# Synthesis of Poly(*m*-phenylene) and Poly(*m*-phenylene)-*block*-Poly(3-hexylthiophene) with Low Polydispersities

# KAORU OHSHIMIZU,<sup>1</sup> AYUMI TAKAHASHI,<sup>1</sup> TOMOYA HIGASHIHARA,<sup>1,2</sup> MITSURU UEDA<sup>1</sup>

 <sup>1</sup>Department of Organic and Polymeric Materials, Graduate School of Science and Engineering, Tokyo Institute of Technology, 2-12-1-H-120, O-okayama, Meguro-Ku, Tokyo 152-8552, Japan
<sup>2</sup>PRESTO, Japan Science and Technology Agency (JST), 4-1-8, Honcho, Kawaguchi, Saitama 332-0012, Japan

Received 28 February 2011; accepted 1 April 2011 DOI: 10.1002/pola.24703 Published online 27 April 2011 in Wiley Online Library (wileyonlinelibrary.com).

**ABSTRACT**: Well-defined poly(*m*-phenylene) (PMP), which is poly(1,3-dibutoxy-*m*-phenylene), was successfully synthesized via Grignard metathesis polymerization. PMP with a reasonably high number-average molecular weight ( $M_n$ ) of 25,900 and a very low polydispersity index of 1.07 was obtained. The polymerization of a Grignard reagent monomer, 1-bromo-2,4-dibutoxy-5-chloromagnesiobenzene, proceeded in a chain-growth manner, probably due to the meta-substituted design producing a short distance between the MgCl and Br groups and thereby making a smooth nickel species (-C-Ni-C-) transfer to the intramolecular chain end (-C-Ni-Br) over a

**INTRODUCTION** Well-defined architectures of polymers are quite important to clarify the relationships between structures and properties. However, the control of the molecular weights (MWs) and polydispersity indices (PDIs) of condensation polymers is generally very difficult compared to a controlled system based on the addition or ring-opening living polymerization. Since Yokozawa<sup>1,2</sup> and McCullough<sup>3,4</sup> independently discovered the quasi-living system of Grignard metathesis (GRIM) polymerization for synthesizing regioregular poly(3-hexylthiophene) (P3HT) with well-controlled MWs and PDIs, various P3HT-based block copolymers have been reported.<sup>5-9</sup> These materials generally formed nanofiber structures as thin film on various substrates.<sup>10–14</sup> Other well-defined  $\pi$ -conjugated polymers, such as poly(*p*-phenylene)s (PPPs)<sup>15</sup> and polypyrroles,<sup>16</sup> have also been successfully prepared based on the GRIM polymerization system.

Although some controlled systems for  $\pi$ -conjugated polymers other than P3HT were discovered,<sup>17–21</sup> attention has focused only on the AB type diblock copolythiophenes, and new combination of different main chains is very limited. Three synthetic examples of well-defined block copolymers with different main chains, poly(2,5-dihexyloxy-1,4-phenylene)(PPP)-*b*-P3HT,<sup>14,22</sup> PPP-*b*-poly(*N*-hexylpyrrole),<sup>23</sup> and P3HT-*b*-poly(9,9-dioctylfluorene),<sup>24</sup> were very recently reported, based on the sequential quasi-living GRIM polymerization. Among them, only one article described the benzene ring. PMP showed a good solubility in the common organic solvents, such as tetrahydrofuran,  $CH_2CI_2$ , and  $CHCI_3$ . Furthermore, a new block copolymer comprised of PMP and poly(3-hexylthiophene) was also prepared. The tapping mode atomic force microscopy image of the surface of the block copolymer thin film on a mica substrate showed a nanofibril morphology with a clear contrast. © 2011 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 49: 2709–2714, 2011

**KEYWORDS**: conjugated polymers; diblock copolymers; GRIM polymerization; molecular weight distribution; poly(*m*-phenylene)

phase-separated behavior of PPP-*b*-P3HT in 2009 by Wu et al.<sup>14</sup> They reported that PPP-*b*-P3HT showed phase-separated crystalline–crystalline domains and a lamellar morphology by differential scanning calorimetry (DSC) and atomic force microscopy (AFM), respectively. With regard to the poly(*m*-phenylene)s (PMPs) having an amorphous nature, there have been neither information about a controlled synthetic system for block copolymers nor even for homopolymers. Therefore, their fundamental properties and morphologies are still unknown.

