Macromol. Symp. **2004**, *215,* 179-189

On the Preparation and Polymerization of *p*-Methoxystyrene Miniemulsions in the Presence of Excess Ytterbium Triflate

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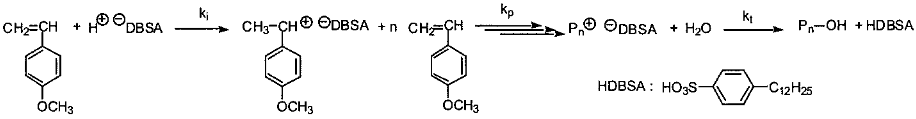
Summary: The cationic polymerization of p-methoxystyrene using an acid initiator and ytterbium triflate as a cocatalyst was studied in miniemulsion. Conductometry measurements revealed that ytterbium triflate dissociates in water. The high ionic strength implemented by ytterbium cation releasing requires the use of an electrosteric surfactant, i.e. sodium dodecylpolyoxyethylene(8) sulfate, as an efficient stabilizer against particle coalescence. The catalyst increases significantly the polymerization rate but only moderately affects the molar masses. A tentative polymerization scheme is proposed based on these results and several other "blank" experiments.

Keywords: cationic polymerization; miniemulsion; p-methoxystyrene; rare earth catalyst

Introduction

Ionic polymerization in emulsion is a subject developed in our team over a decade, both on ring opening polymerization (cyclosiloxanes,[1,2] phenyl glycidyl ether[3]) and polymerization of vinyl monomers (n-butyl cyanoacrylate[4], p-methoxystyrene[5]). We reported in this last study on the cationic polymerization of p-methoxystyrene (*p*MOS) catalyzed by an acid surfactant, namely dodecylbenzene sulfonic acid.

Scheme 1



DOI: 10.1002/masy.200451115

A simple polymerization scheme applies (Scheme 1). All reactions are interfacial. Initiation is the limiting step, whereas propagation is fast because the active centers pair with the surfactant head, which acts as a bulky counter-ion. Termination with water limits strongly the final molar masses. Recently, Sawamoto and coworkers described the polymerization of p-methoxystyrene with the aid of rare earth triflates,[6-8] a water-resistant Lewis acid extensively used in organic synthesis (see ref. [9] for a recent review). The HCl adduct of the monomer was first used as an initiator, and ytterbium triflate as a cocatalyst.[6,7] It was shown that chains could be controlled up to 30% conversion, after which transfer reactions with water were too high to maintain control of the polymerization. Final molar masses were in the order of 3000 g/mol, with low polymolecularities (less than 1.4). Sulfonic acids were also used as initiators,[8] with a neat increase in the rate of polymerization, presumably by bringing protons at the interface. In this latter case, however, molar mass distributions were higher (1.7). Other metal triflate were also found to be efficient Lewis acids for catalyzing *p*MOS polymerization.[10] Another team reported on the polymerization of *p*MOS in water using again ytterbium triflate together with phosphonic acids as initiator, which allowed longer chains to be produced (typically 10,000 g/mol).[11] In all these studies, no mention of the actual colloidal nature of their dispersions were given, though it is revealed to be a striking parameter for the process.

We present here some results on polymerization of *p*MOS in miniemulsion using ytterbium triflate as a catalyst. After considering the molecular structure of ytterbium triflate in water, we focus our discussion on colloidal stability aspects and show how the presence of the catalyst affects the polymerization scheme proposed before (Scheme 1).

Experimental part

All reagents used in this study were characterized at least by ^{1}H NMR before use. *p*-methoxystyrene (*p*MOS) (ACROS, 96%) was used as supplied. Disponil surfactant Fes32is, polyoxyethylene(8) lauryl sulfate sodium (**1**) was kindly donated by Cognis and characterized by MALDI-TOF mass spectrometry. Alkyl chains are predominantly composed of 12 carbons, with less than 30% with 14 and 16 carbon atoms. The ethoxylated part is widely distributed and centered at 8 ethylene oxide units. All chains bear a sulfate moiety.

$$C_{12}H_{25}\!-\!\left(O\!-\!CH_2\!-\!CH_2\right)_8\!-\!OSO_3^-\,Na^+$$

1

HCl 35% (Prolabo) and H_2SO_4 98% (BDH) were diluted in distilled water prior to their addition in the emulsion. Ytterbium triflate was donated by Rhodia Terres Rares (La Rochelle, France). The pH of ytterbium triflate solution is unchanged compared to pure water, which is an indication that no triflic acid formed in the sample during storage.

