

Synthesis and Characterization of Hyperbranched Polyurethanes via Monomeric A₂ Plus Monomeric B₃ Approach

Biao Wang, Yuhong Liu, Guangqiong Li

Department of Chemical Engineering, School of Energy and Power Engineering, Xi'an Jiaotong University, Xi'an 710049, People's Republic of China

Correspondence to: Y. Liu (E-mail: liuyuh@mail.xjtu.edu.cn)

ABSTRACT: The monomeric A₂ plus monomeric B₃ approach was employed to prepare hyperbranched polyurethanes (HBPU)s based on 4,4'-methylenediphenyl diisocyanate and trimethylolpropane with the molecular weights ranging from 20,000 to 59,800 g mol⁻¹. Through controlling the concentration and stoichiometric ratio of monomers, gel was successfully prevented in the monomeric A₂ plus monomeric B₃ system. The structures of HBPU)s were characterized by ¹³C NMR. Molecular weights of HBPU)s were characterized by gel permeation chromatography. A gradual increase in HBPU molecular weight as well as degree of branching was observed when the stoichiometric ratio of A₂ to B₃ increased. It was exhibited that the solution concentration of the reaction had great effect on the gel point and cyclization of the monomeric A₂ plus monomeric B₃ system. This novel isocyanate terminated HBPU)s are expected to be capable of modifying the curing performance of benzoxazine resin. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 128: 3919–3924, 2013

KEYWORDS: hyperbranched polymers; gels; polyurethanes; synthesis

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INTRODUCTION

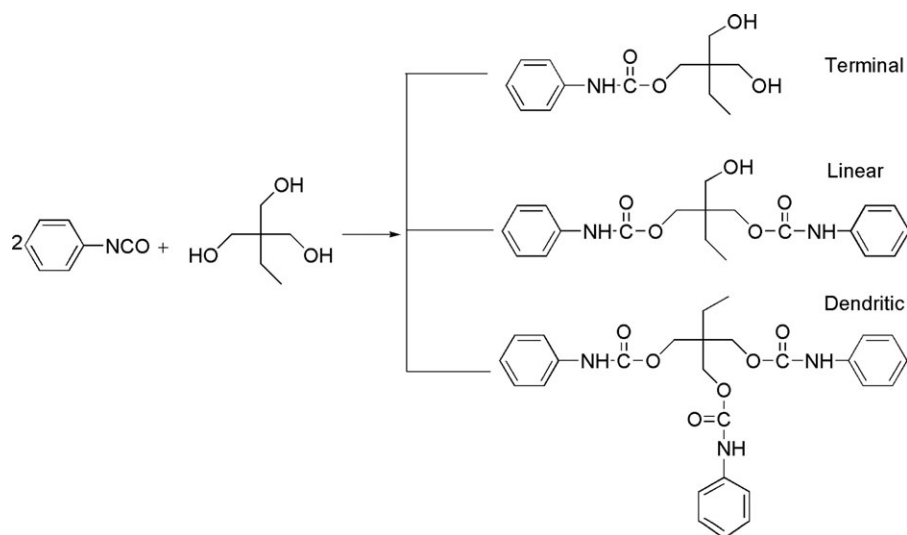
Hyperbranched polymers (HBPs) have received extensive attention during the last 20 years due to their unique features when compared with their linear analogs, such as 3D architecture, good solubility, and low melting viscosity, especially the presence of large numbers of functional end groups.¹ According to the type of monomer, the synthetic methodologies of HBPs can be classified into two categories, i.e., single-monomer methodology (SMM) and double-monomer methodology (DMM). SMM refers to the preparation of HBPs based on AB_n monomers or potential AB_n monomers, while DMM refers to the preparation of HBPs through copolymerization reaction of two types of monomers. A major advantage of the A₂ plus B₃ methodology is the commercial availability of A₂ and B₃ monomers compared to their AB_n counterparts.

