

Asymmetric Polymerization of *N*-Vinylcarbazole with Optically Active Anionic Initiators^{*}

Wei Hu, Jing Cao^{**}, Yi-ling Huang and Sai Liang

Key Laboratory of Environmentally Friendly Chemistry and Applications of Ministry of Education, College of Chemistry, Xiangtan University, Hunan 411105, China

Abstract The anionic polymerization of *N*-vinylcarbazole (NVC) by using optically active anionic initiators such as the lithium salts of (*S*)-1-(9H-fluoren-2-yl)-4-isopropyl-4,5-dihydrooxazole ((*S*)-1-FIDH) and (*S*)-2-(9H-fluoren-2-yl)-4-isopropyl-4,5-dihydrooxazole ((*S*)-2-FIDH) and complexes of (-)-Sparteine with *n*-butyllithium (*n*-BuLi-(-)-Sp) or fluorenyl lithium (Fli-(-)-Sp) was achieved. The yield and specific rotation of poly(*N*-vinylcarbazole)s (poly(NVC)s) were considerably affected by the molar ratio of (*S*)-FIDH to NVC. The highest yield and specific rotation were obtained with Li-(*S*)-1-FIDH as an initiator, with a molar ratio of monomer and initiator [M]/[I] = 10/1. The effects of the chiral initiators, type of solvent and the polymerization temperature were investigated. The obtained optical activity of polymers was attributed to asymmetric induction of the chiral initiators.

Keywords: Helical polymer; Anionic polymerization; Chiral carbon anionic initiator; *N*-vinylcarbazole.

INTRODUCTION

Optically active polymers, a kind of functional polymer, have attracted considerable attention. Recently, development of synthetic processes for polymers having clear helical structure attracts large interests^[1,2]. There are numerous of synthesis methods of optically active polymers. Anionic polymerization is one of the most extremely important polymerization method. A variety of vinyl monomers, such as diene monomers^[3], styrene derivatives^[4], and methacrylic acid derivatives^[5] have been polymerized using this method. *N*-vinylcarbazole (NVC) is a kind of aromatic vinyl monomer, and some aromatic vinyl monomers have been reported to produce polymers with well-defined structures such as helical conformation in the presence of chiral anionic initiator^[6–10]. It is believed that the necessary condition for vinyl monomers to undergo anionic polymerization is the presence of vinyl groups with low electron density. However, NVC having nitrogen atoms (a strong electron-donor) adjoining the vinyl group cannot be polymerized using anionic polymerization.

Until 2006, Natori regarded NVC as a monomer accompanied by an amine as a complexing agent within the same molecule. That is, both a polymerization site and a complexing agent site appear to coexist in this monomer. On the basis of this concept, They reported the first successful example of the anionic polymerization of NVC with RLi^[11].

Although NVC can be polymerized with anionic initiators such as butyllithium, however, the polymerization of the monomer with chiral anionic initiator is not exploited. In the present study, we carried out

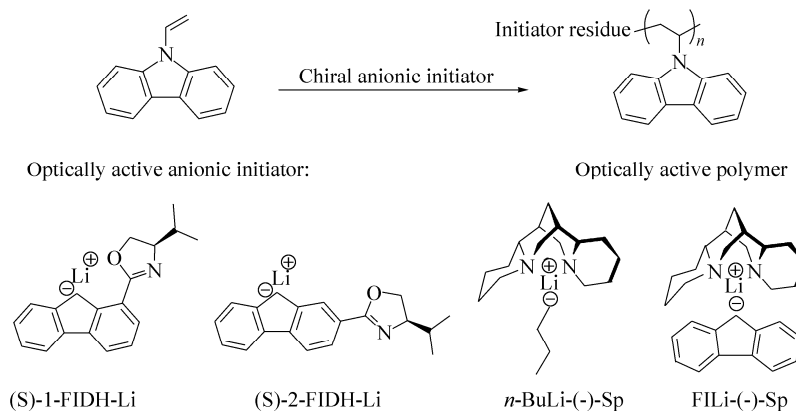
^{*} This work was financially supported by the open project program of Key Laboratory of Environmentally Friendly Chemistry and Applications of the Ministry of Education, China (No. 09HJYH04) and Xiangtan University Doctoral Scientific Research Fund.

