Synthesis and self-assembly of a novel amphiphilic diblock copolymer consisting of isotactic polystyrene and 1,4-trans-polybutadiene-graft-poly(ethylene oxide)

HuaQing Liang, QiHua Zhou, YongJiang Long, WanChu Wei, Shuo Feng, GuoDong Liang and FangMing Zhu

Herein, a novel amphiphilic diblock copolymer consisting of isotactic polystyrene (iPS) and 1,4-trans-polybutadiene-graft-poly(ethylene oxide) (1,4-trans-PBD-g-PEO), was synthesized by the combination of living coordination copolymerization and graft copolymerization. iPS-b-1,4-trans-PBD was firstly synthesized via sequential monomer addition in the presence of 1,4-dithiabutandiyl-2,2’-bis(6-cumyl-4-methylphenoxy) titanium dichloride (complex 1) activated by trisobutyl aluminum modified methylaluminoxane (MMAO). Moreover, hydroboration of double bonds in the 1,4-trans-PBD blocks were performed with 9-borabicyclo[3.3.1]nonane (9-BBN) and subsequent oxidation by NaOH/H2O2 to form hydroxys. Consequently, PEO was grafted into the hydroxylated 1,4-trans-PEO. The insoluble crystalline block (iPS) and the polymerisates were respectively iPS and 1,4-trans-polybutadiene (1,4-trans-PBD) with narrow molecular weight distribution. Furthermore, the diblock copolymer consisting of iPS and 1,4-trans-PBD was synthesized by this [OSSO]-Ti complex via sequential monomer addition, which makes it possible for the research into the self-assembly of iPS-core diblock copolymers in selective solvent.

The self-assembly of crystalline-coil diblock copolymers has drawn general attention at recent years because of their remarkable advantages. The insoluble crystalline block undergoes microphase separation and aggregation to form the core of micelle-like objects, surrounded by a solvent-swollen corona that provides colloidal stability. Crystalline-coil diblock copolymers can enrich the nano structures of the micelles as some complex architectures may be obtained by controlling the crystallization pathway. There are several strategies for the crystallization-driven self-assembly of the crystalline-coil block copolymers, that are, thermally controlled crystallization, morphological transitions, hierarchical assembly, and “living” crystallization. In most cases, the crystalline-coil diblock copolymers contain a crystalline core-forming block such as polyethylene (PE), poly(ferrocenyldimethylsilane) (PFDMs), polyethylene oxide (PEO), poly(l-lactide)
toluene was then rapidly added to this styrene. A 6.3 mL of a 1.9 M solution of MMAO in -heptane, and 5.0 mL of a solution of 10 mol [OSSO]-Ti complex in -dodecane was added dropwise. A reaction mixture was terminated by introducing 2 mL ethanol containing the antioxidant. The polymer was precipitated in 200 mL ethanol acidified with 20 mL concentrated hydrochloric acid, recovered by filtration, washed with an excess of ethanol, and dried to constant weight under vacuum at room temperature.

Preparation of isotic poly(styrene-block-hydroxylated 1,4-trans-polybutadiene). The hydroboration of -b-1,4-trans-PBD was performed in a Schlenk flask equipped with a condenser. -b-1,4-trans-PBD was dissolved in dry THF and then 9-BBN was added dropwise at room temperature. After hydroboration at 75 °C for 48 h, the reaction solution was cooled to 0 °C. The required amount of 6 M NaOH (aq.) and then 30 wt% H2O2 (aq.) was added dropwise. After oxidation at 50 °C for 24 h, the -b-hydroxylated 1,4-trans-PBD was precipitated into water and filtered. The resultant polymer was washed with methanol for several times to remove traces of boric acid.

Preparation of isotic poly(butadiene-graft-poly(ethylene oxide)) (-b-(1,4-trans-PBD-g-PEO)). -b-(1,4-trans-PBD-g-PEO) was prepared by ring-opening graft copolymerization of ethylene oxide on hydroxylated 1,4-trans-PBD block initiated by naphthalene/potassium. The -b-1,4-trans-PBD and dry THF was placed in a Schlenk flask at room temperature. Graft copolymerization of ethylene oxide was initiated by a dark green THF solution of naphthalene/potassium at −40 °C for 5 min. Heating temperature to 25 °C, the reaction was carried out for more than 24 h until the solution turned to light yellow. The copolymerization solution was quenched with concentrated hydrochloric acid acidic methanol, and then the polymer was precipitated in diethyl ether. After isolation by filtration, the polymer was purified by removing poly(ethylene oxide) homopolymer through dialyzed against deionized water. The insoluble fraction of the -b-(1,4-trans-PBD-g-PEO) was dried under vacuum.

