Synthesis of Highly Branched Comblike Polymers Having One Branch in Each Repeating Unit by Linking Reaction of Polystyryllithium with Well-Defined New Epoxy-Functionalized Polystyrene

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Summary: Highly branched comblike polymers having one branch in each repeating unit were successfully synthesized by the linking reaction of polystyryllithium (PSLi) with new epoxy-functionalized polystyrenes, poly(4-(3,4-epoxybutyl)styrenes, (**1**). The reaction of PSLi with **1** proceeded very fast to reach 88 % efficiency after 1 h and was complete within 24 h under the conditions in THF at -78 °C. A high molecular weight PSLi (M_w = 56.2 kg/mol) could be completely reacted with **1** (M_w = 8.36 kg/mol) to introduce into each of all epoxy reaction sites. However, the linking efficiency decreased with increasing the molecular weights of PSLi and especially **1**. With use of a high molecular weight **1** (M_w = 71.8 kg/mol), even a low molecular weight PSLi (M_w = 4.28 kg/mol) could not be quantitatively introduced into all epoxy functions, although a high efficiency of 88 % was achieved. The influence of both molecular weights on linking efficiency was examined in detail.

Keywords: branched; highly branched comblike polymer; living polymerization; poly(4-(3,4-epoxybutyl)styrene); polystyryllithium

Introduction

Poly(macromonomer) is of considerable interest from the standpoint of structure-property relationships because it possesses an extremely high-density branched structure with one branch in each repeating unit. In order to elucidate fundamental understanding regarding the effect of

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branching structure on properties, it is desirable to employ poly(macromonomer)s whose backbone and branch chains are precisely controlled in molecular weight. They are generally prepared by living polymerization of macromonomers with controlled structures.[1-7]

One of the most studied synthetic procedures for the synthesis of branched polymers utilizes "grafting-onto" method in which a backbone polymer chain contains several functional groups, which can react with the active terminal group of another polymer chain.[8] The above-mentioned extremely high-density comblike branched polymers have not been synthesized until recently by the grafting-onto method because of the steric hindering effect of branches and undesirable side reactions during the course of grafting reactions. Moreover, it is generally difficult to synthesize well-defined functionalized backbone polymers with precisely controlled chain lengths.

Recently, Deffieux and Schappacher have first successfully synthesized high-density comblike branched polymers structurally identical to the above-mentioned well-defined poly(macromonomer)s by the coupling reaction of polystyryllithium with the poly(2-chloroethyl vinyl ether)s obtained by living cationic polymerization.[9-12] Very surprisingly, polystyryllithium underwent coupling reaction virtually quantitatively to introduce into all repeating unit of the poly(2-chloroethyl vinyl ether)s whose degrees of polymerization are less than 60. Soon after, we have also been successful in synthesizing similar high-density comblike branched polymers by the coupling reaction of living anionic polymers with the poly(3-bromomethylstyrene)s prepared *via* living anionic polymerization.[13-15] Quantitative coupling efficiency was demonstrated in the reaction of the poly(3-bromomethylstyrene)s with a wide variety of living anionic polymers including even less reactive living polymers of *tert*-butyl methacrylate and ethylene oxide. Very interestingly, a high molecular weight polystyryllithium (M_w = 68 800, M_w/M_n = 1.03) could be introduced into all reaction sites. Almost at the same time, Hadjichristidis and his coworkers have reported the successful synthesis of highly branched comblike polymers by the coupling reaction of poly(isoprenyllithium) end-capped with DPE with the poly(4-chloromethylstyrene) obtained by TEMPO-mediated living radical polymerization.[16] Based on such successful results, it appeared that there is no steric limitation for the introduction of branch chains into backbone polymers under the suitable conditions. Thus, the "grafting-onto method" using well-defined backbone polymers also provides an effective procedure for the synthesis of high-density comblike branched polymers having one branch in each repeating unit. Unfortunately, only a few reliable synthetic examples have so far been reported.

Herein, we report on the possible synthesis of such high-density comblike branched polymers by another type linking reaction of polystyryllithium with a new well-defined epoxy-functionalized polystyrene *via* living anionic polymerization. We also report on the effect of molecular weights of backbone and branch chains on linking efficiency. No systematic study on the effect has been reported at the present time.