^{**} Corresponding author: Jing Cao (曹靖), E-mail: caojing8088@xtu.edu.cn

Received April 25, 2015; Revised May 17, 2015; Accepted May 18, 2015

doi: 10.1007/s10118-015-1689-9

the polymerization of NVC by using optically active anionic initiators such as the lithium salts of (*S*)-1-(9H-fluoren-2-yl)-4-isopropyl-4,5-dihydrooxazole ((*S*)-1-FIDH) and (*S*)-2-(9H-fluoren-2-yl)-4-isopropyl-4,5-dihydrooxazole ((*S*)-2-FIDH)^[12] and complexes of (-)-Sparteine with *n*-butyllithium (*n*-BuLi-(-)-Sp) or fluorenyl lithium (FILi-(-)-Sp) (Scheme 1). The effects of the chiral initiators for polymerization were investigated.



Scheme 1 Asymmetric polymerization of *N*-vinylcarbazole with optically active anionic initiators

EXPERIMENTAL

Materials and Instrumentation

All reagents for syntheses and polymerization were purchased from Aladdin or Acros Company. *N*-Vinylcarbazole (NVC) (98%) was recrystallized in cyclohexane and then dried under reduced pressure in dry nitrogen. Cyclohexane, toluene and tetrahydrofuran (THF) were refluxed over Na wire and then distilled under a nitrogen atmosphere just before use. Other reagents were used as received without further purification.

NMR spectra were recorded using a Bruker 400 MHz spectrometer with CDCl_3 solvent and tetramethylsilane (TMS) as internal standard. Mass spectrum was performed on a Matrix Assisted Laser Desorption Ionization Time of Flight Mass Spectrometry (4800 MALDI-TOF MS) and α -cyano-4-hydroxycinnamic acid (CCA) as matrix. The number-average molecular mass (M_n) and molecular mass polydispersity (M_w/M_n) of the polymer were estimated with a gel permeation chromatography (GPC) apparatus equipped with a Waters 1515 refractive index detector. THF was employed as the eluent at a flow rate of 1.0 mL/min at 38 °C. All GPC curves were calibrated against a series of monodispersed polystyrene standards. Optical rotations were measured using a Perkin-Elmer 341 LC polarimeter at 20 °C. The cell path length was 10 cm. The concentration was 1 mg/mL, and the solvent was CHCl_3 . Circular dichroism (CD) spectra were recorded on a JASCO J-810 spectrometer. The light path length of the quartz cell used was 10 mm. The concentration was about 1×10^{-5} mol/L, and the solvent was CHCl_3 .

Preparation of Initiator Solution

n-BuLi-(-)-Sp complex, Li-(*S*)-1-FIDH and Li-(*S*)-2-FIDH were prepared by adding an equimolar amount of *n*-BuLi in hexane to a cyclohexane or toluene solution of (-)-Sp, (*S*)-1-FIDH and (*S*)-2-FIDH respectively under nitrogen atmosphere at ambient temperature just before use. An equimolar amount of *n*-BuLi was added to a cyclohexane or toluene solution of fluorene to produce FILi. FILi-(-)-Sp complex was prepared by adding an equimolar amount of (-)-Sp to FILi.

