Polymerization of Macromonomers to Cylindrical Brushes Initiated by Organolanthanides

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Regular comblike polymers exhibit the structure of cylindrical brushes if the side chains are densely grafted, i.e., every monomer unit of the main chain carries a side chain, and if the main chain is much longer than the side chain. It is now experimentally and theoretically proven that the steric repulsion of the side chains forces the normally flexible main chain into an extended wormlike conformation with considerable directional persistence which may reach the order of 50−100 nm, depending on the side chain length. The traditional chemical pathway to cylindrical brushes is the free radical homopolymerization of macromonomers. Since the pioneering work of Tsukahara et al.[1,2] on the homopolymerization of methacryloyl end-functionalized polystyrene macromonomers to yield extremely high molar mass poly(macromonomers), several chemically different poly(macromonomers) were successfully synthesized.[3−13] Also, different routes to cylindrical brush polymers by "grafting from"[14−16] and "grafting onto"[17,18] techniques were reported, each of which exhibits certain advantages and disadvantages as outlined in Table 1. Another principal advantage of metallocene-catalyzed polymerizations is the possibility to obtain iso- or syndiotactic samples. Since this was not our goal in the present study, we have omitted this criterion in Table 1.

So far, living anionic, living cationic, or controlled radical polymerizations have not led to significantly larger main chain than side chain degree of polymerizations which would allow the control of main and side chain length as well as of the grafting density.[19−24] A successful living polymerization of macromonomers would also open a chemical pathway to amphipolar block copolymer brushes and cylindrical brush−flexible chain hybrid structures which should exhibit an interesting phase behavior.

Organolanthanides such as metallocenes of the type $[Ln(\eta^5\text{-}C_5R_5)_2X]$ (X = H, alkyl) are capable of polymerizing methacrylates with remarkable control of both degree of polymerization and syndiotacticity via an enolate mechanism to give polymers with very low polydispersity.[25,26] Attempts to polymerize macromonomers with metallocene catalysts have not led to degrees of polymerization of the main chain of above 100.[27]

Table 1. Comparison of Different Chemical Pathways To Prepare Cylindrical Brushes[a]

	grafting onto	grafting from	macromonomer polymerization
main chain polydispersity	+	+	−
side chain polydispersity	+	0	+
control of grafting density	−	0	+

[a] + = good control; − = poor control; 0 = intermediate control.

Table 2. Molar Masses M_w and M_n, Polydispersity M_w/M_n, and Degree of Polymerization P_n of Macromonomers As Determined by MALDI-ToF Mass Spectrometry

	M_w (g/mol)	M_n (g/mol)	M_w/M_n	P_n
MM-PS_{10}	1445	1348	1.05	10
MM-PS_{13}	1740	1658	1.05	13
MM-PS_{17}	2267	2161	1.05	17

We report here the first successful polymerization of methacrylates with oligostyryl side chains to give poly(macromonomers) with degrees of polymerization in the main chain of above 500 utilizing organolanthanide initiators.

Macromonomers 1−3 were prepared by anionic polymerization with the initiator *sec*-butyllithium as described earlier (Table 2).[1,2] The results of the macromonomer polymerization by organolanthanide initiator, as shown in Scheme 1, are summarized along with the reaction conditions in Table 3. The macromonomer was dissolved in benzene or THF and treated with $AlMe_3$. A benzene solution of $[Sm(\eta^5\text{-}C_5Me_4Et)_2Cl(THF)]$[28,29] which was activated with $AlMe_3$ was then added to initiate the polymerization at ambient temperature. The reactions were terminated after 12 h reaction time by diluting the reaction mixture with THF and precipitating the polymer into methanol. All samples were freeze-dried from benzene. At the polymerization temperature applied the catalyst is known to yield atactic polymer chains. Accordingly, this topic was not pursued in the present work.