In this article, we report for the first time the GRIM polymerization of a meta-substituted monomer, 1-bromo-2,4-dibutoxy-5-iodobenzene (2), which yields PMP with very low PDI. We expect that the *meta*-substituted design is favorable for the smooth intramolecular transfer of a nickel species (-C-Ni-C-) to the chain end (-C-Ni-Br), walking over a benzene ring, because of a shorter distance between the MgCl and Br groups than the para-substituted one, which lead to the facile control of the polymerization system. Furthermore, new block copolymers with PMP and P3HT segments can be successfully synthesized, while maintaining a low PDI by a similar addition sequence of monomers to PPP-*b*-P3HT.<sup>22</sup> The phase-separated behavior of poly(1,3dibutoxy-*m*-phenylene)-*b*-poly(3-hexylthiophene) (PMP-b-P3HT) is also observed by DSC and AFM.

Correspondence to: M. Ueda (E-mail: ueda.m.ad@polymer.titech.ac.jp) or T. Higashihara (E-mail: thigashihara@polymer.titech.ac.jp) Journal of Polymer Science Part A: Polymer Chemistry, Vol. 49, 2709–2714 (2011) © 2011 Wiley Periodicals, Inc.



SCHEME 1 Synthesis of compound 2.

# **EXPERIMENTAL**

# Materials

Tetrahydrofuran (THF) was dried over sodium benzophenone and distilled before use under nitrogen. 4-Bromo-6iodoresorcinol<sup>25</sup> and 2-bromo-3-hexyl-5-iodothiophene  $(1)^1$ were prepared according to the literature. 1-Bromo-2,4-dibutoxy-5-iodobenzene (2) was prepared (Scheme 1) by modifying the procedure in a previous report.<sup>25</sup> Lithium chloride was dried by a heat-gun under reduced pressure and used under nitrogen. All other reagents and solvents were used without further purification.

#### Synthesis of 1-Bromo-2,4-dibutoxy-5-iodobenzene (2)

A THF (100 mL) solution of 4-bromo-6-iodoresorcinol (3.67 g, 11.6 mmol), PPh<sub>3</sub> (6.72 g, 25.6 mmol), and 1-butanol (1.90 g, 25.6 mmol) were cooled to 0 °C. To the solution was added diethyl azodicarboxylate in toluene solution (12.0 mL, 26.3 mmol, 40% w/v), and the reaction mixture was warmed to room temperature and stirred for 1 h at the temperature. It was then poured into hexane and filtered. The filtrate was evaporated, and the residue was recrystallized from methanol to give white needles (3.5 g, 70% yield); m.p. = 73.8-74.5 °C.

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, ppm, 25 °C):  $\delta$  = 7.83 (s, ArH, 1H), 6.39 (s, ArH, 1H), 3.99 (q, -OCH<sub>2</sub>-, 4H), 1.81 (m, -CH<sub>2</sub>-, 4H), 1.55 (m, -CH<sub>2</sub>-, 4H), 0.99 (m, -CH<sub>3</sub>, 6H). <sup>13</sup>C NMR (300 MHz, CDCl<sub>3</sub>, ppm, 25 °C):  $\delta$  = 158.1, 156.8, 141.3, 103.7, 98.8, 75.2, 69.5, 69.3, 31.3, 31.2, 19.5, 19.4, 14.0. Anal. Calcd. for C<sub>14</sub>H<sub>20</sub>BrIO<sub>2</sub>; C, 39.37; H, 4.72; Br, 18.71; I, 29.71; 0, 7.49. Found: C, 39.46; H, 4.62.