Conventional procedures adopted for the synthesis of step-growth polymers usually involve adding all reactants into the reactor at first, while A₂ was always added dropwise to B₃ in the monomeric A₂ plus monomeric B₃ polymerizations. Flory² first predicted that care must be taken to avoid the statistically inevitable gel of the A₂ plus B₃ system because of crosslinking as the monomer ratio varies. This was confirmed by Russo et al.,^{3,4} Jikei et al.,^{5,6} and Webster et al.,⁷ later on. It is

indicated that both the stoichiometric balance of A₂ to B₃ and the dropwise addition of A₂ to B₃ can reduce adverse reactions and the possibility of gel during the course of reaction.⁸

Kakimoto et al.⁹ and Fréchet et al.¹⁰ reported the synthesis of HBPs independently using A₂ plus B₃ strategy in 1999. Other HBPs, including poly(arylene ether phosphine oxide)s,¹¹ polyethers,¹² and polyamides⁶ have also been successfully synthesized with the A₂ plus B₃ methodology, whereas, previously in the course of preparing hyperbranched polyurethanes (HBPU)s, gel was observed when the maximum stoichiometric ratio of A₂ to B₃ was 1.12 : 1⁸ with the molecular weights ranging from 16,000 to 63,000 g mol⁻¹. HBPU)s are rarely prepared via monomeric A₂ plus monomeric B₃ approach in that the high reactivity of isocyanate groups can easily lead to gel. To avoid the occurrence of gelation, A₂ or B₃ was usually an oligomeric when A₂ plus B₃ system was adopted to prepare HBPU)s. Fornof et al.¹³ prepared a highly branched polyurethane via the oligomeric A₂ plus B₃ methodology without gelation. Poly(caprolactone) containing highly branched segmented poly(ester urethane)s were synthesized via A₂ with oligomeric B₃ polymerization by Unal et al.¹⁴

In this work, we employed monomeric A₂ plus monomeric B₃ approach to prepare HBPU)s with 4,4'-methylenediphenyl



Scheme 1. Preparation of model compounds

diisocyanate (MDI) as A_2 and trimethylolpropane (TMP) as B_3 . Gel can be successfully avoided when the stoichiometric ratio of A_2 to B_3 even reach 1.5 : 1 by controlling the reaction conditions, such as temperature, the stoichiometric ratio of A_2 : B_3 , and the solution concentration of monomers. In addition, HBPU with different content of functional end groups, i.e., $-OH$ and $-NCO$ can be prepared through tuning to the stoichiometric ratio of A_2 to B_3 . In addition, HBPs with different end-capped groups can be used as reactive modifiers to improve the fracture toughness and impact resistance of the thermosetting polymer without sacrifice the elastic modulus (E) or glass transition temperature (T_g) of the matrix polymer.^{15–17} Therefore, HBPU bearing different end groups implied their potential application in high performance thermosets.

EXPERIMENTAL PART

Materials

4, 4'-MDI with purity of greater than 99.6% (Yantai Wanhua Polyurethanes Co., Ltd.) was used as received. TMP with purity of greater than 98% was purchased from Tianjin Bodi Chemical Co., Ltd. and was dried at 50°C at reduced pressure for 12 h prior to use. Dibutyltin dilaurate (DBTDL, Tianjin Chemical Co., China) was used as received. Phenyl isocyanate (PI) with purity of greater than 99% was obtained from Suzhou Yacoo chemical Reagent Corporation and was used as received. Tetrahydrofuran (THF) and dimethylacetamide (DMAc) were analytical grade and were vacuum distilled.

Preparation of Model Compounds

TMP (1.6100 g, 0.012 mol) was dissolved into 10 mL DMAc to form a 15 wt % solution and was added with PI (2.8608 g, 0.024 mol) to a 100-mL, round-bottom flask. The reaction was carried under strong magnetical agitation in the presence of 100 ppm of DBTDL at 80°C for 1 h till the isocyanate content reached the theoretical value as determined by di-*n*-butylamine backtitration method. Any unreacted isocyanate was removed by precipitating the reaction mixtures in hexane and then the reaction mixtures were dried in vacuum at 110°C for 24 h (Scheme 1). The ¹³C

NMR spectrum of the mixtures, i.e., mono-, di-, and trisubstituted model compounds based on PI and TMP had the following shifts: (dimethyl sulfoxide [DMSO]): $\delta_c = 7.37, 21.38, 21.61, 21.99, 39.71, 41.17, 42.01, 42.79, 60.62, 61.61, 62.03, 63.77, 64.21, 64.48, 118.20, 122.20, 122.31, 122.42, 128.79, 138.99, 139.12, 139.27, 153.38, 153.61, 153.89$.