Conversion of the macromonomer proceeded up to about 60%, at which point the increasing viscosity of the reaction mixture prevented further reaction. The vastly different efficiencies of the initiator (see Table 3) clearly demonstrate that the polymerization of macromonomers is neither living nor controlled. Certainly one major problem lies in the unfavorable polymerization conditions. To obtain high molar mass polymacromonomers, the polymerization has to be conducted at extremely high macromonomer concentration in order to avoid the osmotic repulsion experienced by a macromonomer diffusing toward the highly crowded growing chain ends in dilute solution. Only at high enough average concentration of macromonomer and growing polymacromonomers in the reaction mixture is this concentration gradient eliminated at the expense of an extremely slow mobility of the macromonomer. Moreover, the initiator concentration is extremely small, and the unavoidable loss due to termination by impurities prevents a controlled polymerization. Since impurities have a predominant influence on the polymerization, the initiator efficiencies given in Table 3 do not allow to quantify solvent effects or the influence of macromonomer molar mass. However, as known from radical

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Scheme 1. Polymerization of Macromonomers

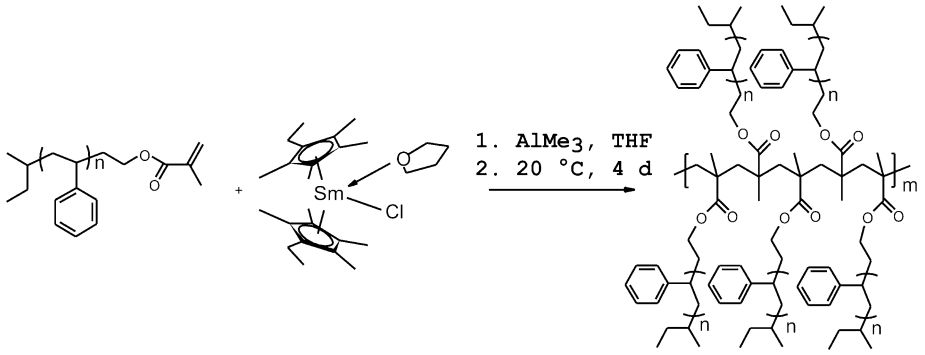

Table 3. Polymerization Conditions of Macromonomers in Benzene (b), THF (T), and a Mixture of Benzene and THF (bT)

	g (mmol)	solvent (mL)	concn (mol L^{-1})	[MM]/[cat.]	cat.[c] (μmol)	% conv	eff (%)
PM-PS_{10}b	3.0 (2.22)	11.0[a]	0.20	3.7	600	54	0.9
PM-PS_{13}T	1.3 (0.78)	3.0[b]	0.26	207	4.0	40	49.3
PM-PS_{17}T	2.0 (0.93)	2.5[b]	0.37	171	5.4	59	9.3
PM-PS_{17}bT	2.4 (1.11)	1.4[a] + 1.4[b]	0.40	277	4.0	28	24.8

[a] Benzene. [b] THF. [c] Activated with 0.2 mL (0.15 g, 2.08 mmol) of $AlMe_3$.

Table 4. Light Scattering and GPC Characterization of Polymacromonomers after Fractionation (Sample Code f)

	% content residual MM	M_w (SLS) (g/mol)	R_g (SLS) (nm)	R_h (DLS) (nm)	P_w (SLS)	M_w/M_n (GPC)
PM-PS_{10}b f	6	513 000	32	16	381	1.86
PM-PS_{13}T f	14	530 000	30	15	305	1.92
PM-PS_{17}T f	4	4.5×10^6	73	39	2082	1.91
PM-PS_{17}bT f	19	2.4×10^6	54	30	1060	3.55[a]

[a] The unfractionated sample exhibits a bimodal molar mass distribution as shown in the Supporting Information. The data are shown for the fractionated sample, which, however, shows very pronounced tailing to small molar masses and still contains a small fraction of the low molar mass peak.

polymerization of macromonomers also for the present system high monomer concentrations are necessary in order to obtain high molar mass polymers as discussed above. Because of the presence of impurities, the effect of small variations in concentration could not be investigated systematically.

Another disadvantage of the high concentrations to be applied for the polymerization is that the extremely high viscosity makes it virtually impossible to take samples for a kinetic investigation during the course of the reaction without additional termination.

