

Synthesis of novel polymeric energy materials with high nitrogen content by double click functionalization

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Received : August 20, 2015 Accepted : March 1, 2016

Abstract

A novel approach to produce polymeric energy materials with high nitrogen contents is described. Electron-rich alkynes in the polymer side chain are sequentially functionalized by two different click reactions. A [2+2] cycloaddition-retroelectrocyclization with tetracyanoethylene (TCNE) proceeds at room temperature without any side reactions yielding the 1,1,4,4-tetracyanobutadiene (TCBD) unit. This transformation efficiently increases the nitrogen content of the resulting polymer. The cyano groups of the TCBD unit are subjected to the cyano-azide cycloaddition reaction in the presence of zinc chloride (ZnCl₂) or silver trifluoromethanesulfonate (AgOTf). The successful formation of tetrazole products is suggested from elemental analyses and thermal analysis.

Keywords : click chemistry, elemental analysis, functionalization of polymers, polystyrene

1. Introduction

Nitrogen-rich compounds are some of the most common energetic materials, and significant efforts have been devoted to develop novel high-performance energetic nitrogen compounds¹⁻⁸. To this end, the synthetic route to the target compounds as well as the chemical and thermal stabilities of the intermediate compounds must be carefully considered. During the course of our research program about the click postfunctionalization of aromatic polymers, we have shown that the nitrogen content of the precursor polymers can be efficiently enhanced by the [2+2] cycloaddition-retroelectrocyclization between alkynes and tetracyanoethylene (TCNE), namely, the alkyne-acceptor click reactions, yielding the 1,1,4,4-tetracyanobutadiene (TCBD) unit⁹⁻¹¹. We now propose a further increase in the nitrogen content in terms of the second click postfunctionalization of the resulting TCBD polymer with sodium azide (NaN₃). It was previously reported that the cyano-azide cycloaddition yielding tetrazole products could be promoted by zinc chloride (ZnCl₂)¹². In addition to ZnCl₂, silver trifluoromethanesulfonate (AgOTf) was also investigated,

because this metal ion was selectively coordinated to the cyano-nitrogen atoms of the TCBD units¹³. The nitrogen contents of the resulting polymers were carefully determined by elemental analyses.

2. Experimental

2.1 General

¹H- and ¹³C-Nuclear magnetic resonance (NMR) spectra were measured on a JEOL model AL300 spectrometer at 20°C. Chemical shifts are reported in ppm downfield from tetramethylsilane (SiMe₄), using the solvent's residual signal as an internal reference. The resonance multiplicity is described as s (singlet), d (doublet), and m (multiplet). Attenuated total reflectance Fourier transform infrared (ATR-FT-IR) spectra (4000-1000 cm⁻¹) were recorded on a JASCO FT/IR-4100 spectrometer. Gel permeation chromatography (GPC) was measured on a JASCO system equipped with polystyrene gel columns using tetrahydrofuran (THF) as an eluent at the flow rate of 1.0 mL min⁻¹ after calibration with standard polystyrenes. Matrix assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectra were measured on a

Shimadzu/Kratos AXIMA-CFR mass spectrometer using dithranol as a matrix. Ultraviolet-visible (UV-Vis) spectra were recorded on a JASCO V-670 spectrophotometer. Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) measurements were carried out on a Rigaku TG8120 under a nitrogen flow or air. A small portion (0.5–1.0 mg) of a sample was placed in an aluminum pan and heated at the scan rate of 10 °C min⁻¹.

2.2 Materials

All chemical were purchased from Kanto, TCI, and Aldrich, and used without further purifications.