Preparation of HBPU

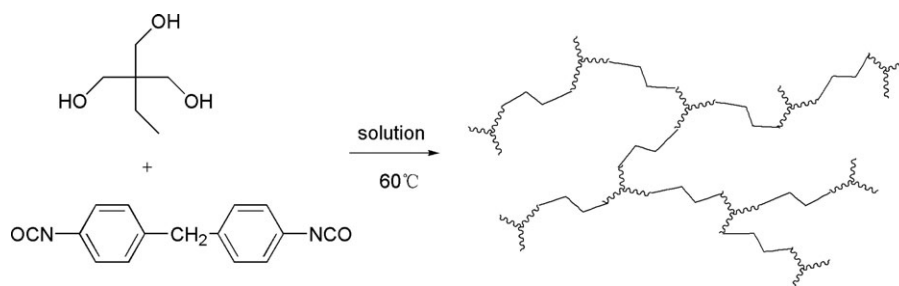
All reactions were carried out in three-necked, round-bottom flasks equipped with a magnetic stirrer, condenser, addition funnel, and nitrogen inlet. THF was used to dissolve MDI and then the solution was added dropwise to TMP solution in DMAc at 60°C. The reaction was allowed to proceed for 24 h until the isocyanate content reached the theoretical value as determined by di-*n*-butylamine backtitration method (Scheme 2).

In experiments where the influence of the monomer concentration on gel point was researched at 60°C, a series of different concentration of MDI solutions and TMP solutions were prepared. TMP solution was decanted into the flask and the MDI solution into the addition funnel. The dropwise addition of MDI solution into the flask was stopped once the gel was observed. The appearance of insoluble species in the mixture was regarded as the gel point, at the same time the mixture became so viscous that the agitation can hardly to continue. The concentration of MDI solution and TMP solution were always the same in all experiments.

In experiments where the effect of A_2 to B_3 ratio on molecular weight and degree of branching (DB) was investigated, different amounts of MDI solutions were added to a certain amount of TMP solution in a series of experiments. In these experiments the concentration of both MDI and TMP solutions was 10 wt %. Other reaction conditions, as mentioned above, were always the same.

Polymer Characterization

The molecular weights of the polymers were characterized by means of gel permeation chromatography (GPC) with Waters 2414 refractive index detector at 40°C in dimethylformamide



Scheme 2. Preparation of HBPU via monomeric A₂ plus monomeric B₃ strategy

with a flow rate of 1 mL min⁻¹ using polystyrene standards. The ¹³C NMR measurements were performed on a Bruker AVANCE 500 MHz NMR spectrometer with dimethyl sulfoxide-*d*₆ as solvent and tetramethylsilane as internal standard. The inverse-gated spectra were taken when the quantitative analysis of ¹³C NMR data was done due to the nuclear overhauser effect.

RESULTS AND DISCUSSION

Synthesis of HBPU

HBPU were synthesized via the monomeric A₂ plus monomeric B₃ route. In the study, MDI was chosen as A₂ and TMP as B₃. NMR spectra were widely used in polymer characterization and can provide us with a clear outline of polymer structure. The ¹³C NMR spectrum of HBPU was showed in Figure 1.

The methyl resonance that was attributed to the TMP appeared at 7.46 ppm (a) and the methylene resonances adjacent to the methyl appeared in the region of 23–21 ppm (b). The resonances in the range of 65–63 ppm (d) were assigned to the methylene adjacent to the unreacted hydroxy from TMP. Three well-resolved resonances were discernable in the range of 43–41 ppm (c) and were assigned to the quaternary carbon for the dendritic, linear, and terminal groups from TMP. The resonances in the region of 138–137 ppm (1), 136–134 (2) ppm, 128.86 ppm (3), and 118.30 ppm (5) were attributed to the benzene ring from MDI. The peak at 40.15 ppm (6) was attributed to the methylene from MDI and the DMSO-*d*₆ reso-

nance overlapped in this region. The carbonyl resonances (154–152 ppm) (4) and the methylene resonances adjacent to the ester group (63–60 ppm) (7) were also observed.