Experimental Section

All reagents used in this study were purchased from Aldrich, Japan unless otherwise stated and purified using standard procedures described elsewhere.[12] Living anionic polymerization and linking reaction were carried out by standard high-vacuum line (10^{-6} torr) technique using break seals. 4-(3-Butenyl)styrene was synthesized and anionically polymerized in a living manner as reported recently.[17-18]

Size exclusion chromatography (SEC, in THF at 30 °C), laser static light scattering (SLS, in THF at 25 °C), and ^{1}H and ^{13}C NMR ($CDCl_3$) measurements were performed following procedures described elsewhere.[12]

Epoxidation Reaction of Poly(4-(3-butenyl)styrene) with 3-Chloroperbenzoic Acid

Poly(4-(3-buteny)styrene) was treated with a 1.1-fold excess of *m*-chloroperbenzoic acid (MCPBA) towards each butenyl group in CH_2Cl_2 at 0 °C for 12 h. The reaction was terminated with 10 % K_2CO_3 and the organic layer was washed with water. The polymers were obtained in 80 ~ 90 % yields by usual work-up, followed by reprecipitation twice. The resulting polymers were finally freeze-dried from their absolute benzene solutions for 24 h. ^{1}H NMR (300 Mz, $CDCl_3$); δ 7.1 – 6.7 (br, 4H, aromatic), 2.8 (br, 1H, epoxy CHO), 2.6 (br, 3H, epoxy CHO and benzyl-CH_2), 2.3 (br, 1H, epoxy CHO), 2.1 – 1.6 (br, 3H, methine CH and butenyl CH_2), 1.6 –

1.1 (br, 2H, methylene CH_2), 08 – 0.5 (br, *sec*-butyl CH_3 (initiator residue). ^{13}C NMR (75 MHz, $CDCl_3$); δ 142.7, 138.4, 128.1, 127.8, 51.8, 47.3, 40.1, 34.4, 31.8, 30.4.

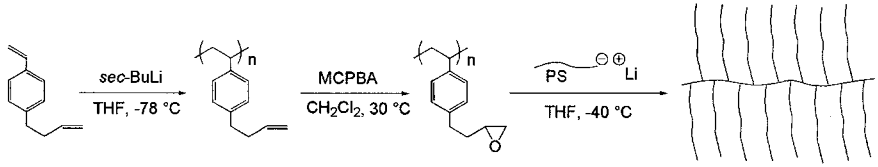
Linking Reaction of Polystyryllithium with New Epoxy-Functionalized Polymer

Polystyryllithium was prepared by the anionic polymerization of styrene with *sec*-BuLi in THF at -78 °C for 30 min. The linking reaction was then carried out by adding epoxy-functionalized polystyrene to a 2.0-fold excess of polystyryllithium in THF at -40 °C. The reaction mixture was allowed to stir at -40 °C for additional 24 ~ 168 h. The reaction was terminated with acetic anhydride and the reaction mixture was poured into a large amount of methanol to precipitate polymers. The objective comblike branched polymer was isolated nearly quantitatively by fractional precipitation as follows: To the polymer mixture dissolved in cyclohexane (0.3 wt-%), hexane (cyclohexane/hexane = 1/5, v/v) was slowly added and the mixture was allowed to stand at 5 °C for overnight. The branched polymer precipitated was collected by filtration, reprecipitated twice from THF to methanol, and freeze-dried from its absolute benzene solution for 24 h.

Results and Discussion

Synthesis of Well-Defined Epoxy-Functionalized Polystyrene Used as a Backbone Polymer

Our methodology for the synthesis of highly branched comblike polymers involves the following three reaction steps as illustrated in Scheme 1: In the first reaction step, the precisely controlled poly(4-(3-butenyl)styrene) in chain length was prepared by the living anionic polymerization of 4-(3-butenyl)styrene. In the second reaction step, the resulting polymer was quantitatively oxidized with MCPBA to transform into poly(4-(3,4-epoxybutyl)styrene) (**1**) used as a backbone polymer, keeping its precisely controlled chain structure. In the third step, the linking reaction of **1** with the preformed polystyryllithium (PSLi) was carried out to form a highly branched comblike polymer.



Scheme 1. Synthesis of highly branched comblike polymers.

As recently reported,[17-18] 4-(3-butenyl)styrene underwent living anionic polymerization under the conditions in THF at -78 °C using *sec*-BuLi as an initiator. The results of the polymerization carried out with different monomer to initiator ratios are summarized in Table 1. As can be seen, agreement of M_n values between calculated and determined by ^{1}H NMR and/or SLS is quite satisfactory in each case. Their molecular weight distributions were extremely narrow, M_w/M_n values being less than 1.04.