3. Results and discussion

Polystyrene was selected as a common polymer backbone to examine the proposed double click postfunctionalization. *N,N*-Dihexadecyl-4-((4-vinylphenyl)ethynyl) aniline (**1**) was newly designed as a styrene monomer. The hexadecyl chains were introduced in order to enhance the solubility of the corresponding polymer in organic solvents, which allowed for the quantitative structure analysis by spectroscopic techniques. **1** was synthesized by the Sonogashira cross-coupling reaction between 1-ethynyl-4-vinylbenzene and *N,N*-dihexyl-4-iodoaniline in 64% yield. ¹H-NMR (300 MHz, CDCl₃): δ 0.89 (t, J = 7.3 Hz, 6H), 1.27 (m, 52H), 1.55 (m, 4H), 3.27 (t, J = 7.3 Hz, 4H), 5.27 (d, J = 9.9 Hz, 1H), 5.76 (d, J = 18.3 Hz, 1H), 6.57 (d, J = 9.3 Hz, 2H), 6.70 (dd, J = 9.9, 18.3 Hz, 1H), 7.36 (d, J = 8.1 Hz, 4H), 7.45 ppm (d, J = 9.0 Hz, 2H). ¹³C-NMR (75 MHz, CDCl₃): δ 14.28, 22.85, 27.28, 27.36, 29.52, 29.67, 29.76, 29.81, 29.86, 32.08, 51.11, 87.30, 91.82, 108.77, 111.32, 114.22, 123.84, 126.21, 131.50, 133.01, 136.56, 136.59, 148.09 ppm. IR (neat): ν 2954, 2917, 2848, 2206, 1623, 1608, 1595, 1521, 1469, 1409, 1365, 1317, 1287, 1267, 1247, 1227, 1209, 1193, 1179, 1163, 1130 cm⁻¹. MALDI-TOF MS (dithranol): m/z: calcd for C₄₈H₇₇N 667.61 g mol⁻¹; found 668.57 g mol⁻¹ [M+H]⁺.

Poly(*N,N*-dihexadecyl-4-((4-vinylphenyl)ethynyl) aniline) (**P1**) was prepared by atom transfer radical polymerization of **1** (Figure 1). To an ample bottle, **1** (0.47 g, 0.70 mmol), *N,N,N',N''*-tetramethylethylenetriamine (PMDETA, 1.2 mg, 7 μmol), copper (I) bromide (CuBr, 1.0 mg, 7 μmol), ethyl 2-bromopropionate (1.3 mg, 7 μmol), and toluene (1.0 mL) were added, and the solution was vacuum sealed after freeze-thaw cycles (x6). The mixture was heated to 110 °C for 24 h, cooled to 20 °C, and THF (3 mL) was added. The solution was passed through

a plug (neutral aluminium oxide (Al₂O₃), THF), concentrated in vacuo, and poured into methanol (MeOH, 500 mL). The precipitate was collected by filtration, and reprecipitation from dichloromethane (CH₂Cl₂) to MeOH afforded **P1** (0.11 g, 23%). ¹H-NMR (300 MHz, C₆D₆): δ 0.94 (br s, 6nH), 1.37–1.51 (m, 59nH), 3.10 (br s, 4nH), 6.56 (m, 4 nH), 7.68 ppm (m, 4nH). IR (neat): ν 2921, 2850, 2209, 1602, 1520, 1465, 1398, 1367, 1196, 1136 cm⁻¹. GPC (THF): M_w 16800, M_n 13100. Elemental analysis calcd. (%) for (C₄₈H₇₇N)_n: C 86.29, H 11.62, N 2.10; found: C 85.61, H 11.48, N 2.08. As described above, the chemical structure of **P1** was characterized by ¹H NMR and IR spectra, and the molecular weight (M_w) and polydispersity (M_w/M_n) were 16800 and 1.27, respectively.