The self-assembly of -b-1,4-trans-PBD in -dodecane. 1,4-trans-PBD can rapidly dissolve in -dodecane after slightly heated, while -b can not dissolve in -dodecane after heated to 150 °C, which demonstrate that -dodecane is a selective solvent for -b-1,4-trans-PBD. Moreover, tetrahydrofuran (THF) is a good solvent for both -b and 1,4-trans-PBD. The solvent-induced self-assembly of -b-1,4-trans-PBD can be generally proceeding as follows. Taking the preparation of self-assembled solution of 0.5 mg mL⁻¹ for example, 5.0 mg of -b-1,4-trans-PBD was dissolved in about 2 mL THF and the solution was added to 10 mL -dodecane dropwise to obtain a light blue solution indicating the self-assembly of -b-1,4-trans-PBD in -dodecane. Then the THF was completely removed by vacuum evaporation for several hours proved by ¹H NMR.

The self-assembly of -b-(1,4-trans-PBD-g-PEO) in aqueous solution. Water is a suitable selective solvent for the self-assembly of -b-(PBD-g-PEO). The solvent-induced self-assembly of -b-(PBD-g-PEO) is generally proceeding as follows. 5.0 mg of -b-(1,4-trans-PBD-g-PEO) was dissolved in about 2 mL of THF and the solution was added to 10 mL of deionized water to obtain a light blue solution, implying the self-assembly of -b-(1,4-trans-PBD-g-PEO) in aqueous solution.

### Experimental

#### Materials

All reagents were purchased from Aladdin and J&K Scientific. Styrene was dried with calcium hydride and distilled on a vacuum line. 1,3-butadiene was dried with calcium hydride at −40 °C and distilled at room temperature to form a toluene solution. Tetrahydrofuran (THF) was dried by distilling from potassium with benzophenone as an indicator. Toluene was dried by distilling from sodium with benzophenone as an indicator. 9-Borabicyclo[3.3.1]nonane (9-BBN) (Aladdin, 0.5 M in THF) was used as received. NaOH and H2O2 (30 wt%) were used as received. Naphthalene/potassium was prepared using naphthalene/potassium at −75 °C. The polymerization was started by injecting 0.7 mL styrene. After 2 h, 4.6 mL of a 4.3 M solution of 13-butadiene in toluene was then rapidly added to this flask. The copolymerization continuously proceeded for an additional 2 h. The reaction mixture was terminated by introducing 2 mL ethanol containing the antioxidant. The polymer was precipitated in 200 mL ethanol acidified with 20 mL concentrated hydrochloric acid, recovered by filtration, washed with an excess of ethanol, and dried to constant weight under vacuum at room temperature.
solution. Then the THF was completely removed by dialysis against deionized water for a week proved by $^1$H NMR.

**Measurements**

$^1$H NMR (400 MHz) and $^{13}$C NMR (100 MHz) spectra were recorded in CDCl$_3$ at 25 °C on a Varian Unity Inova 400 spectrometer. Molecular weight and molecular weight distribution ($M_w/M_n$) were determined by gel permeation chromatography (GPC) against narrow molecular weight distribution polystyrene standards on a Waters 2414 refractive index detector at 40 °C with THF as the eluent.

The morphology of the micelles was observed by scanning electron microscope (SEM) (Hitachi S-4800) with an accelerating voltage of 10.0 kV and transmission electron microscope (TEM) (JEM 1400Plus) with an accelerating voltage of 120 kV. For the SEM observation, a drop from the previously prepared micellar solution was deposited onto a carbon-coated copper grid.

Dynamic light scattering (DLS) measurements were conducted on a Brookhaven BI-200SM apparatus with a BI-9000AT digital correlator and a He–Ne laser at 632 nm. Data were analyzed by the CONTIN algorithm, while the average hydrodynamic diameter ($D_h$) and size polydispersity of the particles were obtained by a cumulant analysis of the experimental correlation function.