Table 1. Synthesis of **1** by means of anionic living polymerization of 4-(3-butenyl)styrene followed by epoxidation reaction with MCPBA.

sec-BuLi	Monomer	Poly[4-(3-butenyl)styrene]			**1**				
		$M_n \times 10^{-3}$			$M_n \times 10^{-3}$		DP_w	M_w/M_n	Functionality (%)
		calc	obs	M_w/M_n	calc	obs			
0.182	8.00	7.02	7.27	1.03	8.00	8.00	47.8	1.04	~100
0.0410	7.25	28.0	28.1	1.02	30.9	31.7	191	1.05	~100
0.0270	12.0	70.0	69.7	1.03	76.8	75.8	453	1.04	96

The butenyl C=C bond of the resulting polymers was carefully oxidized with MCPBA. SEC profiles of the polymers before and after the epoxidation reaction are shown in Figures 1(a) and (b). Both polymers exhibited monomodal narrow SEC distributions and were very similar in shape to each other. In their ^{1}H NMR spectra shown in Figures 2(a) and (b), two characteristic resonances at 4.99 and 5.84 ppm corresponding to vinyl protons of the butenyl group disappear completely, while new peaks at 2.30, 2.60, and 2.80 ppm assignable to the epoxy protons are observed at the expected ratios. The molecular weights calculated are in good agreement with those determined in all cases (see also in Table 1). These results in addition to SEC and ^{1}H NMR analyses clearly indicate that the epoxidation reaction proceeds cleanly and quantitatively to afford new well-defined epoxy-functionalized polystyrenes, **1**, with precisely controlled in chain length and with epoxy function in each repeating unit.

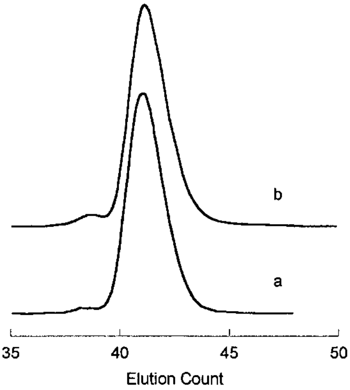


Figure 1. SEC profiles for polymers before (a) and after (b) oxidation reaction.

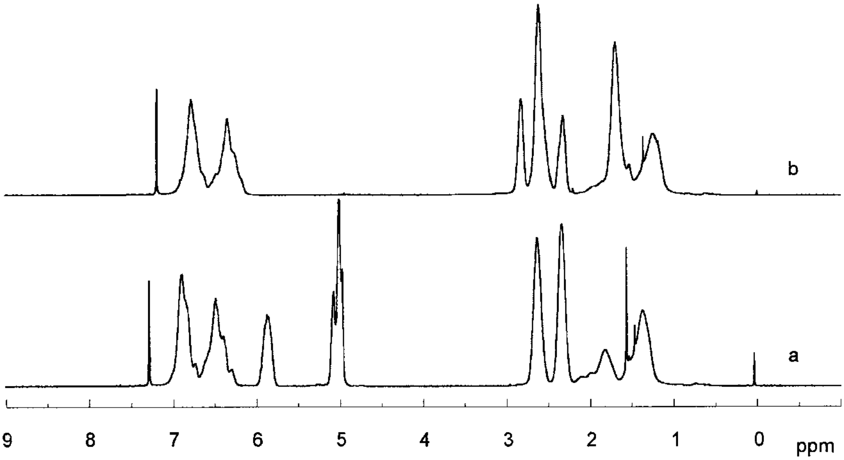


Figure 2. ^{1}H NMR Spectra of polymers before (a) and after (b) epoxidation reaction.

Synthesis of Highly Branched Comblike Polymers by Linking Reaction of 1 with Polystyryllithium

It is known that the reaction of living anionic polymers of styrene and 1,3-diene monomers with ethylene oxide is virtually quantitative under usual conditions and therefore often used as one of the most efficient functionalization reactions for the preparation of hydroxyl-terminated polymers.[19-21] By using similar reactions of living anionic polymers with epoxy-functionalized polymers, several branched polymers were previously prepared with limited branching efficiencies.[22-23]

For the synthesis of highly branched comblike polymers, the linking reaction of **1** with PSLi was carried out under the conditions in THF at -40 °C for 24 ~ 168 h. A 2.0-fold excess of PSLi toward each epoxy function of **1** was used to complete the reaction. In order to study the effect of molecular weights of backbone and branch chains on linking efficiency, three polymer samples of **1** with different degrees of polymerization from 47.8, 191 to 453 and (PSLi)s with M_w values in the range from 4 kg/mol to 56 kg/mol were used.