P1 possessed the side chain alkynes activated by the dialkylaniline donor. Therefore, the TCBD units were quantitatively constructed in the monomer repeat unit by the [2+2] cycloaddition-retroelectrocyclization with TCNE in a click chemistry fashion as follows: Poly(2-(4-(dihexadecylamino)phenyl)-3-(4-vinylphenyl)buta-1,3-diene-1,1,4,4-tetracarbonitrile) (**P2**) was prepared by click postfunctionalization of **P1** with TCNE. To a solution of **P1** (96.9 mg, 0.145 mmol repeat unit⁻¹) in chloroform (CHCl₃, 8.6 mL), a solution of TCNE (18.6 mg, 0.145 mmol) in 1,2-dichloroethane (4.0 mL) was added. The mixture was stirred at 20 °C for 1 h, and the solvent was evaporated, yielding **P2** (115.4 mg, 99.9%). ¹H-NMR (300 MHz, C₆D₆): δ 0.94 (br s, 6nH), 1.39 (m, 59nH), 2.94 (br s, 4nH), 6.56 (m, 4 nH), 7.90 ppm (m, 4nH). IR (neat): ν 2922, 2851, 2214, 1602, 1540, 1485, 1455, 1415, 1343, 1297, 1264, 1210, 1181, 1082 cm⁻¹. GPC (THF): M_w 16400, M_n 12700. Elemental analysis calcd. (%) for (C₅₄H₇₇N₅)_n: C 81.46, H 9.75, N 8.80; found: C 80.63, H 9.75, N 8.54. It should be noted that the experimentally determined nitrogen content dramatically increased from 2.08% (**P1**) to 8.54% (**P2**) by this click reaction. The nitrogen contents were in good agreement with the calculated values, supporting the clean transformation of the polymer structures.

The different side chain structures of **P1** and **P2** were also suggested by the UV-Vis absorption spectra. Due to the intramolecular charge-transfer of the dialkylaniline-substituted TCBD, **P2** showed a low energy absorption at 486 nm in 1,2-dichlorobenzene. In contrast, the precursor polymer **P1** did not display such a low energy band. Interestingly, we have previously found from the comprehensive cation recognition experiments using

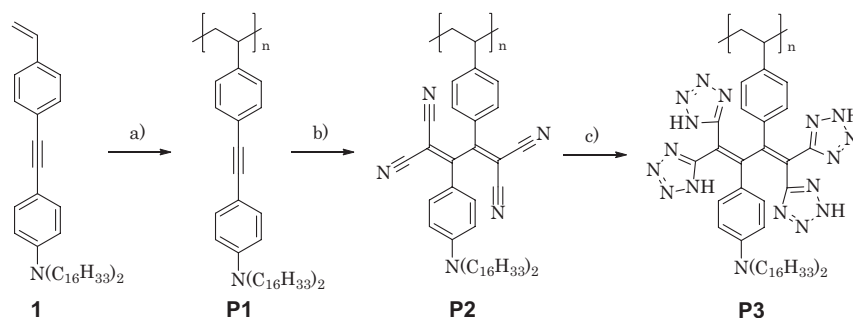


Figure 1 Click synthesis of tetrazole-containing polystyrene. a) CuBr, PMDETA, ethyl 2-bromopropionate, toluene, 110 °C, 24 h; b) TCNE, CHCl₃/1,2-dichloroethane, 20 °C, 1 h; c) NaN₃, ZnCl₂ or AgOTf, DMF or 1,2-dichlorobenzene, 140 °C, 48 h.