The final product was soluble in DMAc, THF, DMSO, etc. (Table I). The molecular weights and distribution of HBPU were tabulated on Table II.

Influence of A₂/B₃ Ratio on DB and Molecular Weight (M_w) of HBPU

In order to investigate the change of DB as well as the growth of the molecular weight with an increase in A₂ /B₃ ratio in the monomeric A₂ plus monomeric B₃ system, HBPU were prepared in the range of 0.5 : 1–1.2 : 1 for the stoichiometric ratio of A₂ : B₃. The stoichiometric ratio of A₂ : B₃ refers to the monomeric species. The solution concentration of both monomers was constant 10 wt % during the research.

DB is a representative parameter of the branching efficiency of HBPU. Müller,¹⁸ Frey,¹⁹ and Hawker²⁰ independently proposed calculations of DB for HBPU. In this study, both A₂ and B₃ were monomers, hence Hawker's equation was employed to evaluate DB of HBPU:

$$DB = \frac{D + T}{D + L + T} \quad (1)$$

where *D* represents the number of dendritic units, *L* represents the number of linear units, and *T* represents the number of terminal units.¹³

¹³C NMR spectroscopy was adopted to evaluate the DB for HBPU. For the purpose of confirming the assignments of the

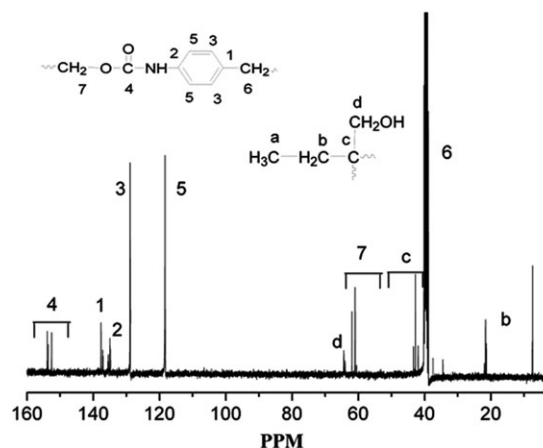


Figure 1. ¹³C NMR spectrum of HBPU.

Table I. Solubility of HBPU in Different Solvents

Sample	A ₂ : B ₃	Solvent					
		DMF	DMAc	DMSO	THF	Acetone	Methanol
1	0.5 : 1	++	++	++	+-	-	-
2	0.9 : 1	++	++	++	++	-	-
3	1 : 1	++	++	++	++	-	-
4	1.1 : 1	++	++	++	++	-	-
5	1.2 : 1	++	++	++	++	-	-

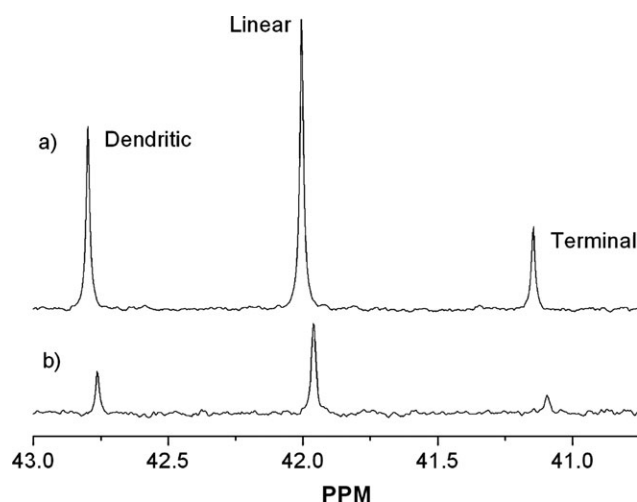
++: soluble; +-: partially soluble; -: insoluble.