All analysis methods, e.g. ^{1}H NMR, particle size measurements by QELS, SEC in THF were described previously.[5] Conductometric measurements were performed on a Consort K120 digital conductometer, equipped with a platinum electrode and a temperature probe. KCl and acetic acid were used as, respectively, strong and weak electrolytes to validate the conductometry measurements. TEM analysis was performed on a JEM100CXII UHR microscope from JEOL, with a 100 kV acceleration tension. One drop of the sample was deposited on a carbon coated grid and allowed to evaporate before analysis.

Regular miniemulsions were obtained by sonication using a 450 Branson Ultrasonics Corporation sonifier at power 7 (25 W). *p*MOS was added to the surfactant solution maintained by means of an ice bath at a temperature of 25°C during sonication (1 min 30 sec). Small volumes of HCl or H_2SO_4 solutions were then added to the reactor to start the polymerization (typically 3 to 5 equivalents compared to surfactant content). The emulsion was then transferred into the reactor where polymerization proceeded under thermal regulation (60°C) and mechanical stirring (350 rpm).

At regular time intervals, 0.5 mL aliquots were withdrawn. One drop from the sample was poured in a diluted surfactant solution ($c=10^{-4}$ M< CMC) prior to QELS particle diameter measurement. 1 mL of methanol and 1 mL of water were poured into the sample to stop the reaction and break the emulsion (adding NaOH better inhibits the reaction but also catalyzes the formation of ytterbium oxides, which precipitate and disturb the emulsion treatment). CH_2Cl_2 was also systematically added in the tube to ensure that no organic product remained in water. The organic phase was efficiently separated from the aqueous one by centrifugation (30 mins at 5300 rpm on a bench centrifugator), dried with $MgSO_4$, evaporated, redissolve in THF and filtered (0.45 μm filters from MILIPORE) prior to SEC analyses.

Results and discussion

1. Yb(OTf)$_3$ molecular structure in water

Among the numerous reports that use ytterbium triflate as a catalyst in water, none really described so far the actual configuration of this salt in water. Triflate is, similar to chloride or perchlorate, a non-coordinating ligand linked to ytterbium through its outer-sphere, as revealed by various analytical methods.[12] Since ytterbium triflate has been shown to dissociate totally in polar solvents such as acetonitrile,[13] it is suspected that dilution in water would also produce the 1:3 electrolytes.

To confirm this point, conductometric analyses were carried out on Yb(OTf)$_3$ and YbCl$_3$ solutions of various concentrations. Only one paper reports values for conductometry of Yb(OTf)$_3$ in water at two concentrations.[12] YbCl$_3$ is known to totally dissociate in water.[14] Figure 1 shows ytterbium equivalent molar conductance ($\Lambda_{\mathrm{mol,Yb}}$) as a function of YbCl$_3$ and Yb(OTf)$_3$ water concentrations expressed as the square root of their normality, for the purpose of comparison with the literature.[14] Equivalent molar conductances were calculated by dividing the molar conductance by 3 (the valence of the ytterbium cation) and substracting the molar conductance for Cl$^-$ (76.3 S/m^2/mol) and OTf$^-$ (44.5 S/m^2/mol).

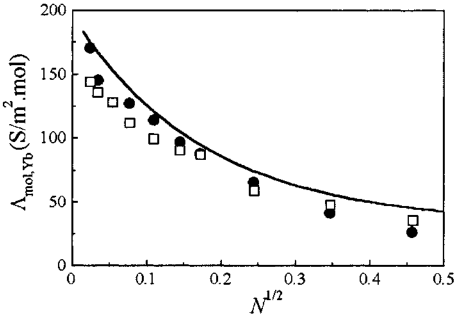


Figure 1: Equivalent molar conductance for ytterbium cation as revealed by conductometric measurements. (□) YbCl$_3$; (●) Yb(OTf)$_3$; (—) YbCl$_3$ from the literature.[14]

$\Lambda_{\mathrm{eq,Yb}}$ slowly decreases with ytterbium triflate concentration. Similar behavior is observed for YbCl$_3$, in agreement with previous reports from the literature (line in Figure 1). Such a decrease is not due to a weak electrolyte behavior. Instead, rare earth cations can complex with 8 or 9 molecules of water, depending on the type of lanthanide and its concentration in water, which readily affect their ionic sphere and thus their mobility in water. Note that our results compare well with those from the literature (Figure 1), although we used a typical conductometer.