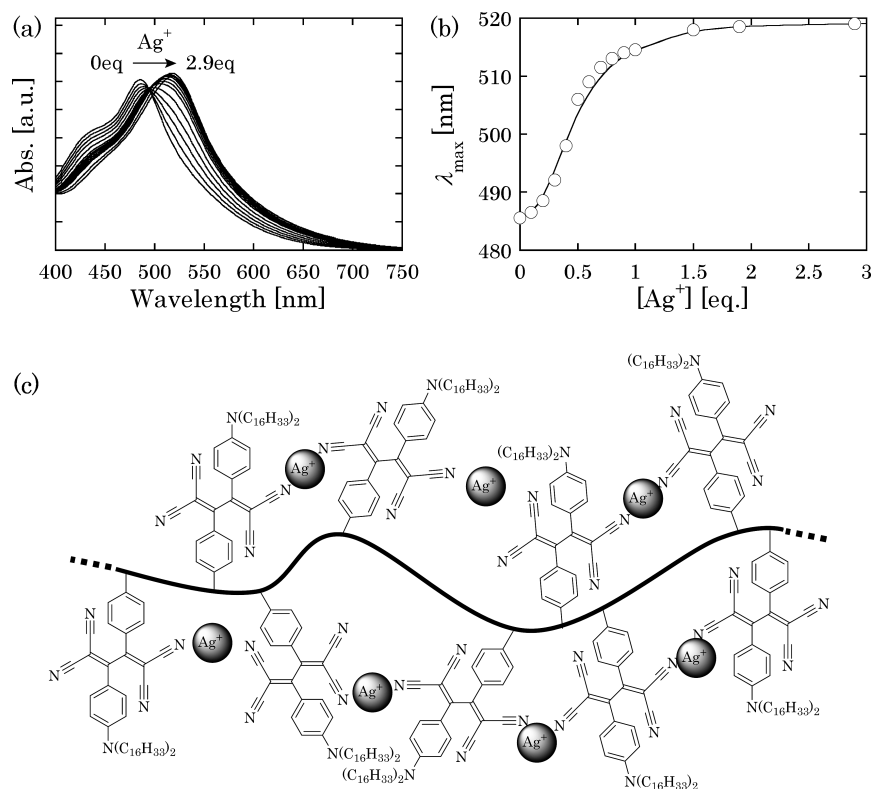


Figure 2 (a,b) UV-vis absorption spectral change of **P2** in 1,2-dichlorobenzene upon the addition of AgOTf and (c) schematic illustration of the Ag⁺ ion recognition by the TCBD side chains.

lithium (Li⁺), sodium (Na⁺), potassium (K⁺), magnesium (Mg²⁺), scandium (Sc³⁺), titanium (Ti³⁺), manganese (Mn²⁺), iron (Fe²⁺ and Fe³⁺), cobalt (Co²⁺), copper (Cu⁺ and Cu²⁺), zinc (Zn²⁺), palladium (Pd²⁺), silver (Ag⁺), tin (Sn²⁺), and gold (Au⁺) ions that the side chain TCBD units specifically interact with silver (Ag⁺) ions in chlorinated solvents.¹⁴ This event resulted in the change in the absorption spectra. Similar to previous reports,^{15–17} the longest wavelength absorption maximum (λ_{\max}) of **P2** gradually shifted in the longer wavelength direction as more Ag⁺ ions were recognized at the side chain TCBD units (Figure 2). Plots of the λ_{\max} versus the added Ag⁺ ion amount suggested that the bathochromic shift saturates at 518 nm when 2.0 equiv. of Ag⁺ ions with respect to the polymer repeat unit are added. This result implied that the average coordination number of the Ag⁺ ion is 2. It should also be noted that this multiple coordination of the cyano groups occurs only when polymeric TCBDs are designed^{15–17}.

Based on the specific recognition behavior of Ag⁺ ions by the TCBD cyano groups, we expected that the Ag⁺ ions serve as a catalyst for the addition reactions of the cyano groups. Therefore, further transformation of the polymer side chain was attempted using click postfunctionalization based on the cyano-azide cycloaddition in the presence of metal catalysts. It was previously reported that the cyano-azide cycloaddition is an effective click reaction to prepare polymeric tetrazole derivatives. For example, polyacrylonitrile was successfully converted into poly(vinyl tetrazole) through the reaction with NaN₃ in the presence of ZnCl₂.¹² We first applied the same reaction conditions to the

postfunctionalization of **P2** for the conversion of the TCBD cyano groups into the tetrazole groups. The synthetic procedure of poly(4-(1,1-di(1*H*-tetrazol-5-yl)-4,4-di(2*H*-tetrazol-5-yl)-3-(4-vinylphenyl)buta-1,3-dien-2-yl)-*N,N*-dihexadecylaniline) (**P3**) is as follows: To a solution of **P2** (14.9 mg, 0.0188 mmol repeat unit⁻¹) in *N,N*-dimethylformamide (DMF, 1.8 mL), NaN₃ (19.6 mg, 0.301 mmol) and ZnCl₂ (47.9 mg, 0.352 mmol) were added. The mixture was heated to 140 °C for 48 h under nitrogen (N₂). After cooling to 60 °C, 0.1 N hydrochloric acid (HCl, 2.0 mL) was added dropwise. The red precipitate was collected and washed with 0.1 N HCl and water. The solid was dried in vacuo at 40 °C (14.6 mg, 90.6%). ¹H-NMR (300 MHz, THF-d₈): δ 0.90 (br s, 6nH), 1.30 (m, 59nH), 2.54 (br s, 4nH), 10.84 ppm (br s, nH). IR (neat): ν 2922, 2851, 2214, 1602, 1540, 1485, 1455, 1415, 1343, 1297, 1264, 1210, 1181, 1082 cm⁻¹. Elemental analysis calcd. (%) for (C₅₄H₈₁N₁₇)_n: C 66.98, H 8.43, N 24.59; found: C 68.32, H 9.00, N 14.78.

