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Anionic Polymerization of Methyl Methacrylate as Promoted by a N-Butyl Lithium-Pyridazine-Polyether Alkoxide Based Complex Initiator System

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Polymerization of methyl methacrylate was conducted using a n-butyl lithium/pyridazine system as initiator in tetrahydrofuran (THF) and toluene. Special attention was focused on using some lithium polyether alkoxides as polymerization is promoted at ambient temperatures. The positive effects of these μ/σ -type ligands such as lithium 2-(2-methoxyethoxy)ethoxide and lithium 2-(methoxy)ethoxide on controlling the living character, molecular weight, stereoregularity and yield of the produced polymers were all demonstrated. It was found that initiator/lithium-2-(methoxy)ethoxide in a 1/10 ratio gives the most controlled polymerization. All products were then characterized by size exclusion chromatography (SEC), proton nuclear magnetic resonance (^1H NMR) and differential scanning calorimeter (DSC). The molecular weight distributions obtained were as narrow as 1.28 and the glass transition temperatures were comparable with that of a syndiotactic PMMA and approximately 100% conversions achieved. Moreover, the effect of the polarity of the solvents on the association equilibrium has been discussed. It was found that the molecular weight of the produced polymethylmethacrylate could be better controlled in THF than in toluene.

Key Words: Pyridazine complex initiator, Polyether alkoxide, PMMA.

Introduction

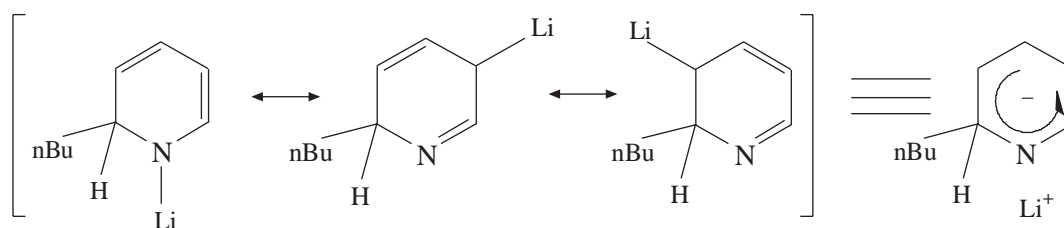
Poly [alkyl (meth)acrylate] based products are nowadays the basis of an increasingly diversified range of applications. However, although they are in principle good candidates to undergo anionic polymerization, this method suffers from severe limitations related to side reactions (inherent to the propagating enolate species) with the ester carbonyl group of (meth) acrylates and α -hydrogen of acrylates. As a result, polymerization yield is low, and molecular weight distribution is broad¹.

Several methods have emerged as breakthroughs in the control of the anionic polymerization of (meth) acrylates, such as group transfer polymerization (GTP) by the DuPont research team², metal-free anionic

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polymerization by Reetz et al.³, and ligated anionic polymerization by the contribution of Teyssie et al.⁴, Lochmann et al.⁵ and Hatada et al.⁶ as well as covalent living polymerization by Yasuda et al.⁷. Earlier investigations in Teyssie's laboratory have shown that inorganic and organometallic μ -bonded additives, such as alkali and alkaline earth metal salts, metal alkyls, alkoxides and amides, and cation σ -bonding organic ligands, such as polyethers and polyamines¹ as well as μ - σ type ligands, such as polydentate lithium alkoxide, are efficient ligands in promoting the living anionic polymerization of alkyl methacrylates and bulky acrylates^{8,9} at low temperature.

McGrath et al.¹⁰ proposed a special anionic polymerization mechanism for methyl methacrylate (MMA) involving the formation of active σ -complex of n-butyllithium (n-BuLi) with pyridine. Unfortunately, side reactions unavoidably occur during the polymerization upon either increasing the polymerization temperature or decreasing the pyridine content in the pyridine/toluene mixture. It has been also reported that butyllithium (BuLi) adds to pyridine with subsequent elimination of lithium hydride to give 2-butylpyridine¹¹ and a negative charge has a 20 % chance of being located at positions 3 and 5, the rest being associated with position 1, i.e., the lithium cation delocalized at the ring¹² (Scheme 1). In addition, the uncontrolled polymerization of 2-vinylpyridine in hydrocarbon solutions and at high temperatures has been ascribed to this well known susceptibility of the pyridine ring to nucleophilic addition of organolithium compounds^{13,14}.



Scheme 1

In an attempt to avoid the above-mentioned problems, the anionic polymerization of MMA was conducted using a n-BuLi/pyridazine complex initiator system in the presence and absence of various lithium polydentate alkoxides as ligands. The question is addressed to determine whether the initiator system has a "self ligated" character or not. The effects of the temperature, nature of the solvents (THF and toluene) and ligands such as (2-(2-methoxyethoxy) ethoxide (LiOEEM) and 2-methoxy ethoxide (LiOEM)) on the course of anionic polymerization in terms of polymer tacticity, molecular weight and yield were all examined.