Dissolution of Lewis acids in water is known to involve two steps: first, dissociation of the salt and water complexation, and second, hydrolysis of the metal cation (scheme 2).[15] Rare earth atoms are considered "water-resistant" due to their stability towards hydrolysis at neutral pH;[16] where other Lewis Acids, such as $AlCl_3$ or $TiCl_4$, form hydroxides and quickly deactivate through aggregation.[15] By evaporation, the crystal salts reform and the catalyst can thus be reused.

Scheme 2

$$Yb(OTf)_3 \xrightleftharpoons{\text{dissociation}} 3\ OTf^- + Yb(H_2O)_m^{\ 3+} \xrightleftharpoons{\text{hydrolysis}} Yb(H_2O)_{m-n}(OH)_n^{(3-n)+} + nH^+$$

There are three main implications for the polymerization process studied here: i) a high ionic strength will develop in the water medium, and thus extremely robust surfactants are sought to produce stable emulsions; ii) the catalyst dissociated in water will not be capable of catalyzing a polymerization reaction under this state; however, by saturating the water, a few ytterbium triflate molecules may reach the interface and catalyze the polymerization; iii) some ligands are known to penetrate the inner sphere of the ytterbium atom and thus form stable complexes even in water. Sulfates were for instance demonstrated by conductometry to inner-coordinate rare earth atoms.[17] Recent studies from organic chemistry showed that this property was actually used to prepare Lewis Acid Surfactant Complex (LASC) by mixing sodium dodecyl sulfate and ytterbium chloride in water.[16]

2. Colloidal stability during the preparation and polymerization of *p*MOS

Table 1 summarizes the various experiments carried out in the present study. Increasing loads of ytterbium triflate were added and different blank experiments, e.g. without catalyst or adding only sodium triflate and ytterbium chloride in excess, were also performed. HCl and H_2SO_4 were added as a proton source for starting the polymerization.

As stated above, the dissociation of ytterbium triflate to release trivalent cation and monovalent anions has profound impact on the ionic strength of the dispersion. Usual surfactants, e.g. non-ionic, cationic or anionic ones, could not stabilize the particles even at low catalyst content. One family of surfactants, i.e. Disponil™ from Cognis, is used in conventional radical emulsion polymerization in industry, when efficient stability against particle coalescence is sought. These surfactants indeed bear a polyethylene oxide moiety between the alkyl chain and the sulfate end-group, which provides rather efficient electrosteric stabilization. Among these, polyoxyethylene(8) lauryl sulfate sodium was chosen since it provides satisfactory resistance against a trivalent cation such as ytterbium.

Table 1: Recipes for all experiments reported in this article.[a]

Run	m_{pMOS} (g)	m_1 (g)	m_{water} (g)	m_{acid} (g)	$m_{additive}$ (g)	Additive[d]	Particle size (nm)	σ[b]	R_p (%/h)	$\overline{M_n}$ (g/mol)	$\overline{M_w}/\overline{M_n}$
1	2.40	0.56	4.14	0.14	-	-	240	0.04	8.5	990	1.17
2	2.43	0.57	4.07	0.14	0.22	$Yb(OTf)_3$	240	0.19	13.0	950	1.22
3	2.41	0.56	4.00	0.14	0.58	$Yb(OTf)_3$	-	-	16.0	1180	1.22
4	2.41	0.56	4.00	0.15	1.11	$Yb(OTf)_3$	325	0.90	24.0	1230	1.30
5[c]	1.83	0.44	3.02	0.09	0.83	$Yb(OTf)_3$	740	1	12.5	1260	1.31
6[c]	2.41	0.56	4.07	0.12	1.11	$Yb(OTf)_3$	620	1	9.0	1270	1.29
7	2.41	0.56	4.09	0.16	0.31	$YbCl_3$	-	-	14.5	850	1.15
8	1.83	0.43	3.02	0.05	0.89	Alun salt	-	-	16.0	800	1.18
9	2.40	0.56	4.02	0.16	0.69	NaOTf	-	-	16.5	970	1.21

[a] Other parameters: temp. 60°C, stirring rate: 350 rpm; [b] Particle size distribution ($0<\sigma<1$); [c] Catalyst: H_2SO_4;
[d] Alun salt: $AlKO_8S_2,12H_2O$: NaOTf: sodium triflate.