DSC experiments were carried out on a TA Instruments (New Castle, DE, USA) Q10 calorimeter. Calibration was performed with indium and tin, and all tests were run employing ultrapure nitrogen as the purge gas. DSC heating and cooling scans were performed at 10 °C min$^{-1}$ over the temperature range 0 °C to 250 °C for standard measurements.

**Results and discussion**

**Synthesis and characterization of $i$PS-Containing diblock copolymers**

In recent years, [OSSO]-based titanium complexes have attracted much attention because of the isospecific polymerization of styrene and α-olefins. In 2003, Okuda et al. first reported that [OSSO]-Ti complexes could promote polymerization of styrene upon activation with methylaluminoxane (MAO) to give $i$PS. Subsequently, the living stereospecific polymerization of styrene and 1,3-butadiene catalyzed by 1,4-dithiabutandiyl-2,2′-bis(6-cumenyl-4-methylphenoxy) titanium dichloride (complex 1) activated with MAO was reported by Capacchione in 2010. In this case, we synthesized the diblock copolymers of $i$PS-$b$-1,4-trans-PBD with complex 1 and MMAO used as cocatalyst via sequential monomer addition as shown in Scheme 1 and Table 1.

Moreover, the resultant diblock copolymers were characterized by GPC, NMR and DSC. The $^1$H NMR and $^{13}$C NMR (Fig. 1 and 2) shows that the PS block is $i$PS ($m_{m}$ $\approx$ 95%) and the PBD block is 1,4-trans-PBD ($1,4$-trans addition $\approx$ 95%). In addition, the relative length of the $i$PS block and the 1,4-trans-PBD block could be calculated from the $^1$H NMR. To study the thermal properties, one of the prepared diblock copolymers of $i$PS-$b$-1,4-trans-PBD with no other heat treatment or mechanical treatment was used for DSC scan at a heating rate of 10 °C min$^{-1}$ (the first heating curve for solution crystallization, as shown in Fig. 3a), which exhibits that the melting temperature ($T_m$) of $i$PS block ($M_n = 9.2 \times 10^4$) is 220 °C and 1,4-trans-PBD block ($M_n = 2.9 \times 10^4$) is 45 °C/82 °C, indicating these two blocks were crystalline. After cooling at a rate of 10 °C min$^{-1}$, this copolymer was heating again at a rate of 10 °C min$^{-1}$ (the second heating curve, as shown in Fig. 3b). In this case, the area of crystal-melting peak of $i$PS at 220 °C was much smaller than that in the first heating curve, suggesting the very slow crystallization rate of $i$PS. To confirm this, the third heating

| Entry | St/BD in feed (mmol mmol$^{-1}$) | $C_{PS}^{b}$ (%) | $C_{trans}^{c}$ (%) | $M_n^{d} \times 10^{-4}$ | $M_w/M_n^{d}$ | $T_{mPS}^{e}$ (°C)$^{f}$ |
|-------|--------------------------------|----------------|-----------------|---------------------|----------------|-----------------|
| 1     | 0/8.0                          | 100            | 95              | 4.6                 | 1.30           | —               |
| 2     | 1.3/8.0                         | 78.7           | 96              | 7.0                 | 1.36           | 222             |
| 3     | 2.0/8.0                         | 71.4           | 96              | 7.9                 | 1.39           | 220             |
| 4     | 3.4/8.0                         | 57.1           | 96              | 10.0                | 1.30           | 222             |
| 5     | 8.0/18.7                        | 54.1           | 95              | 15.8                | 1.27           | 220             |
| 6     | 8.0/8.0                         | 39.1           | 95              | 14.6                | 1.20           | 220             |
| 7     | 8.0/3.4                         | 28.8           | 97              | 13.1                | 1.25           | 221             |
| 8     | 8.0/0                           | 0              | —               | 11.3                | 1.20           | 221             |