# Synthesis of Poly(1,3-dibutoxy-m-phenylene)

A round-bottomed flask equipped with a three-way stopcock was charged with lithium chloride (0.10 g, 2.36 mmol) and heated by a heat-gun under reduced pressure. After the flask was cooled to room temperature under a nitrogen atmosphere, 2 (214 mg, 0.501 mmol) and THF (10 mL) were added, and the mixture was stirred at room temperature. To the mixture was added <sup>i</sup>PrMgCl (2.0 M solution in THF, 0.287 mL, 0.574 mmol) via a syringe, and the mixture was stirred for 30 min. Next, a suspension of Ni(dppp)Cl<sub>2</sub> (3.0 mg, 0.0055 mmol) in dry THF (3.0 mL) was added to the mixture via a syringe, and then the mixture was stirred for 24 h. The polymerization was quenched by the addition of 5M HCl solution. The polymer solution was poured into a mixture solution of methanol (200 mL) and water (200 mL). and the residue was filtered, washed with methanol, and dried under reduced pressure to give PMP ( $M_{\rm p} = 25,900$ , PDI = 1.07) as a yellow solid (64.0 mg, 62%).<sup>1</sup>H NMR (300

MHz, CDCl<sub>3</sub>, ppm, 25 °C):  $\delta$  = 7.16 (s, ArH, 1H), 6.47 (s, ArH, 1H), 3.84 (m, -OCH<sub>2</sub>-, 4H), 1.56 (m, -CH<sub>2</sub>-, 4H), 1.27 (m, -CH<sub>2</sub>-, 4H), 0.75 (m, -CH<sub>3</sub>, 6H).

# Synthesis of PMP-b-P3HT

A round-bottomed flask equipped with a three-way stopcock was charged with lithium chloride (0.21 g, 4.95 mmol) and heated by a heat-gun under reduced pressure. After the flask was cooled to room temperature under a nitrogen atmosphere, **2** (428 mg, 1.00 mmol) and THF (20 mL) were added, and the mixture was stirred at room temperature. To the mixture was added <sup>*i*</sup>PrMgCl (2.0 M solution in THF, 0.551 mL, 1.10 mmol) via a syringe, and the mixture was stirred for 30 min at the temperature. Then, a suspension of Ni(dppp)Cl<sub>2</sub> (6.8 mg, 0.0125 mmol) in dry THF (5.0 mL) was added to the mixture via a syringe. The polymerization continued for 1 h at room temperature, and then a solution of the Grignard exchanged compound **1** in dry THF (5 mL) was added to the mixture. The Grignard exchanged compound **1** solution was prepared as follows.

A round-bottomed flask equipped with a three-way stopcock was charged with lithium chloride (0.21 g, 4.95 mmol), and heated by a heat-gun under reduced pressure. The flask was cooled to room temperature under a nitrogen atmosphere. Then, compound **1** (0.365 mg, 0.978 mmol) and THF (5 mL) were added, and the mixture was stirred at 0 °C for 30 min. To the mixture was added <sup>i</sup>PrMgCl (2.0 M solution in THF, 0.538 mL, 1.076 mmol) via a syringe, and the mixture was stirred for 30 min at 0 °C.

The polymerization of the second monomer was continued for 1 h at room temperature and quenched by addition of 5M HCl solution. Then, the polymer solution was poured into a mixture solution of methanol (200 mL) and water (200 mL), and the residue was filtered and purified via a Soxhlet extraction with methanol. The residue was extracted again with chloroform using a Soxhlet apparatus. Chloroform was removed by evaporation under reduced pressure, and the polymer was dried overnight under reduced pressure to give PMP-*b*-P3HT ( $M_n = 16,400$ , PDI = 1.15) as a purple solid (0.185 g, 52%).

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, ppm, 25 °C):  $\delta = 7.18$  (s, Ar H, 1H), 6.99 (s, thiophene, 1H), 6.51 (s, ArH, 1H), 3.86 (t,  $-\text{OCH}_2-$ , 4H), 2.83 (t,  $-\text{CH}_2$  (P3HT), 2H), 1.80–0.75 (m, alkyl, 7H + 11H(P3HT)).