Polymerization Procedure

A well-dried 25 mL Schlenk tube with NVC (0.4 g) was purged with dry nitrogen, and solvent, such as cyclohexane or toluene (5.0 mL) was added at room temperature. The above optically active anionic initiators were then supplied to this solution with a hypodermic syringe under a dry nitrogen atmosphere. The reaction mixture was magnetically stirred for 24 h. After polymerization, dry MeOH was added to the reaction mixture in

an equimolar amount to the lithium (Li) atoms present in the reaction mixture, to terminate the reaction. The polymerization mixture was then poured into a large volume of MeOH to precipitate the polymer, which was then isolated by filtration. The product was dried under reduced pressure at 50 °C for 24 h, resulting in a white powdery polymer.

RESULTS AND DISCUSSION

Polymerization of NVC with Optically Active Carbon Anionic Initiators

Chiral initiators are often used in the anionic polymerization of achiral monomers to give optically active polymers^[13, 14]. Chiral initiators could be obtained not only by consisting of optically inactive initiator, such as *n*-BuLi, and chiral ligand, but also from compounds containing chiral centre. Recently, our research group exploited two kinds of novel carbon anionic chiral initiators, Li-(*S*)-1-FIDH and Li-(*S*)-2-FIDH, the asymmetric polymerizations of monomers such as N-substituted maleimide and isocyanates by these initiators were investigated.

Anionic polymerization of NVC with optically active carbon anionic initiators, Li-(*S*)-1-FIDH and Li-(*S*)-2-FIDH, were investigated with various molar ratios of NVC and initiator in cyclohexane or toluene at room temperature for 24 h. The results obtained from these polymerizations are shown in Table 1.

Table 1. Polymerization of NVC in cyclohexane or toluene at room temperature^a

Run	Initiator	Solvent	[M]/[I]	Yield ^b (%)	$[\alpha]_{546}^{20}$ ^c	$M_n^d (\times 10^3)$	M_w/M_n^d
1	Li-(<i>S</i>)-1-FIDH	cyclohexane	1/0.35	10.4	−10°	3.60	2.67
2	Li-(<i>S</i>)-1-FIDH	cyclohexane	10/1	18.6	−17°	3.88	2.52
3	Li-(<i>S</i>)-1-FIDH	cyclohexane	20/1	12.8	−12°	4.05	2.34
4	Li-(<i>S</i>)-2-FIDH	cyclohexane	1/0.35	14.0	−5°	3.76	3.26
5	Li-(<i>S</i>)-2-FIDH	cyclohexane	10/1	23.1	−12°	3.99	3.14
6	Li-(<i>S</i>)-2-FIDH	cyclohexane	20/1	18.8	−8°	4.29	2.86
7	Li-(<i>S</i>)-1-FIDH	toluene	10/1	10.7	−13°	2.14	1.32
8	Li-(<i>S</i>)-2-FIDH	toluene	10/1	15.2	−9°	2.38	1.73
9	Li-(<i>S</i>)-1-FIDH	THF	10/1	—			
10	Li-(<i>S</i>)-2-FIDH	THF	10/1	—			

^a NVC, 0.4 g; solvent, 5 mL; time, 24 h; ^b Methanol-insoluble part; ^c 1 mg/mL in CHCl₃; ^d By GPC

We found all of the polymers initiated by Li-(*S*)-1-FIDH initiator (runs 1–3, $[\alpha]_{546}^{20} = -10^\circ$ to -17°) showed larger specific rotation than that with Li-(*S*)-2-FIDH initiator (runs 4–6, $[\alpha]_{546}^{20} = -5^\circ$ to -12°). As mentioned in our previous work^[12], due to steric interaction, the (*S*)-1-FIDH initiator showed more efficient twisting power for controlling the screw sense of the polymer than the (*S*)-2-FIDH initiator, its active centre was farer from the crowded chiral oxazoline group compared to that of (*S*)-1-FIDH. Furthermore, yields of poly(NVC)s initiated by Li-(*S*)-2-FIDH were obviously higher than those with Li-(*S*)-1-FIDH. On the basis of these results, the crowded substituent of the initiator seemed to reduce the polymerizability of NVC and yet enhanced the chiral induction ability in the polymerization.