Experimental

Reagents and Solvents

MMA monomer (Fluka) was dried by refluxing over CaH_2 , distilled under reduced pressure, and stored under nitrogen atmosphere in the dark at $-20\text{ }^\circ\text{C}$. Just before polymerization, triethylaluminum (TEA) (Fluka-Germany) (10 % solution in hexane) was added until a persistent yellow-green color was observed, followed by distillation under reduced pressure.

THF (Aldrich, Germany) was purified by refluxing over a fresh sodium-benzophenone complex until a deep purple color appeared which indicates oxygen and moisture free solvent. Toluene (Merck, Germany)

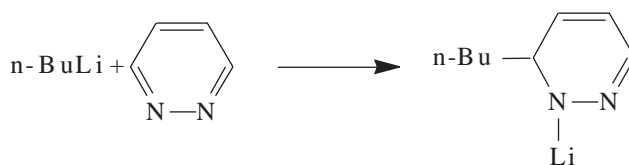
was refluxed over CaH_2 for 48 h and redistilled over polystyryllithium immediately prior to use. *n*-butyl lithium (*n*-BuLi) (Aldrich, Germany) was used as received. The alcohols (Aldrich, Germany) used in the ligand synthesis were purified by distillation over CaH_2 and stored under nitrogen. Pyridazine (Aldrich, Germany) was purified by the slow addition of a few drops of *n*-BuLi/hexane until a persistent red color was observed.

Preparation of Polydentate Alkoxides

Lithium 2-(2-methoxyethoxy)ethoxide (LiOEEM) and lithium 2-methoxy ethoxide (LiOEM) were prepared by reaction of an excess of lithium with the parent alcohol, 2-(2-methoxyethoxy)ethanol and 2-methoxy ethanol, respectively, in THF according to the previously reported procedure ⁹.

Preparation of Initiator

Synthesis of the initiator was performed by reacting an equal amount of *n*-BuLi with pyridazine in THF or toluene at room temperature (Scheme 2). In each case a deep-red color of the initiator was attained.

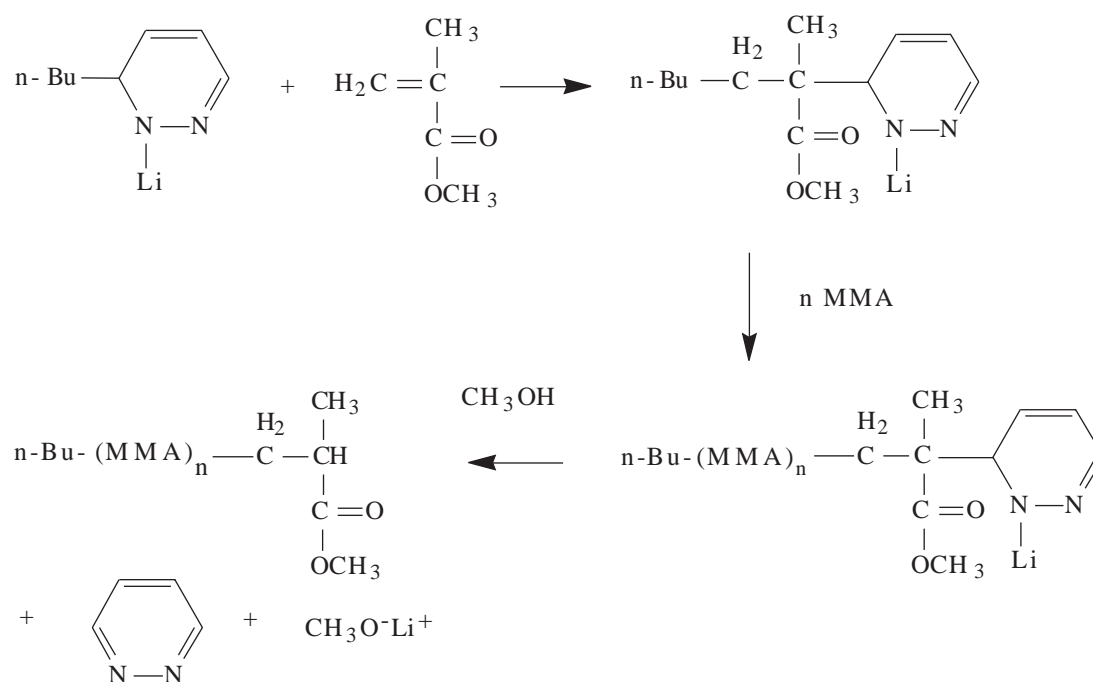


Scheme 2

Polymerization and Characterization

Anionic polymerization of MMA was conducted in a previously flamed glass reactor under nitrogen atmosphere. The solvent and then the required amount of pyridazine were transferred into the reactor through a short stainless-steel capillary and with a syringe. A small amount of *n*-BuLi/hexane was added dropwise to the reaction mixture for blank titration until the pale red color of *n*-BuLi/pyridazine complex persisted. Subsequently, 3.5×10^{-4} moles of *n*-BuLi was added to a solution containing a slight molar excess of pyridazine at room temperature. A deep red color developed, indicating the formation of pyridazyl lithium¹⁰. After maintaining the required reaction temperature, purified methyl methacrylate monomer (6% by weight) was charged into the reactor via syringe or capillary. The polymerization was terminated with distilled methanol after 15 min and the polymer was recovered by precipitation into excess methanol, washed and dried under vacuum at 40 °C for 24 h (Scheme 3).