# Measurement

The <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded with a Bruker DPX300S spectrometer. Size exclusion chromatography (SEC) was performed on an Asahi Techneion AT-2002 equipped with a Viscotek TDA model 305 triple detector array using THF as a carrier solvent at a flow rate of 1.0 mLmin<sup>-1</sup> at 30 °C. Three polystyrene gel columns of pore sizes (650, 200, and 75 Å) (bead size 9  $\mu$ m) were used. The absolute  $M_n$  values were calculated by collecting data from right-angle laser light scattering (RALLS). Thermal analysis was performed on a Seiko EXSTAR 6000 TG/DTA 6300 thermal analyzer at a heating rate of 10 °C min<sup>-1</sup> for thermogravimetry (TG) and



SCHEME 2 Synthesis of PMP.

on a DSC 6200 at a heating rate of 20 °C min<sup>-1</sup> for DSC under nitrogen. UV-vis spectra of polymer thin films and solutions in CHCl<sub>3</sub> at  $10^{-5}$  mol L<sup>-1</sup> were taken on a Jasco V-560 UV-vis spectrophotometer over a wavelength range of 250-750 nm. AFM images were taken with a SII-NT SPA 400 operating in a tapping mode.

# **RESULTS AND DISCUSSION**

#### Synthesis of Monomer 2

We have already reported the synthesis of PMP by oxidation coupling polymerization of 1,3-di-n-butoxybenzene.<sup>26</sup> However, their molecular weight distributions were broad, based on a conventional polycondensation system. To obtain PMP with a high MW and a low PDI, the monomer **2** was designed and successfully prepared by Scheme 1, as identified by <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra and elemental analysis.

#### Synthesis of Poly(1,3-dibutoxy-m-phenylene)

We first examined the Grignard exchange reaction of monomer **2** with an equivalent molar ratio of <sup>*i*</sup>PrMgCl in the presence of LiCl in THF at room temperature for 30 min, followed by quenching with methanol under the same conditions reported in a previous study.<sup>10</sup> The quantitative and selective Grignard exchange reaction at the iodine-substituted 5-position proceeded as confirmed by the <sup>1</sup>H NMR spectra.

Based on this result, the nickel-catalyzed cross-coupling polymerization of the Grignard exchanged monomer **2** was carried out at room temperature in THF in the presence of LiCl (Scheme 2). The polymerization initiated with Ni(dppp)Cl<sub>2</sub> (dppp = 1,3-bis(diphenylphosphino)propane) successfully proceeded to give PMP with a 67% conversion and the  $M_n$ and PDI values determined by SEC-RALLS were 25,900 and 1.07, respectively. The incomplete monomer conversion might be derived from the deactivation process of the Grignard exchanged monomer **2** during the long polymerization time of 24 h. As Yokozawa and coworkers<sup>15,22</sup> reported, the



FIGURE 1 <sup>1</sup>H NMR spectrum of PMP in CDCl<sub>3</sub>.

monomer conversions of the Grignard exchanged products of 1,4-dibromo-2,5-dihexyloxybenzene and 1-bromo-2,5-dihexy-loxy-4-iodobenzene were also around 70% for the synthesis of the PPPs.

PMP well dissolves in the common organic solvents, such as THF, CH<sub>2</sub>Cl<sub>2</sub>, and CHCl<sub>3</sub>. This good solubility is attributed to the twisted structure of the meta-linked main chain in addition to the dibutoxy side chains. The obtained polymer, PMP, was characterized by a <sup>1</sup>H NMR spectrum and size exclusion chromatography - right-angle laser light scattering (SEC-RALLS) profile. Figure 1 shows the <sup>1</sup>H NMR spectrum of PMP, in which the characteristic signal assignable to the oxymethylene proton appears at 3.84 ppm. The SEC-RALLS profile of PMP is shown in Figure 2, which displays a unimodal peak with the very low PDI of 1.07. This low PDI should be due to the chain-growth polymerization mechanism occurring by a catalyst transfer condensation polymerization.<sup>1-4</sup> For the synthesis of P3HT using the catalyst transfer polycondensation system, Ni(dppp)Cl<sub>2</sub> reacts with 2 equiv. of 1, and the coupling reaction occurs with the concomitant generation of a zero-valent Ni complex. In this case, the Ni(0) species does not diffuse to the reaction solution media but is selectively transferred to the intramolecular C-Br bond. Another **1** reacts with this Ni inserted dimer, followed by the cross-coupling reaction and transfer of the Ni catalyst to the next C-Br bond. The chain-growth reactions continue in such a way that the Ni catalyst transfers to the polymer end group over a thiophene ring without diffusion. This selective Ni transfer system should be due to the proper distance between the C-MgCl and C-Br groups. Because, the polymerization of dihalogenated monomers based on the

![](_page_2_Figure_15.jpeg)

FIGURE 2 SEC-RALLS profile of PMP.