No matter what initiator was used, poly(NVC) exhibited the largest negative specific rotation and the largest yield with molar ratio of monomer and initiator ($[M]/[I] = 10/1$) (Table 1, run 2 and 5) compared with other ratios, such as 1/0.35 or 20/1. The results indicated that the relationship between the molar ratio of $[NVC]/[initiator]$ and the yield of poly(NVC) was not a simple one.

It is well-known that anionic polymerization of conventional monomers, such as butadiene (Bd), isoprene (Ip), styrene (St), and methyl methacrylate (MMA), are strongly affected by the types of solvents used. Consequently, to reveal the effect of solvents, anionic polymerization of NVC with Li-(*S*)-1-FIDH ($[M]/[I] = 10/1$) was performed in three different solvents at room temperature.

The effect of solvents for polymerization of NVC initiated by Li-(*S*)-FIDH was very similar to that by BuLi^[12]. Among the three types of solvents, aliphatic hydrocarbon solvents, such as cyclohexane, gave good

results with high yield (Table 1, run 2 and 5). The poly(NVC) obtained in toluene have narrower M_w/M_n range compared to that in cyclohexane (Table 1, run 7 and 8). No poly(NVC) was obtained when an ether such as THF was used as a solvent due to transfer and decomposition reactions by the polarization of C-Li bonds in organolithium compounds^[15].

From the perspective of basic polymer chemistry, a relatively low polymerization temperature is considered to be appropriate for the anionic polymerization, and the polymer chain conformation becomes much regular. Therefore, the effect of polymerization temperature on the anionic polymerization of NVC with Li-(*S*)-1-FIDH was examined. The polymerization was performed in toluene under a dry nitrogen atmosphere for 24 h. The obtained results are summarized in Table 2.

Table 2. Influence of polymerization temperature on the anionic polymerization of NVC ^a

Run	Initiator	Temp (°C)	Yield ^b (%)	$[\alpha]_{546}^{20}$ ^c	$M_n^d (\times 10^3)$	M_w/M_n^d
1	Li-(<i>S</i>)-1-FIDH	Room temp	10.7	-13°	2.14	1.32
2	Li-(<i>S</i>)-1-FIDH	0	8.7	-15°	1.52	1.28
3	Li-(<i>S</i>)-1-FIDH	-78	—	—	—	—

^a NVC, 0.4 g; toluene, 5 mL; $[M]/[I] = 10/1$; time, 24 h; ^b Methanol-insoluble part; ^c 1 mg/mL in CHCl₃; ^d By GPC

The yield of Poly(NVC) polymerized at 0 °C was significantly reduced. However, the absolute value of the specific rotation of poly(NVC) was larger than that at room temperature. With the decrease of temperature, the M_w/M_n range became narrow. No poly(NVC) was obtained when polymerized at -78 °C since NVC monomer was almost insoluble in toluene under such temperatures.

Polymerization of NVC with Organolithium-(*-*)-Sparteine Complex Anionic Initiators

In the helix-sense-selective polymerization, there are two ways to control the helix sense: ligand control and initiator control^[1]. Although the chiral initiator significantly affects the initial stages of the polymerization, the effect decreases with increasing the degree of polymerization, leading to a relatively low helix-sense selectivity. The chiral ligand control seems more effective. For example, achiral initiator such as *n*-BuLi and FI-Li together with an optically active chelating agent (*i.e.* (*-*)-sparteine) used in the helix-sense-selective polymerization of trityl methacrylate and diphenyl-2-pyridylmethyl methacrylate successfully produced one-handed helical polymers.

