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Anionic Polymerization of (Meth)acrylic Monomers. 20. Controlled Anionic Polymerization of Methyl Methacrylate at Elevated Temperatures with a (Et$_3$Al + Pyridine)/DPHLi Initiator System

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Introduction. It was earlier demonstrated by several workers that a living anionic polymerization of methyl methacrylate (MMA) could be achieved at not too low temperatures (e.g., −45 °C, compared to the normally used ones, ca. <-60 °C), using organolithium initiators, e.g., sBuLi, when pyridine was used as solvent or cosolvent.[1] A new polymerization mechanism, involving the formation of a so-called active "σ-complex", was tentatively proposed.[1b] Unfortunately, since those σ-complexes, crucial active species in promoting the living process, undergo considerable decomposition reactions upon either increasing the polymerization temperature or decreasing the pyridine content in pyridine/toluene mixtures, side termination reactions unavoidably occur during polymerization.

Since our currently developed "ligated" anionic polymerization technique has steadily become a very efficient tool for producing precisely−controlled poly(meth)acrylates,[2] it seemed of interest to us to test whether the use of suitable ligands might purposely enhance the stability of that active σ-complex and subsequently promote the living polymerization of MMA under moderate experimental conditions. The present paper will give a preliminary answer to that question and show how an alkylaluminum compound, i.e., triethylaluminum (Et$_3$Al), substantially improves the living anionic polymerization of MMA in pyridine or pyridine/toluene mixtures at ≥ 0 °C. It is also important to mention that some alkylaluminum derivatives have recently been found to be effective in promoting living anionic polymerization of MMA in toluene.[3]

Experimental Section. Materials. MMA from Aldrich was first dried by refluxing over CaH$_2$, distilled under reduced pressure, and stored under an inert atmosphere at −20 °C. Just before polymerization, MMA was treated with a 10% Et$_3$Al solution in toluene at 0 °C until a persistent yellow−green color was obtained and then distilled under reduced pressure. Pyridine was first refluxed over KOH and then distilled over St^-Li^+ oligomer prior to use. The (diphenylhexyl)lithium (DPHLi) initiator was prepared at 30 °C by reaction of diphenylethylene with nBuLi in toluene for 48 h. n-, s-, tBuLi/heptane solutions from Janssen and Et$_3$Al/toluene solution from Aldrich were used as received.

Polymerization was carried out in a previously flamed glass reactor under a pure nitrogen atmosphere, monomer, solvent, Et$_3$Al/toluene solution, and initiator being transferred by a syringe and/or capillary technique.

In the case of polymerization in pyridine at 0 °C initiated with DPHLi, three different methods were used to prepare the ligated "DPHLi/Et$_3$Al/pyridine" initiator, depending on the mixing order of the three reactive components at 0 °C. **1**, method A: (Et$_3$Al + pyridine)/DPHLi. Et$_3$Al was first added into dried pyridine. After 10 min, the desired amount of DHPLi was added into that mixture. **2**, method B: (DPHLi + Et$_3$Al)/pyridine. Et$_3$Al was first mixed with DPHLi for ca. 10 min. Pyridine was then added into the Et$_3$Al/DPHLi mixture. **3**, method C: (DPHLi + pyridine)/Et$_3$Al. DPHLi was first added into pyridine, and 30 min later Et$_3$Al was added into the DPHLi/pyridine solution. At other temperatures and with mixed solvents, polymerization was performed with the (Et$_3$Al + pyridine)/RLi initiator system. It is also important to point out that, for polymerization in "pure" pyridine, the solution contained ca. 2% toluene (by volume) from the DPHLi or Et$_3$Al solution.

Characterization. Size-exclusion chromatography (SEC) was carried out in THF, using a Hewlett-Packard 1037 A apparatus equipped with a refractive index detector. Polystyrene standards were used for calibration.

Results and Discussion. A first series of PMMA samples was synthesized in pyridine at 0 °C using a (Et$_3$Al + pyridine)/DPHLi initiator system. The characterization data of these polymers are listed in Table 1. It is obvious that the amount of added Et$_3$Al ligand is a crucial parameter in controlling the living process. Indeed, in the absence of Et$_3$Al, the polymerization is not controlled, as evidenced by a very poor initiator efficiency (f: 0.22) and a rather broad bimodal molecular weight distribution (MWD) (M_w/M_n: 1.75), indicative of the coexistence of at least two types of active species. These results are consistent with previously reported data for the same polymerization system, except for using sBuLi as the initiator.[1b] However, when only 2 mol equiv of Et$_3$Al is added, the initiator efficiency increases up to 0.96; at the same time, the MWD decreases down to 1.40. Upon addition of a 5-fold molar excess of Et$_3$Al, polymerization becomes a very well-controlled process (Table 1), i.e., quantitative yield, very high initiator efficiency (0.95 as an average), and very narrow MWD ($M_w/Mn < 1.10$). A further increase in the molar ratio of ligand/initiator over 5 does not provide any additional beneficial influence on the polymerization.