![](_page_3_Figure_1.jpeg)

**FIGURE 3** <sup>1</sup>H NMR spectrum of P3HT-*b*-PMP.

![](_page_3_Figure_3.jpeg)

FIGURE 4 <sup>1</sup>H NMR spectrum of PMP-*b*-P3HT.

fluorene,<sup>27</sup> carbazole,<sup>28</sup> and bithiophene<sup>29</sup> structures, having longer distances than the thiophene monomers, could not maintain the low PDI, probably due to the diffusion of Ni(0) species to the reaction solution media, which leads to the general condensation polymerization. Similarly, in the case of the *meta*-substituted monomer **2**, the shorter distance between the C—MgCl and C—Br groups of PMP than that of PPP leads to the very low PDI.

The thermal property of PMP was evaluated by thermogravimetric analyzer (TGA) and DSC. PMP exhibited the relatively high-degradation temperature (10% weight loss) of 390 °C and the glass transition temperature ( $T_g$ ) of 24 °C (Fig. 6) under nitrogen, which are values similar to those found in a ref. 26.

# Synthesis of PMP-b-P3HT

For the synthesis of the block copolymers of P3HT and PMP, we first conducted the polymerization of **1** in THF initiated by Ni(dppp)Cl<sub>2</sub> in the presence of LiCl, followed by the postpolymerization of **2**. The <sup>1</sup>H NMR spectrum (Fig. 3) of the product showed that a very small amount of the PMP monomer units were contained. The low conversion of **2** may be due to the wrong order (**1** to **2**) of monomer addition as previously reported.<sup>22</sup> Thus, the block copolymerization was then carried out in the reversed order (**2** to **1**) (Scheme 3). This order would be preferable due to the better  $\pi$ -donor ability of P3HT than that of PMP, where  $\pi$ -electrons of the polymers are considered to assist the transfer of the Ni(0) species during the catalyst-transfer polymerization. In practice, the block copolymer, PMP-*b*-P3HT, with the  $M_n$  of

16,400 and low PDI (1.15) was obtained. The obtained block copolymer, PMP-*b*-P3HT, was characterized by <sup>1</sup>H NMR spectroscopy and SEC-RALLS. Figure 4 shows the <sup>1</sup>H NMR spectrum of PMP-*b*-P3HT, in which a triplet signal due to the oxymethylene protons (a) next to the phenylene ring of PMP segment and a triplet signal assignable to the methylene protons (b) of P3HT segment are observed at 3.86 and 2.83 ppm, respectively. The molar ratio of the segment units (n:m) for PMP:P3HT was 21:79 determined by the integration of signals (a) and (b); however, the feed ratio of the monomers was 50:50. This difference is due to the incomplete conversion of monomer **2** due to the deactivation; however, the SEC profile of PMP-*b*-P3HT shows a unimodal peak with a low PDI and without shoulders (Fig. 5), which indicates the formation of the expected block copolymer.

The phase transition temperatures of PMP-*b*-P3HT were measured by DSC in a nitrogen atmosphere (Fig. 6). The DSC profile of the PMP homopolymer is also included for comparison. The block copolymer exhibits two phase transition temperatures at 16 and 220–240 °C, which can be ascribed to the glass transition temperature ( $T_g$ ) of PMP and the melting points ( $T_m$ ) of the P3HT segments, respectively, by comparing the DSC scans of PMP-*b*-P3HT and the PMP homopolymer. The double signals present in the  $T_m$  of the P3HT segment are attributed to a combination of melting processes, which is consistent with a previous report.<sup>30,31</sup> This result clearly indicates the emergence of a microphase separation between the PMP and P3HT segments in the PMP-*b*-P3HT. To further confirm the

![](_page_3_Figure_11.jpeg)

SCHEME 3 Synthesis of PMP-b-P3HT.