Therefore, we carried out the polymerization of NVC by using optically active anionic initiator such as *n*-BuLi-(*-*)-Sp and FILLi-(*-*)-Sp. The results are given in Table 3. The M_n , specific rotation and yield of the polymers were smaller than those from chiral carbon anionic initiators. An interesting phenomenon could be observed that the polymers obtained with *n*-BuLi-(*-*)-Sp showed positive specific rotations but the polymers from other initiators all exhibited negative specific rotations (Table 3 run 1 and 2). It hinted that the chiral initiators exhibit asymmetric induction in the polymerization of NVC since (*-*)-sparteine has negative specific rotations and the NVC monomer used is optically inactive. The fact that the specific rotations of the polymers from organolithium-(*-*)-sparteine complex anionic initiators were not larger than those from chiral initiator (Li-(*S*)-FIDH) suggested the ligand control was not more effective than the initiator control in the polymerization of NVC. There may be two reasons: (1) the serious side reaction in the anionic polymerization of NVC using RLi as an initiator and (2) the effect was small between ligand control and initiator control due to short polymer chain.

Table 3. Anionic polymerization of NVC with amines used as initiator at room temperature ^a

Run	Initiator	Solvent	Yield ^b (%)	$[\alpha]_{546}^{20}$ ^c	$M_n^d (\times 10^3)$	M_w/M_n^d
1	<i>n</i> -BuLi-(<i>-</i>)-Sp	cyclohexane	12.8	+7°	1.46	1.72
2	<i>n</i> -BuLi-(<i>-</i>)-Sp	toluene	10.3	+9°	1.30	1.49
3	FILLi-(<i>-</i>)-Sp	cyclohexane	8.4	-5°	2.88	1.68
4	FILLi-(<i>-</i>)-Sp	toluene	7.0	-6°	2.16	1.35

^a NVC, 0.4 g; solvent, 5 mL; $[M]/[I] = 10/1$; time, 24 h; ^b Methanol-insoluble part; ^c 1 mg/mL in CHCl₃; ^d By GPC

Structures of the Polymers

The ^1H -NMR spectrum of poly(NVC) obtained with Li-(S)-2-FIDH initiator (Table 1, run 5) is shown in Fig. 1. The peaks corresponding to poly(NVC) (Ha, Hb, Hc) were clearly observed. The Ha peaks of aromatic protons on the pendant carbazole groups appear in the range of $\delta = 4.2\text{--}8.0$. The Hb peaks of methine protons in the main chain appear in the range of $\delta = 2.0\text{--}4.0$. The Hc peaks of methylene protons in the main chain in the range of $\delta = 0.5\text{--}2.0$. The spectrum obtained was similar to the ^1H -NMR spectrum by anionic or radical polymerization^[16]. However, whether the polymer was end capped with initiator moiety or not could not be sure from the ^1H -NMR spectrum.