All together these results indicate that increasing amounts of Et$_3$Al substantially promote a MMA living anionic polymerization, in a way that strongly suggests a complexation equilibrium between the growing species and Et$_3$Al.

Extension of these results to more touchy experimental conditions, e.g., at relatively higher polymerization temperatures or in pyridine/toluene mixtures, still gives rather encouraging results as revealed by the experimental values of yield, initiator efficiency, and MWD (M_w/M_n) of polymers, as reported in Table 1. It is obvious that the yield is almost quantitative, the initiator is very close to unity, and the MWD is slightly broader (M_w/M_n: ca. 1.30), when the polymerization is carried out at 20 °C. When the content of pyridine in pyridine/toluene mixtures is decreased down to 70%, the MMA anionic polymerization at 0 °C is still well-

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Table 1. Anionic Polymerization of MMA in Pyridine and Pyridine/Toluene Mixtures Using a (Et_3Al + Pyridine)/DPHLi Initiator System[a]

MMA (mol/L)	Py/Tol (mL/mL)	Et_3Al/DPHLi (mol/mol)	temp (°C)	time (h)	yield (wt %)	M_n(cal)	M_n (SEC)	M_w/M_n (SEC)	f[b]
0.48	50/0		0	0.5	100	12 000	54 400	1.75	0.22
0.40	50/0	2/1	0	3	100	10 000	10 400	1.40	0.96
0.80	50/0	5/1	0	3	100	20 000	21 500	1.09	0.93
0.225	50/0	5/1	0	3	98	5 620	5 870	1.10	0.96
0.60	50/0	10/1	0	3	100	15 000	16 500	1.08	0.91
0.396	50/0	5/1	20	1.5	100	9 900	10 000	1.30	0.99
0.40	35/15	5/1	0	2	99	10 000	11 500	1.12	0.96
0.386	5/45	5/1	0	1.5	100	9 650	10 200	1.60	0.95
0.44	0/50	5/1	0	0.5	50	5 500	42 800	2.50	0.13

[a] Initiator concentration: 4×10^{-3} mol/L. [b] Initiator efficiency, $f = M_n(\text{cal})/M_n(\text{SEC})$, where $M_n(\text{cal}) = (W_{MMA}\,(\text{g})/C_{\text{initiator}}\,(\text{mol})) \times$ yield %.

Table 2. Effect of the Method of Preparing the Initiator System[a] **on the MMA Anionic Polymerization in Pyridine at 0 °C**[b]

method	initiator system[c]	MMA (mol/L)	time (h)	yield (wt %)	M_n(cal)	M_n(SEC)	M_w/M_n (SEC)	f
A	(pyridine + Et_3Al)/DPHLi	0.225	3	100	5620	5870	1.10	0.96
B	(DPHLi + Et_3Al)/pyridine	0.563	1	96	13500	17300	1.52	0.78
C	(DPHLi + pyridine)/Et_3Al	0.339	1	98	8300	9300	1.40	0.90

[a] See the Experimental Section. [b] Initiator concentration, 4×10^{-3} mol/L. [c] Molar ratio of Et_3Al/DPHLi = 5/1.

controlled (Table 1). Even in a 10% pyridine/toluene mixture, the initiator efficiency and the yield are very satisfactory, although there appears a significant increase in MWD (M_w/M_n up to 1.60). That situation is much more promising than the one observed in the absence of pyridine (Table 1), where the polymerization is completely ill-controlled, i.e., limited conversion (ca. 50%), very broad and multimodal MWD ($M_w/M_n \sim 2.50$), and very low initiator efficiency ($f \sim 0.13$). It seems that the interplay of *both* pyridine *and* Et_3Al is at the origin of the well-controlled MMA polymerization reported in this work.

It is worth noting that the livingness of the MMA anionic polymerization somehow depends on the method of preparing the initiator system. Accordingly, and unlike polymerizations initiated with (Et_3Al + pyridine)/DPHLi (method A) in pyridine at 0 °C, the ones with either (DPHLi + Et_3Al)/pyridine (method B) or (DPHLi + pyridine)/Et_3Al (method C) under otherwise identical experimental conditions give rise to relatively broad MWDs (Table 2). Moreover, method C gives a bimodal MWD (Figure 1B), in sharp contrast to the very narrow and symmetrical one observed using method A (Figure 1A). Furthermore, the initiator efficiency is found to be rather low in the case of method B (ca. 80%) (Table 2).