It was found that the resulting red precipitate (**P3**) was insoluble in CHCl₃, partially soluble in DMF, and sufficiently soluble in THF. Therefore, the ¹H NMR of **P3** was measured in deuterized tetrahydrofuran (THF-d₈). Although most of the aromatic peaks were broadened, a low magnetic-field peak ascribed to the tetrazole moieties newly appeared (vide supra). In the IR spectrum of **P3**, the cyano (C≡N) vibrational peak intensity at 2214 cm⁻¹ became weak as compared to that of **P2** (Figure 3). These results again support the progress of the cyano-azide cycloaddition and the formation of tetrazole units. A further strong support was the elemental analysis. The nitrogen content of **P3** prepared in the presence of ZnCl₂ was reasonably increased from 8.54% (for **P2**) to 14.78%

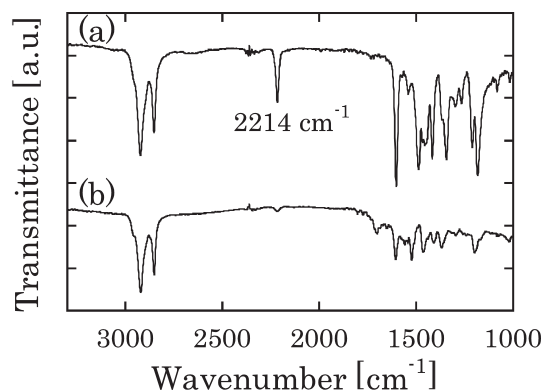


Figure 3 IR spectra of (a) **P2** and (b) **P3** prepared in the presence of ZnCl_2 .

Table 1 Elemental analysis of polystyrene derivatives.

	Calcd. [%]			Found [%]		
	C	H	N	C	H	N
P1	86.29	11.62	2.10	85.61	11.48	2.08
P2	81.46	9.75	8.80	80.63	9.75	8.54
P3^a	66.98	8.43	24.59	68.32	9.00	14.78
P3^b	66.98	8.43	24.59	54.51	6.59	12.03

^a Prepared in the presence of ZnCl_2 . ^b Prepared in the presence of AgOTf .

(Table 1). This result suggested that the cyano-azide cycloaddition is effective even for the conjugated cyano moieties. However, it should be noted that the transformation of the TCBD cyano groups into the tetrazole units was incomplete probably due to the steric reason and limited space of polymer side chains.

The click postfunctionalization of **P2** was also attempted in the presence of Ag^+ ions (AgOTf), because the spectroscopic characterization suggested the strong recognition of the Ag^+ ions by the cyano groups. In this case, the solvent must be carefully selected because the occurrence of Ag^+ ion recognition depends on the solvents. Although the reaction did not proceed in DMF or THF, it was successful in 1,2-dichlorobenzene at 140 °C for 48 h. The synthetic procedure is as follows: To a solution of **P2** (16.9 mg, 0.021 mmol repeat unit⁻¹) in 1,2-dichlorobenzene (1.8 mL), NaN_3 (22.1 mg, 0.340 mmol) and AgOTf (10.8 mg, 0.042 mmol) were added. The mixture was heated to 140 °C for 48 h under N_2 . After cooling to 20 °C, the solvent was evaporated. The solid was washed with 0.1 N HCl and water, and dried in vacuo at 40 °C (17.9 mg, 98.0%). The resulting solid (**P3**) was partially soluble in CHCl_3 and THF, but the well-resolved NMR peaks could not be detected in the deuterized solvents. The elemental analysis of this polymer (Elemental analysis found (%): C 54.51, H 6.59, N 12.03) revealed the nitrogen content of 12.03%, which was lower than that prepared in the presence of ZnCl_2 . The result is reasonable when the ionic radii of Zn^{2+} (74 pm) and Ag^+ (126 pm) are considered. It was thought that the larger Ag^+ ion could not effectively function as a catalyst in the confined polymer side chains.