$^a$ Polymerization conditions: Ti = 1.0 μmol; [Al]/[Ti] = 1200; $T = 25$ °C; $V_{tot} = 20$ mL (styrene + toluene); polymerization time, 2 h (styrene) + 2 h (butadiene). $^b$ PBD content in copolymers, determined from $^1$H NMR spectra. $^c$ trans-1,4-regularities in PBD block, determined from $^1$H NMR spectra. $^d$ Determined by GPC with THF as the eluent. $^e$ Melting temperature relative to the isotactic polystyrene block in the resulting $i$PS-$b$-1,4-trans-PBD, determined by 10 °C min$^{-1}$ heating rate DSC scans.
curve at a rate of 10 °C min⁻¹ as shown in Fig. 3c was displayed after the isothermal crystallization of this sample at 120 °C for 3 hours. As might be expected, the area of crystal-melting peak of iPS at 220 °C greatly increased, which is even bigger than that in the first heating curve.

The hydroxylation of the 1,4-trans-PBD block was carried out as procedures reported.⁴⁹,⁵⁰ Note that the hydroboration of the 1,4-microstructure of polybutadiene was more difficult than the 1,2-microstructure.⁴⁹ Moreover, as reported by Ramakrishnan,⁵⁰ 83% 1,4-cis-polybutadiene synthesized by the ring-opening metathesis polymerization of 1,5-cyclooctadiene can be easily hydroborated at around 60 °C. However, in this case, more than 95% 1,4-trans-PBD block in the copolymer can hardly be hydroborated on the same conditions. Therefore, the temperature of hydroboration was raised to 75 °C and the 1,4-trans-PBD block was almost completely hydroxylated. As shown in Fig. 4, the 1,4-trans-PBD block was almost completely hydroxylated. Compared with the ¹H NMR spectrum of the 1,4-trans-PBD block before hydroxylation, the corresponding peak at 5.44 ppm assigned to the chemical shift of unsaturated bond in 1,4-trans-PBD block almost disappears and the characteristic peak at 3.52 ppm of the methine proton of CHOH appears after hydroxylation.

The graft of PEO into 1,4-trans-PBD block was performed using naphthalene/potassium as initiator via anion ring-opening polymerization of ethylene oxide (as shown in Scheme 2). To remove as completely as possible the PEO homopolymer, the graft copolymerization products were dispersed in water by stirring and dialyzed against deionized water with a dialysis bag molecular weight cut off of 50 000 for a week. The GPC results indicated that the PEO homopolymer was almost removed by dialysis against deionized water. Fig. 5 shows a representative ¹H NMR spectrum of iPS-b-(1,4-trans-PBD-g-PEO) prepared from Entry 6 in Table 1. The high and

Fig. 1 ¹H NMR spectrum of iPS-b-1,4-trans-PBD (Entry 6 in Table 1) synthesized by complex 1/MMAO via sequential monomer addition.

Fig. 2 ¹³C NMR spectrum of iPS-b-1,4-trans-PBD (Entry 6 in Table 1) synthesized by complex 1/MMAO via sequential monomer addition.

Fig. 3 DSC scans of iPS-b-1,4-trans-PBD with \( M_n = 1.21 \times 10^5 \) at 10 °C min⁻¹ heating rate, (a) the first heating curve of the newly prepared sample; (b) the second heating curve after cooling at a rate of 10 °C min⁻¹; (c) the third heating curve after isothermal crystallization at 120 °C for 3 h.

Fig. 4 ¹H NMR spectra of iPS-b-1,4-trans-PBD (Entry 6 in Table 1) before (a) and after (b) hydroxylation.
shark peak at 3.67 ppm is the characteristic chemical shift of PEO and the characteristic peak of the methine proton of CHOHand at 3.52 ppm almost disappears. These results demonstrated that the iPS-b-(1,4-trans-PBD-g-PEO) was successfully prepared.