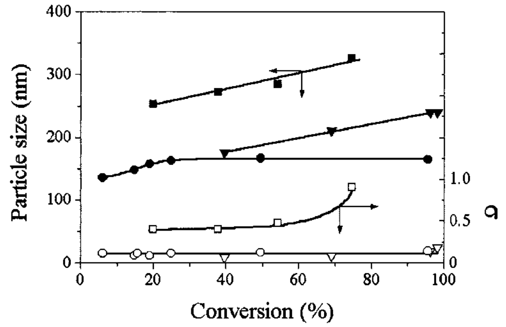


Figure 2: Particle size (diameter d_z, in nm, plain symbols) and polydispersity (σ, without units, open symbols) as a function of conversion for experiments carried out in presence of ytterbium triflate (in wt.%, see Table 1): (●) 0% (run 1). (▼) 2.7% (run 2). (■) 13.5% (run 4).

Figure 2 shows the particle size and polydispersity evolutions with conversion for two contents of catalyst $Yb(OTf)_3$ and one control reaction in the absence of catalyst (other results are provided in Table 1). In all cases, a stable dispersion was obtained with the final particle sizes increasing slightly with ytterbium content (typically between 150 and 500 nm). Emulsion with low content of catalyst gives a fine particle distribution, whereas for the experiment containing 13.5wt.% of ytterbium triflate, a polydispersity coefficient of 1 is reached before the end of polymerization. For experiments carried out with H_2SO_4 as the acid, much larger particles were obtained (Table 1, runs 5 and 6). Such results may be due to a further increase of the ionic strength by sulfate divalent salt.

Figure 3 shows a micrograph of a dispersion obtained for 13.5wt.% $Yb(OTf)_3$. Even if a multi-population of particles is generated in the presence of ytterbium triflate, it still gives a dispersion of monomer droplets in water. The poor contrast and average diameter superior to that obtained by QELS is due to the smoothness of the particles, that spread slightly on the microscope grid.

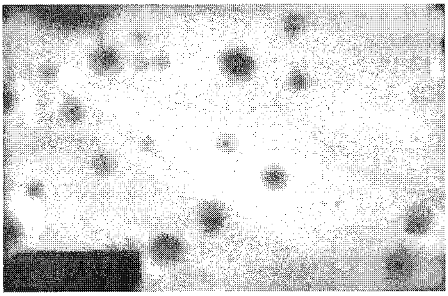


Figure 3: Transmission electron micrograph of the emulsion containing the highest content of ytterbium triflate (13.5wt.%, run 4 in Table 1). Scale: 1μm/cm.

3. Kinetics aspects

Figure 4 plots conversion versus time for experiments conducted at 60°C and various contents of ytterbium triflate. Ytterbium triflate clearly increases the polymerization rate (Table 1), and conversion goes up to a maximum of 85% for the largest ytterbium triflate content. Since particle sizes are slightly higher when the ytterbium triflate is introduced, and thus their surface area is smaller, an increase of the overall rate of polymerization is evidence for co-catalyst participation in the polymerization process.

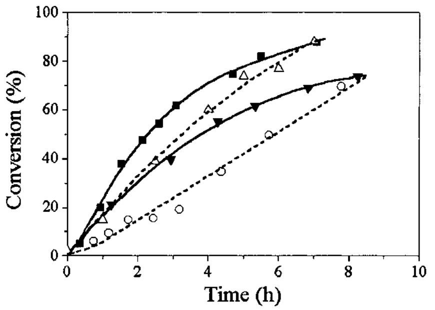


Figure 4: Influence of the content of ytterbium triflate on the conversion to polymer. Ytterbium content (in wt.%, see Table 1): (○) 0% (run 1); (▼) 2.7% (run 2); (△) 6.7% (run 3); (■) 13.5% (run 4).

Figure 5 presents the average molar masses for the above experiments. The molar mass increase more sharply at higher ytterbium triflate content, but to only about two or three monomer unit on average. A pseudo-plateau is observed in all cases, though the molar masses level off at larger conversions at higher ytterbium triflate contents (50%, compared to 20% conversions without ytterbium triflate, see Figure 5).