![](_page_4_Figure_1.jpeg)

FIGURE 5 SEC-RALLS profile of PMP-b-P3HT.

![](_page_4_Figure_3.jpeg)

FIGURE 6 DSC profile of PMP and PMP-*b*-P3HT. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

![](_page_4_Figure_5.jpeg)

**FIGURE 7** AFM image of PMP-*b*-P3HT on mica substrate cast from toluene.

![](_page_4_Figure_7.jpeg)

**FIGURE 8** UV-vis spectra of PMP, P3HT, and PMP-*b*-P3HT in film state, respectively. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

microphase separation of PMP-*b*-P3HT, its thin film was prepared by drop casting from a 1 mg mL<sup>-1</sup> toluene solution onto a mica substrate, and the solution was slowly evaporated at room temperature for 2 days to promote the phase separation. The surface morphology of the thin film was characterized by AFM. As shown in Figure 7, the film clearly exhibited a lamellar-like phase-separated morphology induced by the different nature of the crystalline P3HT and amorphous PMP segments.

The optical properties of PMP and PMP-*b*-P3HT were further investigated by UV-vis spectroscopy. The UV-vis spectra of P3HT, PMP, and PMP-*b*-P3HT in the film state were investigated (Fig. 8). The shoulder at 610 nm of PMP-*b*-P3HT is related to the vibronic absorption of the P3HT segment and is an indicator of the high degree of ordering of the intermolecular P3HT chains, despite the presence of the covalently bonded amorphous PMP segment.

# CONCLUSIONS

Poly(1,3-dibutoxy-*m*-phenylene) (PMP) with a high MW and a very low PDI of 1.07 was successfully synthesized via the GRIM polymerization. PMP showed a relatively high thermal stability and good solubility in the common organic solvents. Furthermore, the PMP-*b*-P3HT diblock copolymer was synthesized by sequential GRIM polymerization. It is quite important to set the addition order of the monomers for the efficient crossover reactions and postpolymerization of the second monomer. The diblock copolymer, PMP-*b*-P3HT, exhibited two endothermal transitions corresponding to the  $T_{\rm g}$  of the PMP blocks and the  $T_{\rm m}$  of the P3HT blocks, respectively, which is indicative of an amorphous–crystalline nature and the existence of microphase-separated domains. The formation of the microphase-separated nanostructures was also supported by AFM observations.

This work was partially supported by the Japan Science and Technology Agency (JST) PRESTO program. This work was also supported in part by Japan and Research Fellowships of the Japan Society for the Promotion of Science for Young Scientists.

# **REFERENCES AND NOTES**

1 Yokoyama, A.; Miyakoshi, R.; Yokozawa, T. Macromolecules 2004, 37, 1169–1171.

**2** Miyakoshi, R.; Yokoyama, A.; Yokozawa, T. J Am Chem Soc 2005, 127, 17542–17545.

**3** Sheina, E. E.; Liu, J.; Iovu, M. C.; Laird, D. W.; McCullough, R. D. Macromolecules 2004, 37, 3526–3528.

4 Iovu, M. C.; Sheina, E. E.; Gil, R. R.; McCullough, R. D. Macromolecules 2005, 38, 8649–8656.

5 Yokozawa, T.; Yokoyama, A. Chem Rev 2009, 109, 5595-5619.

**6** Lim, H.; Huang, K. T.; Su, W. F.; Chao, C. Y. J Polym Sci Part A: Polym Chem 2010, 48, 3311–3322.

**7** Tsai, J. H.; Chueh, C. C.; Chen, W. C.; Yu, C. Y.; Hwang, G. W.; Ting, C.; Chen, E. C.; Meng, H. F. J Polym Sci Part A: Polym Chem 2010, 48, 2351–2360.

**8** Wu, P. T.; Ren, G.; Kim, F.; Li, C.; Mezzenga, R.; Jenekhe, S. A. J Polym Sci Part A: Polym Chem 2010, 48, 614–626.