Table II. Effect of Increasing Addition of MDI on DB of HBPU Prepared at about 10 wt%

Sample	A ₂ : B ₃	A : B	M _w (g mol ⁻¹)	M _w /M _n	D (%)	L (%)	T (%)	DB (%)
1	0.5 : 1	1 : 3	20,041	1.08	14.09	62.82	23.09	37.18
2	0.9 : 1	1.8 : 3	32,678	1.20	26.63	57.84	15.53	42.16
3	1 : 1	2 : 3	45,382	1.08	40.73	56.47	2.79	43.53
4	1.1 : 1	2.2 : 3	52,231	1.20	29.26	55.77	14.97	44.23
5	1.2 : 1	2.4 : 3	59,758	1.22	29.09	55.07	15.84	44.93

resonances from the quaternary carbons in the ¹³C NMR spectrum between 43 and 41 ppm, model compounds which represented dendritic units, linear units and terminal units, respectively, were synthesized using PI and TMP.¹³ There were three possible products for ¹³C NMR spectroscopic assignments, where trisubstituted signifies dendritic, disubstituted is equal to linear, and monosubstituted represents terminal groups in the hyperbranched product. For the PI-based model compounds, the resonances associated with the quaternary carbon in the ¹³C NMR spectrum moved downfield with increasing substitution (Figure 2).¹³ Three distinct resonances were observed for the model compounds in the ¹³C NMR spectra of model compounds in the carbon region of 45–40 ppm. Three well-resolved resonances (43–41 ppm) that corresponded to the quaternary carbon for dendritic (42.76 ppm), linear (41.96 ppm), and terminal (41.09 ppm) groups in the ¹³C NMR spectra of HBPU were all discernable, thus the resonances of the quaternary carbon of the TMP monomer were suitable to calculate the DB of HBPU. The DB results for HBPU prepared at about 10 wt % concentration were tabulated in Table II.

As the stoichiometric ratio of A₂ : B₃ was increased from 0.5 : 1 to 1.2 : 1, DB improved from 37.18% to 44.93%, which was consistent with the theoretical prediction in the earlier literature that DB would increase with increasing the stoichiometric ratio of A₂ : B₃.²¹ As shown in Table II, the increase in DB was attributed to an decrease in the proportion of linear units.

**Figure 2.** Resonances in the quaternary carbon region from ¹³C NMR spectroscopy of model compounds (a) and HBPU (b).

It is worth noting that the DB values of HBPU based on monomeric MDI and monomeric TMP were below the predicted 50% for HBPs. One reason for the lower DB than predicted may be the steric hindrance.²²

GPC of HBPU is presented in Figure 3. The concentration of the monomer was 10 wt %. As the molar ratio of A₂ to B₃ increased the chromatogram obviously moved from long retention time to short retention time. A slow increase in M_w is observed for monomeric A₂ plus B₃ polymerization of HBPU (Table II). When the stoichiometric ratio of A₂ to B₃ was 0.5 : 1, M_w value of the HBPU formed is fairly low, about 20,041 g mol⁻¹. Then as more MDI was added, an obvious increase is observed and M_w reaches to 32,678 g mol⁻¹ when the stoichiometric ratio of A₂ to B₃ was 0.9 : 1. When the stoichiometric ratio of A₂ to B₃ is increased from 1 : 1 to 1.1 : 1, the value is increased from 45,382 to 52,231 g mol⁻¹. M_w reaches to 59,758 g mol⁻¹ when the stoichiometric ratio of A₂ to B₃ is further increased to 1.2 : 1. The dispersity values of HBPU presented in Table II are relatively low, one possibility for the low dispersity values is that the strong intra- or intermolecular hydrogen bonds between the hydroxyl endgroups of HBPU make the data inaccurate as the many HBPU were not modified by esterification prior to GPC measurements. Another reason may be that HBPU were precipitated in methanol many times and most of the low molecular weight polymers may be removed before GPC analysis. The GPC chromatograms are very symmetrical indicating that HBPU formed via monomeric A₂ plus B₃ polymerization are homogeneous. The homogeneity is most likely due to extensive intramolecular cyclization as