At first, we carried out the linking reaction of **1** (M_w = 8.36 kg/mol, DP_w = 47.8) with PSLi (M_w = ca. 10 kg/mol) under the above-mentioned conditions for 10 min, 1 h, 3 h, and 24 h to examine the kinetic feature of the reaction. The SEC profile of the reaction mixture obtained after 24 h is shown in Figure 3(a). A sharp monomodal peak eluted at a high molecular weight side presumably for a comblike branched polymer was observed along with a low molecular weight peak corresponding to the polystyrene used in excess in the reaction. A small amount of dimeric product of the starting polystyrene was also observed in this SEC profile. The dimer formation is likely due to the addition reaction of PSLi to the double bond of another polystyrene chain produced by eliminating LiH from PSLi as pointed out previously.[24-26] The objective comblike branched polymer was isolated nearly quantitatively by fractional precipitation using cyclohexane and hexane mixture at 5 °C.

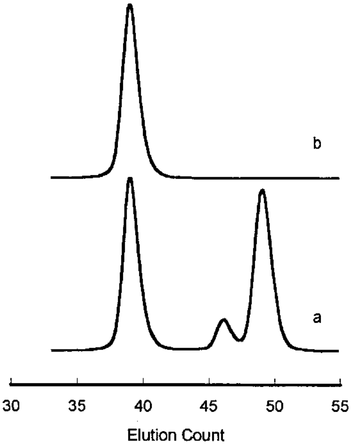
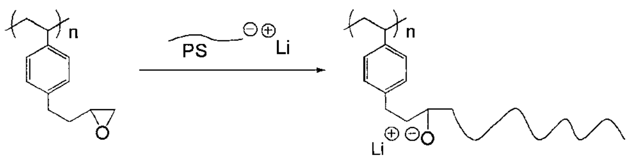


Figure 3. SEC profiles of comlike polymers before (a) and after (b) fractional precipitation.

The single sharp SEC peak as shown in Figure 3(b) implies that the isolated polymer is pure and free of its prepolymers. The absolute M_w value was measured by SLS because the apparent molecular weight estimated by SEC was not reliable due to the branching structure of the polymer. The absolute value was then compared to the calculated value assuming that the PSLi was quantitatively linked with all of the epoxy functions of **1**.

The reaction was fast and reached to 73 % linking efficiency only after 10 min. Efficiencies of 88 and 90 % were obtained after 1 and 3 h, respectively. Quantitative efficiency was achieved after 24 h, although the real reaction time to be completed was presumably less than 24 h. Thus, a high-density comblike branched polymer having one branch in each repeating unit could be obtained by the linking reaction of **1** with PSLi proposed in this study. Furthermore, the linking reaction was almost similar in rate to the coupling reaction of poly(3-chloromethylstyrene) with PSLi end-capped with DPE (76, 88, 90, and 100 % after 10 min, 1 h, 2 h, and 24 h) under the same conditions.[14] It is rather surprising from a viewpoint that the alkoxide anion is produced in every linking point in the reaction as shown below and thereby electrostatic repulsion in addition to steric hindrance is predicted at the final stage of the reaction.



Next, the linking reaction was carried out under the same conditions by changing the molecular weights of **1** and PSLi. The reaction was usually allowed to stand for 24 h. The longer reaction time to 168 h was employed in the cases with high molecular weight polymers. The results are summarized in Table 2.

Table 2. Synthesis of highly branched comblike polymer by linking reaction of **1** with PSLi in THF at -40 °C.