Finally, the thermal decomposition of **P2** and **P3**, prepared in the presence of ZnCl_2 , was investigated by

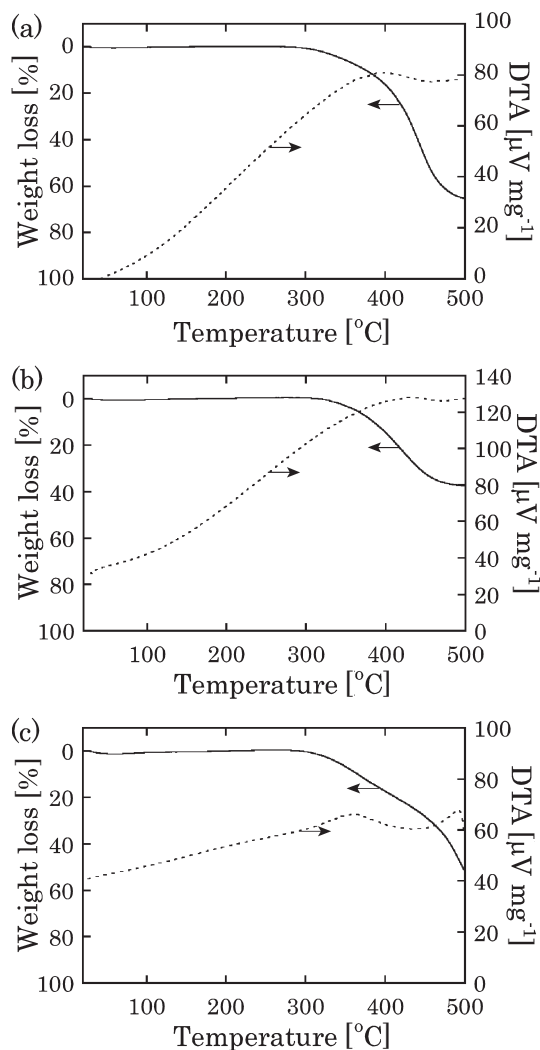


Figure 4 TGA and DTA curves of (a) **P2** under N_2 , (b) **P3** under N_2 , and (c) **P3** under air, at the heating rate of 10 °C min⁻¹. **P3** was prepared in the presence of ZnCl_2 .

TGA and DTA. It was reported that polymeric tetrazole decomposes in two steps under air, i.e., the first degradation of the azole ring ($T_d = 291$ °C) and the second degradation of the polymeric residue ($T_d = 342$ °C).¹⁸⁾ In our case, the first decomposition occurred at slightly lower temperature of ca. 280 °C, which might be due to the higher heating rate (Figure 4(c)). The second decomposition was apparently observed at > 400 °C. The DTA measurements revealed two exothermic peaks at 362 and 492 °C, corresponding to the first and second decompositions, respectively. Both peaks suggested oxidative decomposition, and they explicitly shifted to higher temperature as compared to the reported values (291 and 342 °C)¹⁸⁾. When the TGA measurements of **P3** were performed under N_2 , the onset decomposition temperature shifted to higher temperature (ca. 320 °C), and there was no second degradation (Figure 4 (b)). There was indeed only one peak top at 405 °C in the DTA. Both TGA and DTA results again support the oxidative degradation of **P3** when it was heated under air. Furthermore, it was found that the thermal behavior of **P3** is very similar to that of **P2** (Figure 4 (a)), although the DTA peak values are slightly different (429 °C for **P2** and

405 °C for P3).