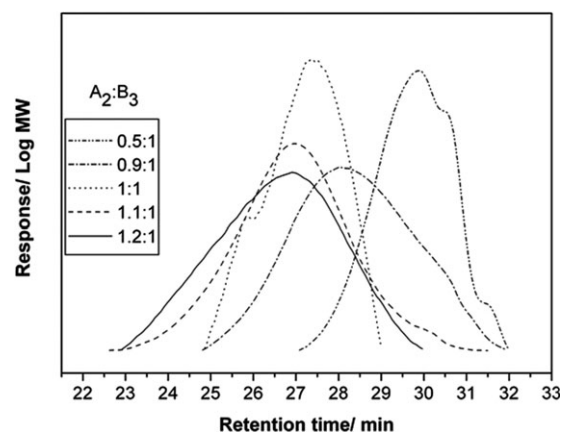
**Figure 3.** GPC chromatograms for increasing addition of MDI.

Table III. Effect of the Concentration of Reactant on Gel Point of HBPU

Solution concentration (%)			
Weight (%)	Volume (%)	Stoichiometric ratio of A ₂ to B ₃	Stoichiometric ratio of A to B
30	24.29	1.28 : 1	2.56 : 3
20	15.75	1.43 : 1	2.86 : 3
20	15.75	1.45 : 1	2.90 : 3
15	11.64	1.61 : 1	3.22 : 3
15	11.64	1.73 : 1	3.46 : 3
10	7.67	2.62 : 1	5.24 : 3
10	7.67	2.5 : 1	5.00 : 3
5	3.79	>4 : 1(no gel)	>8 : 3(no gel)

evidenced by the very high level of dendritic species and very low level of terminal units in the 1 : 1 reaction.

Influence of the Concentration of A₂ and B₃ on Gel Point

According to Flory, at the critical point for gel formation, the extent of reaction for A₂ was 0.75 and for B₃ was 0.50 in the idealized limit of slow A₂ addition into a large excess of B₃.⁸ However, as the extent of reaction for A₂ exceeds 0.75, gel does not necessarily form, but just possible because some other reaction conditions also influence the formation of gel, such as temperature, cyclization²³ and the solution concentration of monomers.⁸ Moreover, Flory's results were based on an assumption that there was no cyclization reaction, but cyclization is inevitable in the polycondensation reaction and cyclization competes with linear polymer formation. Cyclic structure is much easier to generate due to the well-known cage effect when the polycondensation reaction is conducted in solution.²⁴ In order to investigate the effect of the concentration of A₂ and B₃ on gel point in the monomeric A₂ plus monomeric B₃ system, a series of experiments with the solution concentration varying from 5 wt % to 30 wt % were carried out. Dual experiments were conducted to ensure the accuracy of the experiments.

The concentration of monomers and stoichiometric ratio of A₂ to B₃ at each concentration are presented in Table III. Stoichiometric ratio of A₂ to B₃ refers to the molar ratio of MDI to TMP added at the gel point. As the concentration of the monomer is reduced from 30 wt % to 10 wt %, the stoichiometric ratio of A₂ to B₃ increases from 1.28 : 1 to 2.56 : 1. When the concentration of the monomer is further reduced to 5 wt %, gel is never observed even though the stoichiometric ratio of A₂ to B₃ exceed 4 : 1. It is important to note that the amount of A₂ needed for gel at each concentration in the monomeric A₂ plus monomeric B₃ system is much higher than the theoretical value, which may attributed to the inevitable cyclization in the polycondensation. In addition, others have investigated the influence of the concentration of reaction medium on gel point using isopropyl alcohol as solvent, while the A₂ amount needed to reach the gel point was somewhat lower. We have found that the polarity of solvent may have a certain influence on the gel

point in the monomeric A₂ plus monomeric B₃ system, but more experiments need to be conducted.