The self-assembly of iPS-b-1,4-trans-PBD in n-dodecane

The self-assembly of iPS-b-1,4-trans-PBD was performed in n-dodecane, a selective solvent for 1,4-trans-PBD. A solution of the iPS-b-1,4-trans-PBD in THF was added dropwise to n-dodecane to form a light blue solution, indicating the self-assembly process of the iPS-b-1,4-trans-PBD (Entry 6 in Table 1). Then the THF was completely removed by vacuum evaporation. DLS measurement displays that the average hydrodynamic diameter ($D_h$) of the self-assembled micelles of iPS-b-1,4-trans-PBD in n-dodecane were around 80 nm as shown in Fig. 6, which is much larger than that of the individual chain in THF (~35 nm), confirming the self-assembling of iPS-b-1,4-trans-PBD in n-dodecane. Fig. 7 shows the SEM micrographs of the self-assembled micelles of iPS-b-1,4-trans-PBD in n-dodecane after prepared for 0 day, 7 days and 14 days, respectively. Spherical micelles with a diameter of about 60 nm were observed when the micelles were newly prepared. After prepared for two weeks, the micelles aggregated but keep their morphology to be spherical and identical diameter of about 60 nm, which suggests that the iPS core did not crystallize at room temperature as aging. To explain these outcomes, we suppose that the core-forming iPS block could not crystallize or have a very low degree of crystallinity in the nanoconfined space of micelles when the micelles were newly formed by removing the THF. After aged for a period at room temperature, the core-forming iPS block still could not crystallize as a result of the room temperature much lower than the glass transition temperature. The TEM images of self-assembled micelles of iPS-b-1,4-trans-PBD (as shown in Fig. 8) in n-dodecane also suggested the formation of spherical micelles.

To confirm our speculation, the prepared micellar solution was heated to 120 °C for 3 h to promote the crystallization of the
core-forming iPS block. Fig. 9 shows the SEM microscopy of the self-assembled micelles of iPS-b-1,4-trans-PBD (Entry 6 in Table 1) before and after isothermal crystallization. The micellar morphology changed from sphere-like to platelet-like and the diameter changed larger after isothermal crystallization. The TEM images of the self-assembled micelles before and after isothermal crystallization are exhibited in Fig. 10, which also suggests that the micellar morphology changed from sphere-like to bigger platelet-like induced by the crystallization of the iPS core.

The self-assembly of iPS-b-(1,4-trans-PBD-g-PEO) in aqueous solution

The self-assembly of iPS-b-(1,4-trans-PBD-g-PEO) was performed in aqueous solution, which is a selective solvent for PEO. A solution of the iPS-b-(1,4-trans-PBD-g-PEO) in THF was added dropwise to deionized water to form a light blue solution, indicating the self-assembly process of the iPS-b-(1,4-trans-PBD-g-PEO). After the THF was completely removed by dialysis against deionized water, the solution was detected by DLS. As exhibited in Fig. 11, the average hydrodynamic diameter ($D_h$) of the representative self-assembled micelles of iPS-b-(1,4-trans-PBD-g-PEO) prepared from Entry 6 in Table 1 in aqueous solution.
PBD-g-PEO) prepared from Entry 6 in Table 1 were around 90 nm with narrow distribution, confirming the self-assembling of iPS-b-(1,4-trans-PBD-g-PEO) in aqueous solution. In addition, the self-assembled micellar solution was so stable that no obvious precipitation could be observed after prepared for a month. Fig. 12 shows the TEM microscopy of the self-assembled micelles of iPS-b-(1,4-trans-PBD-g-PEO) in aqueous solution after prepared for 0 day, 15 day and 30 day.

Spherical micelles with a diameter of around 70 nm were observed and keep unchanged as time went on. These results were consistent with the DLS detect and its self-assembly behavior was similar to that of iPS-b-1,4-trans-PBD in n-dodecane, suggesting the formation of an amorphous iPS core or with low degree of crystallinity in the micelles as a result of slow crystallization rate of iPS and confined crystallization in nanospace. Fig. 13 displays the TEM images of self-assembled micelles of iPS-b-(1,4-trans-PBD-g-PEO) in aqueous solution. The uniform round dark domains in the images confirm that spherical micelles but not vesicles were formed and the iPS core was amorphous or low crystalline.