The polymacromonomer samples were characterized by GPC vs polystyrene standards in THF and by static and dynamic light scattering (Table 4). For all samples the light scattering results (M_w, R_g) were corrected for residual macromonomer content as described in detail in the Supporting Information. Unfortunately, the amount of samples PM-PS_{13}T and PM-PS_{17}bT was so small that an efficient fractionation could not be conducted, and the residual macromonomer content was quite high, accordingly. For such samples the error in M_w and R_g originates primarily from the uncertainty in polymacromonomer concentration rather than from the neglected scattering intensity of the macromonomer.

The molar masses determined by light scattering are significantly higher than those obtained by GPC. This is expected because the much smaller contour length of the cylindrical brushes due to the large monomer molar mass cannot be compensated by the increase of chain stiffness, and accordingly, a much smaller hydrodynamic volume results.

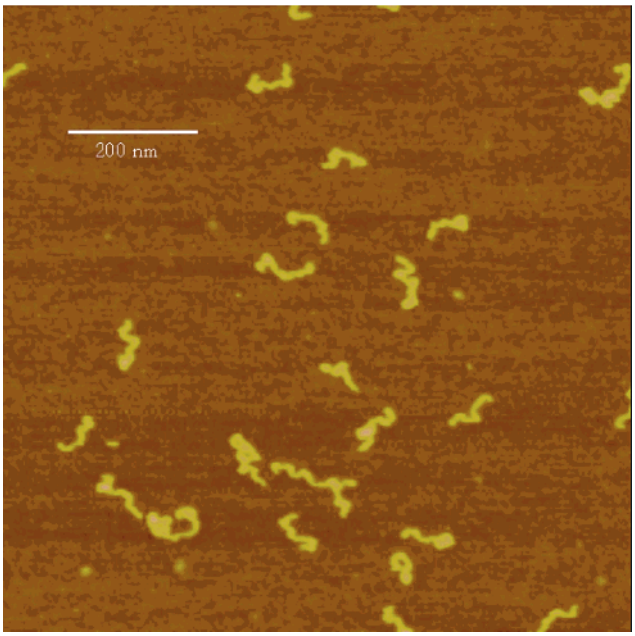

Figure 1. AFM picture of a narrow fraction of polymacromonomer PM-PS_{10}b obtained by collecting a small volume of the eluting polymer during a GPC experiment. The sample was spin-cast from dilute solution in cyclohexane onto carbon-coated mica.

The polydispersities M_w/M_n of the high molar mass samples lie in the regime $\approx$2, which is significantly smaller than obtained by free radical polymerization ($3 \leq M_w/M_n \leq 5$). The elution peaks show a pronounced tailing toward smaller molar masses. Obviously, even rather large chains are terminated during the course of the reaction. This could originate from slow termination by impurities and/or by slow initiation, both caused by the reduced mobilities of the reaction components at the high concentrations applied.

The cylindrical brush conformation of the polymers is documented by AFM (see Figure 1). The sample was dissolved at low concentration ($c = 0.005$ g/L) in cyclohexane and spin-cast onto carbon-coated mica. Cyclohexane is a poor solvent for the PS-polymacromonomers.

This leads to a preferred adsorption onto the surface, thus avoiding monolayer island formation, which was frequently observed for PS-polymacromonomers.[7] However, another consequence of the poor solvent is that the polymer brushes are partially collapsed, as seen in Figure 1. Clearly wormlike molecules are identified which are not as stiff as those polymacromonomers with significantly larger side chains as expected.

In conclusion, we have demonstrated that the organolanthanide-initiated polymerization of macromonomers can be efficiently performed to yield polymacromonomers of high degree of polymerization in the main chain. Because of the extremely unfavorable reaction conditions required for obtaining high molar mass polymacromonomers, the polymerization is neither living nor controlled. At the present state of investigation we have some vague evidence that the polymerization proceeds partly controlled, i.e., that a certain fraction of high molar mass species still contains active polymerization sites. Thus, future work will aim at the realization of block copolymer structures with at least one block having a cylindrical brush structure.

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Supporting Information Available: Details of sample preparation, GPC traces, and Zimm plots. This material is available free of charge via the Internet at http://pubs.acs.org.

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