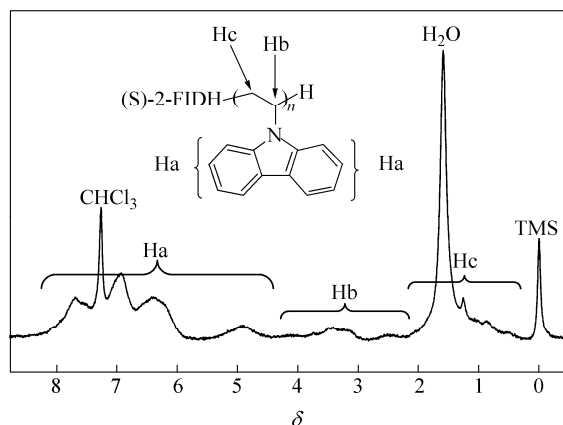


Fig. 1 ^1H -NMR spectrum of poly(NVC) obtained with (S)-2-FIDD-Li in cyclohexane

In order to give proof that chiral FIDH moiety was jointed at the end of the polymer, a polymer sample (Table 1, Run 5) was analyzed *via* matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF-MS) (Fig. 2). A family of peaks (1629, 1822, 2015, 2208, 2401, 2594, 2787, 2980, *etc.*) was clearly detected, and the difference between two adjacent peaks was 193, corresponding to the molecular weight of NVC monomer. This meant that the polymers are composed of poly(NVC) with different degree of polymerization (DP). Then, we could select a peak (*i.e.* 2015) for calculation, the value of nine folds molecular weight of NVC adding 278 equaled to 2015, the molecular weight of FIDH was just 278. Thus, it was undeniable that the polymer was end capped with initiator moiety. We think that the assignment of the other series of peaks (1585, 1779, 1971, 2165, 2358, 2551, 2744, 2938, *etc.*) may be self-polymerized product of NVC, because the exact molar mass correspond to that polymer carrying a cation K^+ .

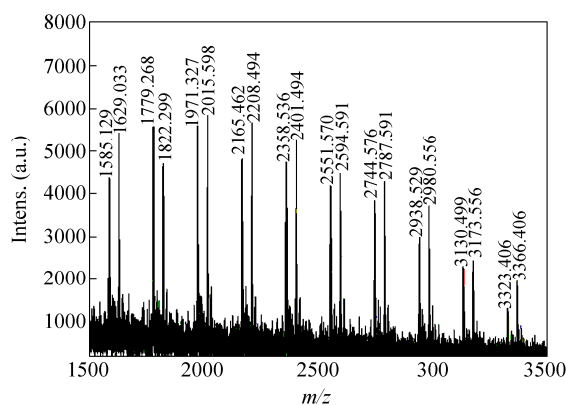


Fig. 2 MALDI-TOF-MS spectrum for poly(NVC) obtained with (S)-2-FIDD-Li in cyclohexane

Figure 3 shows the typical CD spectra of the poly(NVC)s obtained by Li-(*S*)-1-FIDH (Table 1, Run 2) and *n*-BuLi(-)-Sp (Table 3, Run 1). The CD spectra of the poly(NVC)s all exhibited two positive Cotton effect peaks at around 267 nm and 310 nm, and two negative Cotton effect peaks at 255 nm and 285 nm. All indicated that asymmetric induction took place on the main chain and the obtained polymers may have a helical conformation in solution.

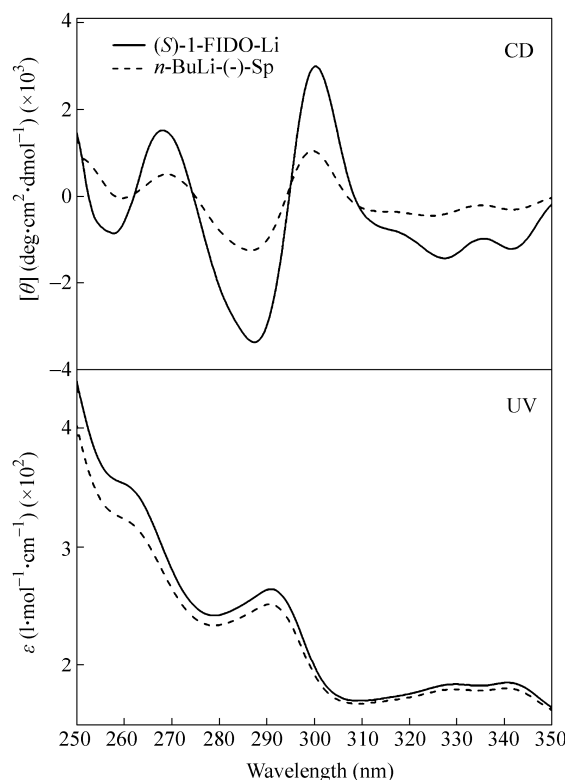


Fig. 3 CD and UV spectra of poly(NVC) obtained with (*S*)-1-FIDH-Li and *n*-BuLi(-)-Sp