Conclusions

iPS-containing diblock copolymers including iPS-b-1,4-trans-PBD and a novel amphiphilic diblock copolymer of iPS-b-(1,4-trans-PBD-g-PEO) with controlled molecular weight, block ratio and narrow molecular weight distribution were synthesized in terms of living coordination polymerization and graft copolymerization. Moreover, this work also demonstrates the morphology and morphology transition of self-assembled micelles of iPS-b-1,4-trans-PBD in n-dodecane and iPS-b-(1,4-trans-PBD-g-PEO) in aqueous solution. These iPS-containing diblock copolymers can all self-assemble into spherical micelles in n-dodecane and in aqueous solution, respectively, implying that the core-forming iPS block could not crystallize or have a very low degree of crystallinity in nanoconfined space of micelles. It is interesting that heating the micellar solution of iPS-b-1,4-trans-PBD in n-dodecane to 120 °C and keeping the constant temperature for 3 hours, the micellar morphology changed from sphere-like to platelet-like as a result of the isothermal crystallization of the core-forming iPS block. We suggest that isothermal crystallization would induce the deformation of the micelles.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (21174167, 51573212) and the NSF of Guangdong Province (S2013030013474, 2014A030313178).

Notes and references

1. A. Proto, A. Avaglino, D. Saviello, R. Ricciardi and C. Capacchione, Macromolecules, 2010, 43, 5919.
2. Z. Y. Li, R. Liu, B. Y. Mai, F. Feng, Q. Wu, G. D. Liang, H. Y. Gao and F. M. Zhu, Polym. Chem., 2013, 4, 954.
3. N. Hadjichristidis, H. Iatou and M. Pitsikalis, Adv. Polym. Sci., 2005, 189, 1.
4. W. Zheng, N. Yan, Y. Zhu, W. Zhao, C. Zhang, H. Zhang, C. Bai, Y. Hu and X. Zhang, Polym., 2015, 6, 6088.
5. N. Yan, Y. Zhang, Y. He, Y. Zhu and W. Jiang, Macromolecules, 2017, 50, 6771.
6. Y. Han, H. Yu, H. Du and W. Jiang, J. Am. Chem. Soc., 2010, 132, 1144.
7. N. Yan, H. Liu, Y. Zhu, W. Jiang and Z. Dong, Macromolecules, 2015, 48, 5980.
8. Y. Zhang, Y. He, N. Yan, Y. Zhu and Y. Hu, J. Phys. Chem. B, 2017, 121, 8417.
9. M. Wu, Y. Zhu and W. Jiang, ACS Macro Lett., 2016, 5, 1212.
10. Y. He, Y. Zhang, N. Yan, Y. Zhu, W. Jiang and D. Shi, Nanoscale, 2017, 9, 15056.
11. W. N. He and J. T. Xu, Prog. Polym. Sci., 2012, 37, 1350.
12. J. Schmelz, F. H. Schacher and H. Schmalz, Soft Matter, 2013, 9, 2101.
13. J. J. Crassous, P. Schuttenberger, M. Ballauff and A. M. Mihut, Polymer, 2015, 62, A1.
14. A. M. Mihut, J. J. Crassous, H. Schmalz, M. Drechsler and M. Ballauff, Soft Matter, 2012, 8, 3163.
15. J. Raez, J. P. Tomba, I. Manners and M. A. Winnik, J. Am. Chem. Soc., 2003, 125, 9546.
16. J. Raez, I. Manners and M. A. Winnik, Langmuir, 2002, 18, 7229.
17. S. F. M. Yusoff, J. B. Gilroy, G. Cambridge, M. A. Winnik and I. Manners, J. Am. Chem. Soc., 2011, 133, 11220.
18. E. K. Lin and A. P. Gast, Macromolecules, 1996, 29, 4432.
19. H. Schmalz, J. Schmelz, M. Drechsler, J. Yuan, A. Walther, K. Schweimer and A. M. Mihut, Macromolecules, 2008, 41, 3235.
20. T. Li, W. J. Wang, R. Liu, W. H. Liang, G. F. Zhao, Z. Y. Li, Q. Wu and F. M. Zhu, Macromolecules, 2009, 42, 3804.