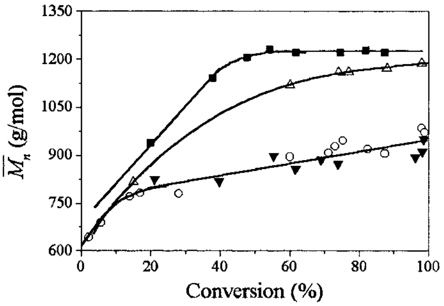


Figure 5: Influence of ytterbium triflate content on the average molar masses with conversion. Same symbols as Figure 4.

The type of acid introduced as a proton source is quite important. We saw before that adding H_2SO_4 dramatically affects the particle sizes, but even more sharply the polymerization rates (Table 1, runs 5 and 6), surely due to the strong complexation of sulfate with ytterbium. However, neither the acid content nor the type of acid modify the average molar mass evolution with conversion (Figure 6). This result may indicate that chloride and sulfate ions, in the presence of excess ytterbium triflate, are only "spectators" of the polymerization.

4. Understanding the mechanism of polymerization

Since some obvious variations were found in terms of polymerization rates and average molar masses while adding ytterbium triflate to the recipe, designed experiments were conducted to show the roles of each actor in the polymerization scheme. $YbCl_3$ or triflate sodium in respective molar contents to $Yb(OTf)_3$ did not show striking differences in kinetics and produced molar masses similar to the polymerization carried out without ytterbium catalyst (Table 1, runs 7,8). Increasing consequently the ionic strength resulted in lower final average molar masses (Table 1, run 9). The presence of ytterbium *and* triflate is important for the process.

Molar mass/conversion plots presented here (Figures 5 and 6) are close to those obtained in our previous study using DBSA as an INISURF.[5] Two main conclusions can be drawn from our previous observations: i) the fact that the molar masses reach a plateau shows that, in the present system, polymerization is interfacial and the critical DP limits the average molar masses;[5] ii) the polymolecularity always evolve with conversion (Figure 6), showing that chains are stopped by water and not reactivated. Indeed, a controlled/living system would show a decrease of polymolecularity with conversion.[18] Another indicator against controlled polymerization is given by the evolutions of molar mass with conversion, which are independent of the type and content of acid introduced in the recipe (Figure 6).

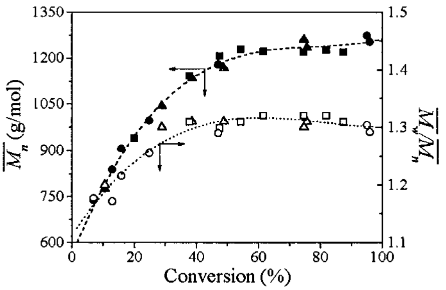
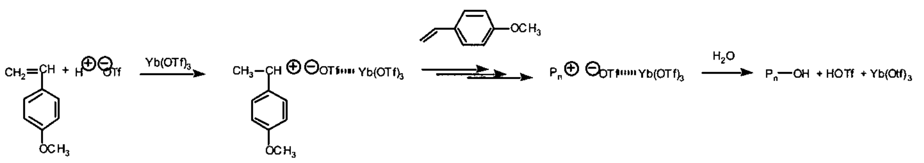


Figure 6: Influence of type and content of acid on the average molar masses (plain symbols) and polymolecularity index (open symbols) with conversion. (■) HCl, 3.5 eq; (●) H_2SO_4, 1.9 eq; (▲) H_2SO_4, 2.1 eq.

Scheme 3



A tentative polymerization scheme is proposed in Scheme 3. A triflate anion, released from ytterbium triflate dissociation in water, captures a proton and reaches the interface to start *p*MOS polymerization. Triflic acid is believed to be the initiator, since triflate ions are in large excess compared to chloride ions and HCl partitions preferentially in water compared to triflic acid or other superacids.[19] This is relevant to experiments with H_2SO_4, where sulfates are inactivated by complexing ytterbium. One of the few ytterbium triflate molecules present in the dispersion then associates with the triflate to form a bulky counter-anion. Such Lewis Acid/Brønsted Acid complexes have been proposed previously by Sawamoto and coworkers as the main catalyst of *p*MOS polymerization.[6-8] Besides, polymerization is obviously interfacial and chain-stopping events with water are predominant. The fact that longer chains are produced when ytterbium triflate is used, may be due either to the lower content of water at the particle interface due to high ionic strength, or the faster propagation (compared to termination) rates, or both.