It is worth recalling that there are convincing evidences[3a] that side reactions unavoidably occur, when RLi is mixed with Et_3Al at relatively high temperature in toluene, e.g., at 0 °C. This might explain why method B (i.e., DPHLi is first mixed with Et_3Al, followed by addition of pyridine) gives rise to a rather low initiator efficiency. Quite similarly, it has been previously reported by Hatada[3a] that the tBuLi/Et_3Al initiator system induces a living polymerization of MMA in toluene at −78 °C but not at 0 °C. Moreover, this low initiator efficiency was also observed by Ballard[3b] and us[3c] for MMA anionic polymerization in toluene at 0 °C initiated with bulk monosubstituted[3b] or bisubstituted [3c] aluminum phenolates−complexed tBuLi.

Therefore, it is reasonable to assume that, for MMA polymerization with a (Et_3Al + pyridine)/DPHLi initiator system, complexation of Et_3Al (a Lewis acid) with pyridine (a Lewis base) prior to interaction with DPHLi might promisingly minimize the extent of side reactions between DPHLi and Et_3Al to the point where a living polymerization process is obtained.

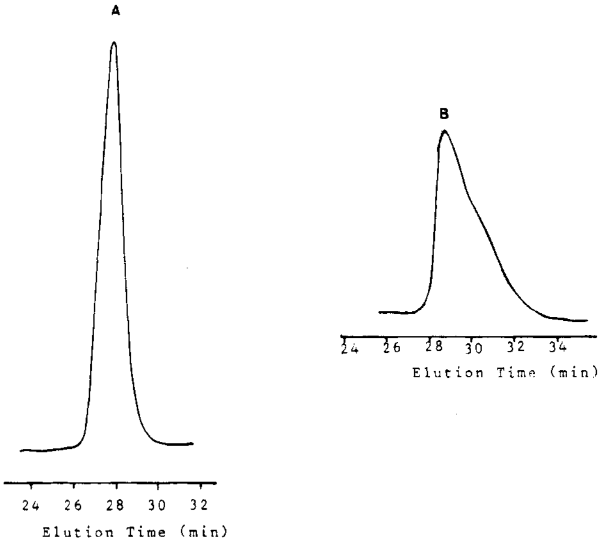

Figure 1. SEC trace of PMMA synthesized in pyridine at 0 °C: (A) M_n, 21500; M_w/M_n, 1.09; prepared using a (pyridine + Et_3Al)/DPHLi initiator system. (B) M_n, 9300; M_w/M_n, 1.30; prepared using a (pyridine + DPHLi)/Et_3Al initiator system.

Conversely, as demonstrated elsewhere,[1] the active σ-complex may tend to decompose into free alkyllithium and pyridine upon increasing temperature. Should this occur at 0 °C, method C possibly leads to at least two types of initiators in pyridine, i.e., Et_3Al-complexed DPHLi and Et_3Al-complexed σ-complex. However, it is still not clear whether a broad and even bimodal MWD using method C is a consequence of side reactions or of a slow exchange equilibrium[4] between the two species described above. Since (pyridine + Et_3Al)/DPHLi promotes a living MMA polymerization in pyridine at 0 °C (see above) and a relatively high initiator efficiency (ca. 0.90) is obtained by method C, it seems reasonable to assume that there is a slow exchange between two types of active complexes compared to the MMA addition rate.

Finally, it is noteworthy that using tBuLi instead of DPHLi in a (pyridine + Et_3Al)/DPHLi initiator system provides MMA polymerization at 0 °C in pyridine with a narrow MWD ($M_w/M_n \sim 1.12$) and a poor initiator efficiency (ca. 0.65). Again, both (pyridine + Et_3Al)/sBuLi and (pyridine + Et_3Al)/nBuLi systems give rise to even less controlled PMMAs, i.e., rather low initiator efficiency (<0.60) and broad MWD ($M_w/M_n > 1.30$). It might then be concluded that decreasing RLi's nucleophilicity and increasing its steric hindrance is an efficient pathway to protect the MMA anionic polymerization from noxious termination reactions at early stages.

As a conculsion, it is obvious from these results that the (Et_3Al + pyridine)/DPHLi initiator system can effectively promote a well-controlled MMA anionic polymerization in pyridine at 0 °C. The important role of both Et_3Al and pyridine in controlling that process, although most probably related to their ability to form μ- and/or σ-type complex species, is however not completely clear, calling for further detailed investigation.

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