4. Conclusion

In conclusion, an efficient way of synthesizing polymeric materials with high nitrogen contents was developed by the sequential double click postfunctionalization. The alkyne-acceptor click chemistry produced the tetracyanated (TCBD) chromophores in the polystyrene side chains. This quantitative transformation of the polymer side chains dramatically increased the nitrogen content to 8.54%. A further increase in the nitrogen content was achieved by cyano-azide click chemistry. Although the transformation into the tetrazole unit was not quantitative, the nitrogen content of the polystyrene derivative successfully exceeded 10%. In the future, the replacement of hexadecyl groups, which was used for the solubility increase in this study, by shorter alkyl chains will definitely enhance the nitrogen content, e.g., 43% nitrogen in the case of methyl groups. The methodology of synthesizing oligo and poly(tetrazole)s from simple alkyne compounds will lead to the development of novel advanced energetic materials.

Acknowledgements

This research was supported by the Foundation for the Promotion of the Industrial Explosives Technology, JSPS KAKENHI Grant Number 15KT0140, and the Support for Tokyotech Advanced Researchers (STAR). The authors thank the Center for Advanced Materials Analysis, Tokyo Institute of Technology, for the elemental analyses.

References

- 1) O. Kwon and M. L. McKee, *Theor. Comput. Chem.*, **12**, 405–420 (2003).

- 2) B. M. Rice, E. F. C. Byrd, and W. D. Mattson, "Structure and Bonding", Vol. 127, pp. 153–194, Springer (2007).
- 3) W. Liu, S.-h. Li, Y.-c. Li, Y.-z. Yang, Y. Yu, and S.-p. Pang, *J. Mater. Chem. A*, **2**, 15978–15986 (2014).
- 4) J. Zhang, D. A. Parrish, and J. M. Shreeve, *Chem. Commun.*, **51**, 7337–7340 (2015).
- 5) K. Yin, Y. Wang, H. Liu, F. Peng, and L. Zhang, *J. Mater. Chem. A*, **3**, 4188–4194 (2015).
- 6) H. Wei, J. Zhang, and J. M. Shreeve, *Chem. Asian J.*, **10**, 1130–1132 (2015).
- 7) D. Fischer, T. M. Klapötke, M. Reymann, J. Stierstorfer, and M. B. R. Völkl, *New. J. Chem.*, **39**, 1619–1627 (2015).
- 8) Y. Ling, X. Ren, W. Lai, and J. Luo, *Eur. J. Org. Chem.*, **2015**, 1541–1547 (2015).
- 9) T. Michinobu, *Pure Appl. Chem.*, **82**, 1001–1009 (2010).
- 10) T. Michinobu, *Chem. Soc. Rev.*, **40**, 2306–2316 (2011).
- 11) T. Michinobu, *Macromol. Chem. Phys.*, **216**, 1387–1395 (2015).
- 12) N. V. Tsarevsky, K. V. Bernaerts, B. Dufour, F. E. Du Prez, and K. Matyjaszewski, *Macromolecules*, **37**, 9308–9313 (2004).
- 13) T. Michinobu, Y. Li, and T. Hyakutake, *Phys. Chem. Chem. Phys.*, **15**, 2623–2631 (2013).
- 14) Y. Washino and T. Michinobu, *Macromol. Chem. Phys.*, **215**, 1485–1490 (2014).
- 15) Y. Li, M. Ashizawa, S. Uchida, and T. Michinobu, *Macromol. Rapid Commun.*, **32**, 1804–1808 (2011).
- 16) Y. Li, M. Ashizawa, S. Uchida, and T. Michinobu, *Polym. Chem.*, **3**, 1996–2005 (2012).
- 17) Y. Li and T. Michinobu, *J. Mater. Chem.*, **22**, 9513–9521 (2012).
- 18) S. V. Levchik, E. E. Bol'vanovich, A. I. Lesnikovich, O. A. Ivashkevich, P. N. Gaponik, and S. V. Vyazovkin, *Thermochim. Acta*, **168**, 211–221 (1990).