Conclusion

This short communication has disclosed some of the constraints imposed by the addition of a catalyst salt in an emulsion process. Ytterbium triflate dissociation increases drastically the ionic strength; only surfactants that provide electrosteric stability avoid particle coalescence. It seems clear that very few ytterbium triflate molecules participate in the reaction,[6-8] which requires concentrated catalyst conditions. In this case, the co-catalyst helps at generating, with the triflate anion, a reactive bulky ion pair at the interface, which increase the polymerization rates and produce slightly higher final average molar masses.

Obviously, average molar masses in the present *direct emulsion* process are much lower than those obtained in other studies (typically 3000 g/mol).[6-8] We will present later on results obtained using DBSA as surfactant and excess ytterbium triflate, for which an *inverse (water-in-monomer) emulsion* process explains such discrepancies.[20]

Acknowledgments

This work was supported by a grant from ADEME and Rhodia Recherches. FG thanks Joël Belleney for analyzing the surfactant by MALDI-TOF and Franck D'Agosto for his comments on the manuscript. SC acknowledges Rosalina Dos Santos for assisting her on some of the experiments. TEM micrograph was kindly provided by Patricia Beaunier.

[1] De Gunzbourg, A.; Favier, J.-C.; Hémery, P. *Polym. Int.* **1994**, *35*, 179.

[2] Barrère, M.; Ganachaud, F.; Bendejacq, D.; Dourges, M.-A.; Maitre, C.; Hémery, P. *Polymer* **2001**, *42*, 7239.

[3] Maitre, C.; Ganachaud, F.; Ferreira, O.; Lutz, J.-F.; Paintoux, Y.; Hémery, P. *Macromolecules* **2000**, *33*, 7730.

[4] Limouzin, C.; Caviggia, A.; Ganachaud, F.; Hémery, P. *Macromolecules* **2003**, *36*, 667-674.

[5] Cauvin, S.; Sadoun, A.; Dos Santos, R.; Belleney, J.; Ganachaud, F.; Hémery, P. *Macromolecules* **2002**, *35*, 7919.

[6] Satoh, K.; Kamigaito, M.; Sawamoto, M. *Macromolecules* **1999**, *32*, 3827.

[7] Satoh, K.; Kamigaito, M.; Sawamoto, M. *Macromolecules* **2000**, *33*, 4660.

[8] Satoh, K.; Kamigaito, M.; Sawamoto, M. *J. Polym. Sci. Part A* **2000**, *38*, 2728.

[9] Kobayashi, S.; Sugiura, M.; Kitagawa, H.; Lam, W. W.-L. *Chem. Rev.* **2002**, *102*, 2227.

[10] Satoh, K.; Kamigaito, M.; Sawamoto, M. *Macromolecules* **2000**, *33*, 5836.

[11] Scheuer, A. D.; Storey, R. F. *Polym. Prep.* **2002**, *43 (2)*, 932.

[12] Seminara, A.; Rizzarelli, E. *Inorg. Chim. Acta* **1980**, *40*, 249.

[13] Di Bernardo, P.; Choppin, G. R.; Portanova, R.; Zanonato, P. L. *Inorg. Chim. Acta* **1993**, *207*, 85.

[14] Spedding, F. H.; Porter, P. E.; Wright, J. M. *J. Am. Chem. Soc.* **1952**, *74*, 2055.

[15] Fringuelli, F.; Pizzo, F.; Vaccaro, L. *J. Org. Chem.* **2001**, *66*, 4719.

[16] Kobayashi, S.; Nagayama, S.; Busujima, T. *J. Am. Chem. Soc.* **1998**, *120*, 8287.

[17] Spedding, F. H.; Jaffe, S. *J. Am. Chem. Soc.* **1954**, *76*, 882.

[18] Litvinenko, G.; Müller, A. H. E. *Macromolecules* **1997**, *30*, 1253.

[19] Walker, F. H.; Dickenson, J. B.; Hegedus, C. R.; Pepe, F. R. *Prog. Org. Coat.* **2002**, *45*, 291.

[20] Cauvin, S.; Ganachaud, F.; Hémery, P. *Macromolecules* **2004**, submitted.