21. R. Liu, Z. Y. Li, B. Y. Mai, Q. Wu, G. D. Liang, H. Y. Gao and F. M. Zhu, J. Polym. Res., 2013, 20, 64.
22. A. Radulescu, R. T. Mathers, G. W. Coates, D. Richter and L. J. Fetters, *Macromolecules*, 2004, 7, 6962.
23. J. Massey, K. N. Power, I. Manners and M. A. Winnik, *J. Am. Chem. Soc.*, 1998, 20, 9533.
24. G. Guerin, J. Raez, I. Manners and M. A. Winnik, *Macromolecules*, 2005, 38, 7819.
25. X. S. Wang, K. Liu, A. C. Arsenault, D. A. Rider, G. A. Ozin, M. A. Winnik and I. Manners, *J. Am. Chem. Soc.*, 2007, 129, 5630.
26. J. T. Xu, J. P. A. Fairclough, S. M. Mai and A. J. Ryan, *J. Mater. Chem.*, 2003, 13, 2740.
27. J. T. Xu, G. D. Liang, S. M. Mai and A. J. Ryan, *Chem. J. Chin. Univ.*, 2004, 25, 1978.
28. A. M. Mihut, M. Drechsler, M. Moller and M. Ballauff, *Macromol. Rapid Commun.*, 2010, 31, 449.
29. D. Portinha, F. Boue, L. Bouteiller, G. Carrot, C. Chassenieux, S. Penese and G. Reiter, *Macromolecules*, 2007, 40, 4037.
30. J. Fu, B. Luan, X. Yu, Y. Cong, J. Li, C. Y. Pan, Y. C. Han, Y. M. Yang and B. Y. Li, *Macromolecules*, 2004, 37, 976.
31. K. Rajagopal, A. Mahmud, D. A. Christian, J. D. Pajerowski, A. E. X. Brown, S. M. Loverde and D. E. Discher, *Macromolecules*, 2010, 43, 9736.
32. Z. X. Du, J. T. Xu and Z. Q. Fan, *Macromolecules*, 2007, 40, 7633.
33. Z. X. Du, J. T. Xu and Z. Q. Fan, *Macromol. Rapid Commun.*, 2008, 29, 467.
34. W. N. He, J. T. Xu, B. Y. Du, Z. Q. Fan and X. S. Wang, *Macromol. Chem. Phys.*, 2010, 211, 1909.
35. S. C. Chan, S. W. Kuo, C. H. Lu, H. F. Lee and F. C. Chang, *Polymers*, 2007, 48, 5059.
36. Z. C. Li, R. J. Ono, Z. Q. Wu and C. W. Bielawski, *Chem. Commun.*, 2011, 47, 197.
37. A. C. Kamps, M. Fryd and S. J. Park, *ACS Nano*, 2012, 6, 2844.
38. M. Lazzari, D. Scalarone, C. E. Hoppe, C. Vazquez-Vazquez and M. A. Lopez-Quintela, *Chem. Mater.*, 2007, 19, 5818.
39. M. Lazzari, D. Scalarone, C. Vazquez-Vazquez and M. A. Lopez-Quintela, *Macromol. Rapid Commun.*, 2008, 29, 352.
40. G. Natta, P. Corradini and I. W. Bassi, *Nuovo Cimento*, 1960, 15, 68.
41. P. J. Lemstra and G. Challa, *J. Polym. Sci., Part B: Polym. Lett.*, 1975, 13, 1809.
42. P. J. Lemstra, J. Postma and G. Challa, *Polymer*, 1974, 15, 757.
43. G. Xue, Y. Wang, X. Gu and Y. Lu, *Macromolecules*, 1994, 27, 4016.
44. C. Capaccione, A. Proto, H. Ebeling, R. Mulhaupt, K. Moller, T. P. Spaniol and J. Okuda, *J. Am. Chem. Soc.*, 2003, 125, 4964.
45. K. Beckerle, R. Manivannan, T. P. Spaniol and J. Okuda, *Organometallics*, 2006, 25, 3019.
46. C. Capaccione, R. Manivannan, M. Barone, K. Beckerle, R. Centore, L. Oliva, A. Proto, A. Tuzi, T. P. Spaniol and J. Okuda, *Organometallics*, 2005, 24, 2971.
47. A. Rodrigues, E. Kirillov, T. Roisnel, A. Razavi, B. Vuillemin and J. F. Carpentier, *Angew. Chem., Int. Ed.*, 2007, 46, 7240.
48. T. Kawasaki, C. Hohberger, Y. Araki, K. Hatase, K. Beckerle, J. Okuda and K. Soai, *Chem. Commun.*, 2009, 5621.
49. T. C. Chung, M. Raate, M. Berluche and D. M. Schulz, *Macromolecules*, 1988, 21, 1903.
50. S. Ramakrishnan, *Macromolecules*, 1991, 24, 3753.