**9** Lee, Y.; Fukukawa, K. Bang, J.; Hawker, C. J.; Kim, J. K. J Polym Sci Part A: Polym Chem 2008, 46, 8200–8205.

10 Ohshimizu, K.; Ueda, M. Macromolecules 2008, 41, 5289-5294.

**11** Zhang, Y.; Tajima, K.; Hirota, K.; Hashimoto, K. J Am Chem Soc 2008, 130, 7812–7813.

**12** Zhang, Y.; Tajima, K.; Hashimoto, K. Macromolecules 2009, 42, 7008–7015.

**13** Wu, P. T.; Ren, G.; Li, C.; Mezzenga, R.; Jenekhe, S. A. Macromolecules 2009, 42, 2317–2320.

**14** Wu, S.; Bu, L.; Huang, L.; Yu, X.; Han, Y.; Geng, Y.; Wang, S. Polymer 2009, 50, 6245–6251.

**15** Miyakoshi, R.; Shimono, K.; Yokoyama, A.; Yokozawa, T. J Am Chem Soc 2006, 128, 16012–16013.

**16** Yokoyama, A.; Kato, A.; Miyakoshi, R.; Yokozawa, T. Macromolecules 2008, 41, 7271–7273. **17** Holder, E.; Tessler, N.; Rogach, A. L. J Mater Chem 2008, 18, 1064–1078.

**18** Tsami, A.; Yang, X. H.; Galbrecht, F.; Farrell, T.; Li, H.; Adamczyl, S.; Heiderhoff, R.; Balk, L. J.; Neher, D.; Holder, E. J Polym Sci Part A: Polym Chem 2007, 45, 4773–4785.

**19** Tsami, A.; Yang, X. H.; Farrell, T.; Neher, D.; Holder, E. J Polym Sci Part A: Polym Chem 2008, 46, 7794–7808.

20 Kanelidis, I.; Ren, Y.; Lesnyak, V.; Gasse, J. C.; Frahm, R.; Eychmueller, A.; Holder, E. J Polym Sci Part A: Polym Chem 2011, 49, 392–402.

**21** Kanelidis, I.; Vaneski, A.; Lenkeit, D.; Pelz, S.; Elsner, V.; Stewart, R. M.; Rodriguez-Fernandez, J.; Lutich, A. A.; Susha, A. S.; Theissmann, R. Adamczyk, S.; Rogach, A. L.; Holder, E. J Mater Chem 2011, 21, 2656–2662.

**22** Miyakoshi, R.; Yokoyama, A.; Yokozawa, T. Chem Lett 2008, 37, 1022–1023.

23 Yokoyama, A.; Kato, A.; Miyakoshi, R.; Yokozawa, T. Macromolecules 2008, 41, 7271–7273.

24 Javier, A. E.; Varshney, S. R.; McCullough, R. D. Macromolecules 2010, 43, 3233–3237.

**25** Shimizu, H.; Fujimoto, K.; Furusyo, M.; Maeda, H.; Nanai, Y.; Mizuno, K.; Inouye, M. J Org Chem 2007, 72, 1530–1533.

**26** Okada, T.; Fujiwara, N.; Ogata, T.; Haba, O.; Ueda, M. J Polym Sci Part A: Polym Chem 1997, 35, 2259–2266.

27 Huang, L.; Wu, S.; Qu, Y.; Geng, Y.; Wang, F. Macromolecules 2008, 41, 8944–8947.

**28** Stefan, M. C.; Javier, A. E.; Osaka, I.; McCullough, R. D. Macromolecules 2009, 42, 30–32.

29 Beryozkina, T.; Senkovskyy, V.; Kaul, E.; Kiriy, A. Macromolecules 2008, 41, 7817–7823.

**30** Causin, V.; Marega, C.; Marigo, A.; Valentini, L.; Kenny, J. M. Macromolecules 2005, 38, 409–415.

**31** Boudouris, B. W.; Frisbie, C. D.; Hillmyer, M. A. Macromolecules 2008, 41, 67–75.