CONCLUSIONS

The anionic polymerization of NVC by using optically active anionic initiators such as the lithium salts of (*S*)-1-(9H-fluoren-2-yl)-4-isopropyl-4,5-dihydrooxazole ((*S*)-1-FIDH) and (*S*)-2-(9H-fluoren-2-yl)-4-isopropyl-4,5-dihydrooxazole ((*S*)-2-FIDH) and complexes of (-)-Sparteine with *n*-butyllithium (*n*-BuLi(-)-Sp) or fluorenyl lithium (FLi(-)-Sp) was achieved. The yield and specific rotation of poly(*N*-vinylcarbazole)s (poly(NVC)s) were considerably affected by the molar ratio of (*S*)-FIDH to NVC. The highest yield and specific rotation were obtained with Li-(*S*)-1-FIDH as an initiator, with a molar ratio of monomer and initiator ($[M]/[I] = 10/1$). The effects of the chiral initiators, type of solvent and the polymerization temperature were investigated. Aliphatic hydrocarbons with relatively low solubility for NVC and poly(NVC) are considered to be appropriate solvents for the anionic polymerization of NVC.

The ^1H -NMR spectroscopic measurements and the MALDI-TOF-MS results strongly support the polymer chain structure of poly(NVC). All of the obtained poly(NVC)s exhibited specific rotation in solution, and significant Cotton effects were observed in circular dichroism (CD) absorption bands of poly(NVC)s. All these suggested that the obtained optically active poly(NVC)s were attributed to asymmetric induction of the chiral initiators, and kept stable single-handed helical conformation in solution.

REFERENCES

- 1 Okamoto, Y., Oike, H. and Yonezawa, N., *Tcichemicals*, 2011, 145: 2
- 2 Nakano, T. and Okamoto, Y., *Chem. Rev.*, 2001, 101(12): 4013
- 3 Natori, I. and Inoue, S., *Macromolecules*, 1998, 31(15): 4687
- 4 Sugiyama, K., Watanabe, K. and Hirao, A., *Macromolecules*, 2008, 41(12): 4235
- 5 Sugiyama, K., Azuma, H., Watanabe, T., Ishizone, T. and Hirao, A., *Polymer*, 2003, 44(15): 4157
- 6 Yu, Z.N., Wan, X.H., Zhang, H.L., Chen, X.F. and Zhou, Q.F., *Chem. Commun.*, 2003, 8: 974
- 7 Cui, J.X., Liu, A.H., Zhi, J.G., Zhu, Z.G., Guan, Y., Wan, X.H. and Zhou, Q.F., *Macromolecules*, 2008, 41: 5245
- 8 Zhi, J.G., Guan, Y., Cui, J.X., Liu, A.H., Zhu, Z.G., Wan, X.H. and Zhou, Q.F., *J. Polym. Sci., Part A: Polym. Chem.*, 2009, 47(9): 2408
- 9 Zhao, Z.Y., Bai, J.W., Zhang, J., Liu, A.H. and Wan, X.H., *Sci. China Chem.*, 2014, 57(7): 982
- 10 Wang, R., Li, X.F., Bai, J.W., Zhang, J., Liu, A.H. and Wan, X.H., *Macromolecules*, 2014, 47(5): 1153
- 11 Natori, I., *Macromolecules*, 2006, 39(18): 6017
- 12 Huang, Y.L., Cao, J., Hu, W. and Liang, S., *Polym. Int.*, 2015, 64(4): 563
- 13 Zang, Y., Ohishi, T., Aoki, T., Teraguchi, M. and Kaneko, T., *Chem. Lett.*, 2013, 42(4): 430
- 14 Nakano, T., Matsuda, A., Mori, M. and Okamoto, Y., *Polym. J.*, 1996, 28: 330
- 15 Rembaum, A., Hermann, A.M. and Haack, R., *J. Polym. Sci., Part B: Polym. Lett.*, 1967, 5(5): 407
- 16 Karali, A., Froudakis, G.E. and Dais, P., *Macromolecules*, 2000, 33(8): 3180