					Branched polymer				
Backbone polymer		Time	Polystyryllithium		M_w x 10^{-3}				GE
M_w x 10^{-3}	DP_w	(h)	M_w x 10^{-3}	DP_w	Calc	SLS	SEC	M_w/M_n	(%)
8.36	47.8	10 min	10.8	103	524	384	159	1.04	73
8.36	47.8	1	9.84	94.1	481	422	122	1.03	88
8.36	47.8	3	9.99	95.5	488	439	130	1.04	90
8.36	47.8	24	9.70	92.7	474	493	144	1.03	~100
8.36	47.8	168	5.19	49.4	257	257	79.7	1.03	~100
8.36	47.8	168	10.0	95.6	487	499	142	1.03	~100
8.36	47.8	168	56.2	540	2700	2790	498	1.04	~100
33.2	191	168	6.03	57.4	1180	1180	220	1.06	~100
33.2	191	168	11.1	107	2140	2230	323	1.06	~100
33.2	191	168	23.2	222	4450	3550	497	1.04	80
33.2	191	168	53.5	514	10200	7050	965	1.05	69
71.8	453	168	4.28	40.6	2016	1790	384	1.04	88
71.8	453	168	10.2	97.5	4710	3750	528	1.03	79

As expected, a lower molecular weight PSLi (M_w = 5.19 kg/mol) was quantitatively reacted with **1** (DP_w = 47.8). Interestingly, quantitative efficiency was realized in the reaction with the same **1** with a very high molecular weight PSLi (M_w = 56.2 kg/mol) to afford a high-density comblike branched polymer having one branch in each repeating unit (M_w = 2790 kg/mol).

With the use of another **1** (M_w = 33.2 kg/mol, DP_w = 191) as a backbone polymer, the linking reaction with either of (PSLi)s having M_w values of 6.03 and 11.1 kg/mol proceeded quantitatively as evidenced from agreement between M_w values calculated and observed by SLS in each case. On the other hand, PSLi with a M_w value of 23.2 kg/mol efficiently reacted with **1** with 80 % efficiency but not completely even after 168 h. The efficiency was further dropped to 69 % in the reaction with a higher molecular weight PSLi (M_w = 53.5 kg/mol). In the reaction using the highest molecular weight backbone polymer (M_w = 71.8 kg/mol and DP_w = 453) in this study, even low molecular weight (PSLi)s (M_w = 4.28 kg/mol and 10.2 kg/mol) could not be completely linked after 168 h, although high efficiencies of 88 and 79 % were realized. The efficiency was not improved at all by extending the reaction time up to 504 h.

All of the results indicate that the linking reaction proceeded quantitatively with suitable combinations of **1** and PSLi. Therefore, the linking reaction proposed herein provides an effective procedure for the synthesis of well-defined high-density comblike branched polymer having one branch in each repeating unit. However, the results also indicate that the degree of linking efficiency is significantly influenced by the molecular weights of both **1** and PSLi. In fact, the linking reactions using higher molecular weight **1** and PSLi were not complete even after longer reaction times (168 ~ 504 h). The similar trend was observed in the synthesis of high-density comblike polymers using analogous reactions previously reported by Deffieux et al,[9-12] Hadjichristidis et al,[16] and our group.[13-15]

We are tentatively considering the reason by a conformation change of the backbone chain. In the case of the short backbone chain (M_w = 8.36 kg/mol, DP_w = 47.8), the backbone chain can permit a free rotation as branch chain is introduced, providing less sterically crowding spaces to make the reaction more facile. On the other hand, the longer backbone chains (M_w = 33.2, 71.8 kg/mol, DP_w = 191, 453) might restrict the free rotation after certain numbers of branch chain are introduced, resulting in rod-like stiff chain conformation due to the steric crowding among adjacent branches. Further introduction of branch chain becomes more difficult by increasing steric crowding of the already introduced branches as the reaction proceeds. Tsukahara et al[27] and Schmidt et al[28-29] reported that the structure of poly(macromonomer) was changed from spherical or starlike to comblike or cylindrical molecular brush as increasing molecular weight of the backbone chain where the backbone chain was also changed from flexible to stiff chain conformation. Since poly(macromonomer) is not a suitable model, but similar in structure to the densely branched polymers synthesized herein, the similar conformation change of the backbone may occur in our case.

Further synthesis of highly branched graft copolymers is in progress, since epoxy function is cable of reacting with other living anionic polymers and chain-end-functionalized polymers with amino and hydroxyl functions.

Conclusions

For the synthesis of highly branched comblike polymers, the linking reaction of new well-defined epoxy-functionalized polystyrenes, **1**, with PSLi was carried out in THF at -40 °C. In the following combinations, **1** ($DP_w = 47.8$) *vs*. PSLi ($M_w = 5.19$, 10.0, or 56.2 kg/mol) and **1** ($DP_w = 191$) *vs*. PSLi ($M_w = 6.03$ or 11.1 kg/mol), the linking reaction proceeded quantitatively under the conditions employed here. We have successfully demonstrated that the "grafting-onto" method using the linking reaction proposed here is effective for the synthesis of well-defined high-density comblike branched polymers having one branch in each repeating unit. We have also found that both backbone and branch chains are limited in molecular weight for achieving quantitative efficiency in this linking reaction.