CONCLUSION

HBPU with molecular weights ranging from 20,000 to 59,800 g mol⁻¹ were facily prepared via monomeric A₂ plus monomeric B₃ approach with MDI as A₂ and TMP as B₃. Quantitative ¹³C NMR spectrum based on the quaternary carbon of TMP was employed to calculate the DB of HBPU. The DB was increased from 37.18% to 44.93%. as the stoichiometric ratio of A₂ to B₃ was increased from 0.5 : 1 to 1.2 : 1. As the concentration of monomer was decreased from 30 wt % to 10 wt %, the stoichiometric ratio of A₂ to B₃ at the gel point increased from 1.28 : 1 to 2.56 : 1. In addition, it is indicated that when the concentration of monomer was 5 wt %, no gel takes place, which may attribute to the inevitable cyclization or the effect of solvent. Further work is needed to fully understand the question.

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REFERENCES

1. Jikei, M.; Kakimoto, M. *Prog. Polym. Sci.* **2001**, *26*, 1233.
2. Flory, P. J. *J. Am. Chem. Soc.* **1941**, *63*, 3083.
3. Russo, S.; Boulares, A.; Rin, A. D.; Mariani, A.; Cosulich, M. E. *Macromol. Symp.* **1999**, *143*, 309.
4. Monticelli, O.; Mariani, A.; Voit, B.; Komber, H.; Mendichi, R.; Pitto, V.; Tabuani, D.; Russo, S. *High. Perform. Polym.* **2001**, *13*, S45.
5. Jikei, M.; Chon, S. H.; Kakimoto, M.-A.; Kawauchi, S.; Imase, T.; Watanebe, J. *Macromolecules* **1999**, *32*, 2061.
6. Hao, J.; Jikei, M.; Kakimoto, M.-A. *Macromolecules* **2002**, *35*, 5372.
7. Webster, O. W.; Gentry, F. P.; Farlee, R. D.; Smart, B. E. *Macromol. Rep. A* **1994**, *31*, 935.
8. Unal, S.; Oguz, C.; Yilgor, E.; Gallivan, M.; Long, T. E.; Yilgor, I. *Polymer* **2005**, *46*, 4533.
9. Jikei, M.; Chon, S. H.; Kakimoto, M.; Kawauchi, S.; Imase, T.; Watanebe, J. *Macromolecules* **1999**, *32*, 2061.
10. Emrick, T.; Chang, H. T.; Fréchet, J. M. J. *Macromolecules* **1999**, *32*, 6380.
11. Czapik, M.; Fossum, E. *J. Polym. Sci. Part A* **2003**, *41*, 3871.
12. Kricheldorf, H. R.; Schwarz, G. *Macromol. Rapid Commun.* **2003**, *24*, 359.
13. Fornof, A. R.; Glass, T. E.; Long, T. E. *Macromol. Chem. Phys.* **2006**, *207*, 1197.
14. Unal, S.; Ozturk, G.; Sisson, K.; Long, T. E. *J. Polym. Sci. Part A* **2008**, *46*, 6285.

15. Mezzenga, R.; Plummer, C. J. G.; Boogh, L.; Månson, J. A. E. *Polymer* **2001**, *42*, 305.
16. Foix, D.; Fernández-Francos, X.; Salla, J. M.; Serra, A.; Morancho, J. M.; Ramis, X. *Polym. Int.* **2011**, *60*, 389.
17. Sangermano, M.; Sayed, H. E.; Voit, B. *Polymer* **2011**, *52*, 2103.
18. Yan, D. Y.; Müller, A. H. E.; Matyjaszewski, K. *Macromolecules* **1997**, *30*, 7024.
19. Hölter, H.; Frey, H. *Acta Polym.* **1997**, *48*, 298.
20. Hawker, C. J.; Lee, R.; Fréchet, J. M. J. *J. Am. Chem. Soc.* **1991**, *113*, 4583.
21. Schmaljohann, D.; Voit, B. *Macromol. Theory Simul.* **2003**, *12*, 679.
22. Ishida, Y.; Sun, A. C. F.; Jikei, M.; Kakimoto, M. *Macromolecules* **2000**, *33*, 2832.
23. Reisch, A.; Komber, H.; Voit, B. *Macromolecules* **2007**, *40*, 6846.
24. Ziegler, K. *Ber. Dtsch. Chem. Ges.* **1934**, *67A*, 139.