreversible oxidation peak at 1.1 V vs. ferrocene.

The second catalyst explored for the polymerization of BSDDT-1 was AlCl<sub>3</sub>. The reaction of BSDDT-1 solution (1 equivalent) with AlCl<sub>3</sub> (2 equivalent) in dry toluene led to a color change from dark red to purple over 3 days. The color of the mixture disappeared immediately upon dilution with dry THF, CH<sub>2</sub>Cl<sub>2</sub>, or CH<sub>3</sub>CN. When a large excess of AlCl<sub>3</sub> (> 10 equivalent) was used, the solution separated into two liquid layers: the upper layer was colorless, and the bottom layer was dark brown or dark green. After removal of most AlCl<sub>3</sub> by passing through diatomaceous earth, the final product (denoted as PBSDDT-2) was insoluble in toluene, but easily soluble (up to 10 mg mL<sup>-1</sup>) in THF, CH<sub>3</sub>CN, CHCl<sub>3</sub>, and CH<sub>2</sub>Cl<sub>2</sub>. The

polymer solution in each of these solvents maintained its color (dark red to brown) for a few hours at relatively high concentration (5–10 mg mL<sup>-1</sup>). But the color changed to pale yellow quickly upon further dilution, accompanied by formation of a white precipitate that was possibly from hydrolysis of AlCl<sub>3</sub>. The <sup>1</sup>H NMR spectrum (Fig. S5†) of this product showed a significant amount of *p*-toluenesulfonamide impurity that was difficult to remove. The FTIR spectrum (Fig. S6†) of this product showed a new band at 1186 cm<sup>-1</sup>, corresponding to the asymmetric vibration of the -N=S=N- group.

### 4. Summary

We have synthesized and characterized a solution-processable conjugated polymer containing alternating 1,2,4-triazole and N=S=N units. We have investigated two reagents for the polymerization of bis-*N*-sulfinyl-3,5-diamino-1-decyl-1,2,4-triazole (BSDDT). While AlCl<sub>3</sub> is effective for obtaining polymers with an extended  $\pi$ -conjugated electronic structure, it is difficult to remove AlCl<sub>3</sub> from the polymer, possibly because it may form complexes with the polymer.

We found that DMAP is effective to polymerize BSDDT. The polymers (PBSDDT), appearing as dark brown or black solids, are stable under inert atmosphere but hydrolyze upon exposure to air. These polymers are easily soluble in a variety of non-polar solvents, including tetrahydrofuran, chloroform, dichloromethane, and chlorobenzene. Visually smooth films can be obtained by spin-coating of the polymer solution (~10 mg mL<sup>-1</sup>) from chlorobenzene. Further research towards improving the stability of these polymers is under investigation. Such polymers containing N=S=N units may find applications in optoelectronic devices fabricated from a solution process.

### Acknowledgements

We are indebted to the Mitsubishi Center for Advanced Materials (MC-CAM) for support. M. Wang thanks the Natural Sciences and Engineering Research Council (NSERC) of Canada for support through a Postdoctoral Fellowship.

### References

- 1 J. M. Rawson and J. J. Longridge, Chem. Soc. Rev., 1997, 26, 53.
- 2 (a) M. J. Cohen and J. S. Harris, *Appl. Phys. Lett.*, 1978, 33, 812; (b)
  A. E. Thomas, J. Woods and Z. V. Hauptman, *J. Phys. D: Appl. Phys.*, 1983, 16, 1123; (c) V. V. Walatka, M. M. Labes and J. H. Perlstein, *Phys. Rev. Lett.*, 1973, 31, 1139.
- 3 (a) F. Wudl, E. T. Zellers and D. Nalewajek, J. Org. Chem., 1980, 45, 3211; (b) J. C. W. Chien and M. Y. Zhou, J. Polym. Sci., Part A: Polym. Chem., 1986, 24, 2947.
- 4 (a) S. H. Chen, C. S. Shiau, L. R. Tsai and Y. Chen, *Polymer*, 2006, 47, 8436; (b) A. W. Grice, A. Tajbakhsh, P. L. Burn and D. D. C. Bradley, *Adv. Mater*, 1997, 9, 1174; (c) Y. Shirota and H. Kageyama, *Chem. Rev.*, 2007, 107, 953.
- 5 L. D. Yagodarova, E. A. Danilova and R. P. Smirnov, *Russ. J. Gen. Chem.*, 2003, **73**, 308.
- 6 (a) G. Kresze, A. Maschke, K. Bederke, H. P. Patzschke, R. Albrecht,
   H. Smalla and A. Trede, *Angew. Chem., Int. Ed.*, 1962, 74, 135; (b)
   G. Kresze and W. Wucherpf, *Angew. Chem., Int. Ed.*, 1967, 6, 149.
- 7 J. Kuyper and G. B. Street, J. Am. Chem. Soc., 1977, **99**, 7848.
- 8 G. Kresze and W. Wucherpfennig, Tetrahedron Lett., 1966, 7, 1671.