[1] Y .Tsukahara, J. Inoue, Y. Ohta, S. Kohjiya, Y. Okamoto, *Polymer J.* **1994**, *26,* 1013.
[2] V. Heroguez, S. Breunig, Y. Ganou, M. Fontanile, *Macromlecules* **1996**, *29*, 4459.
[3] Y. Ederle, F. Isel, S. Grutke, P. J. Lutz, *Macromol. Symp.* **1998**, *132*, 197.
[4] K. L. Beers, S. G. Gaynor, K. Matyjaszewski, S. S. Sheiko, M. Moller, *Macromolecules* **1998**, *31*, 9413.
[5] D. M. Haddleton, S. Perrier, S. A. F. Bon, *Macromolecules* **2000**, *33*, 8246.
[6] K. Nomura, S. Takahashi, Y. Imanishi, *Macromolecules* **2001**, *34*, 4712.
[7] D. Pantazis, I. Chalari, N. Hadjichristidis, *Macromolecules* **2003**, *36*, 3783.
[8] H. L. Hsieh, R. P. Quirk, in: "*Anionic Polymerization. Principle and Practical Applications*", D. E. Hudgin, Ed., Marcel Dekker, New York, Basel, Hong Kong pp369-392, 1996.
[9] M. Schappacher, A. Deffieux, *Macromol. Chem. Phys.* **1997**, *198*, 3953.
[10] M. Schappacher, A. Deffieux, *Macromol. Symp.* **1998**, *132*, 45.
[11] M. Schappacher, C. Billaud, C. Paulo, A. Deffieux, *Macromol. Chem. Phys.* **1999**, *200*, 2377.
[12] M. Schappacher, A. Deffieux, *Macromolecules* **2000**, *33*, 7371.
[13] S. W. Ryu, A. Hirao, *Macromolecules* **2000**, *33*, 4765.
[14] S. W. Ryu, A. Hirao, *Macromol. Chem. Phys.* **2001**, *202,* 1727.
[15] A. Hirao, H. Kawano, S. W. Ryu, *Polym. Adv. Technol.* **2002**, *13*, 275.

[16] T. Tsukatos, S. Pispas, N. Hadjichristtidis, *Macromolecules*, **2000**, *33*, 9504.
[17] H. Zhang, E. Ruckenstein, *Macromolecules* **1999**, *32*, 5495.
[18] A. Hirao, S. Kubota, T. Sueyoshi, K. Sugiyama, *Macromol. Chem. Phys.* **2001**, *202*, 1044.
[19] R. P. Quirk, G. M. Lizarraga, *Macromolecules* **1998**, *31*, 3424.
[20] R. P. Quirk, J. Ma, G. Lizarraga, Q. Ge, H. Hasegawa, Y. J. Kim, S. H. Jang, Y. Lee, *Macromol. Symp.* **2000**, *161*, 37.
[21] R. P. Quirk, Q. Ge, M. A. Arnould, C. Wesdemiotis, *Macromol. Chem. Phys.* **2001**, *202*, 1761.
[22] M. Takaki, R. Asami, M. Mizuno, *Macromolecules* **1977**, *10*, 845.
[23] E. Ruckenstein, H. Zhang, *J. Polym. Sci. Polym. Chem.* **1999**, *37*, 105.
[24] J. W. Burley, R. N. Young, *J. Chem. Soc. B* **1971**, 1018.
[25] M. D. Glasse, *Prog. Polym. Sci.* **1983**, *9*, 133.
[26] H. L. Hsieh, R. P. Quirk, "*Anionic Polymerization. Principle and Practical Applications*", Marcel Dekker, New York 1996, p.173.
[27] Y. Tsukahara, Y. Ohta, K. Senoo, *Polymer*, **1995**, *36*, 3413.
[28] P. Dziezok, S. S. Sheiko, K. Fischer, M. Schmidt, M. Möller, *Ang. Chem. Int. Ed. Engl.* **1997**, *36*, 2812.
[29] S. S. Sheiko, M. Gerle, K. Fischer, M. Schmidt, M. Möller, *Macromolecules* **1997**, *13*, 5368.