Molecular weight was determined by size exclusion chromatography (SEC)-PL equipped with a deflection type refractive index detector. Polystyrene standards were used for calibration. The microstructure of the polymers was determined by ¹H-NMR using a Bruker AM 200 spectrometer. Glass transition temperature was measured by differential scanning calorimeter (DSC) using a Rheometric Scientific apparatus. Samples were scanned with a heating rate of 10 °C/min.



Results and Discussion

The results of polymerization performed with the n-BuLi/pyridazine initiator system in the presence of LiOEEM as ligand at -33 °C are summarized in Table 1.

Table 1. Polymerization of MMA in THF using monofunctional initiator of n-BuLi/pyridazine complex.

No	T(°C)	M/I ^a	M _n s x10 ⁻³	HI ^b	Conversion (%)
1	-33	0	78	1.3	72
2	-33	5	143	1.5	~ 100

a: the mole ratio of LiOEEM to initiator (mole/mole).

b: heterogeneity index

It is quite clear that in the absence of the ligand, yield is not quantitative, indicating the presence of some unavoidable side reactions leading to termination. This shows that the initiator itself cannot act as a perfect self ligated initiator. On the other hand, the addition of 5 molar equivalents of LiOEEM results in a quantitative polymerization. It is reasonable to assume that the complexation occurred between the lithium ester enolate and a lithium containing μ - σ type dual ligand where a lithium ethoxide moiety may function as a μ -type of coordination site and polyether component as a σ - one as proved by Teyssie et al.⁴. It can also be assumed that π -electron deficient pyridazine behaves as a ligand that may form a coordinative bond with the electron rich chain end. So both LiOEEM and pyridazine can form a bulky and relatively large charge separated μ - σ and/or σ type complex, thus minimizing the extent of secondary reactions.

In order to see the effect of another ligand, LiOEM was used for anionic polymerization of MMA initiated with the n-BuLi/pyridazine system at different temperatures (Table 2).

Table 2. Polymerization of MMA in THF using n-BuLi/pyridazine complex initiator system in the presence of LiOEM.

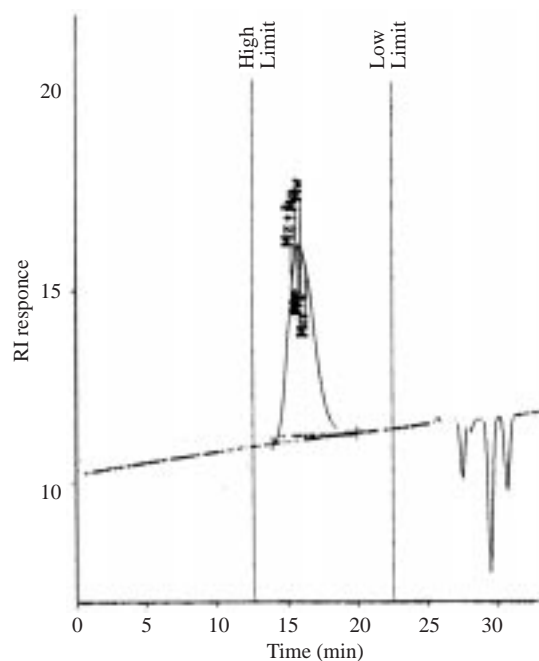
No	T(°C)	M/I ^a	M _n s x10 ⁻³	HI ^b	Conversion (%)
3	-45	5	68	1.73	93
4	-33	5	53	1.61	100
5	0	5	49	1.64	100
6 ^c	0	5	39	1.29	100
7 ^c	0	5	60	2.01	100
8	20	5	40	2.00	92

a: the molar ratio of LiOEM to initiator, b: heterogeneity index, c: monomer resumption experiment (first sequence: no 6).

It is worth noting here that the addition of 5 molar folds of LiOEM has also a great positive effect on the polymer yield as reported before ⁴.

It is also clear that polymerization proceeds quantitatively from -45C up to 0C. At 20C, incomplete monomer conversion occurs, which may be attributed to early termination of the polymer chains and/or dissociation of “n-BuLi/pyridazine complex” at relatively high temperatures.

On the other hand, in spite of the monomodal molecular weight distribution of all PMMA samples (Figure 1), sample 7, prepared by sequential addition of monomer to determine the living character of growing chain ends, has a bimodal molecular weight distribution (Figure 2).

**Figure 1.** SEC chromatogram of PMMA sample 7.

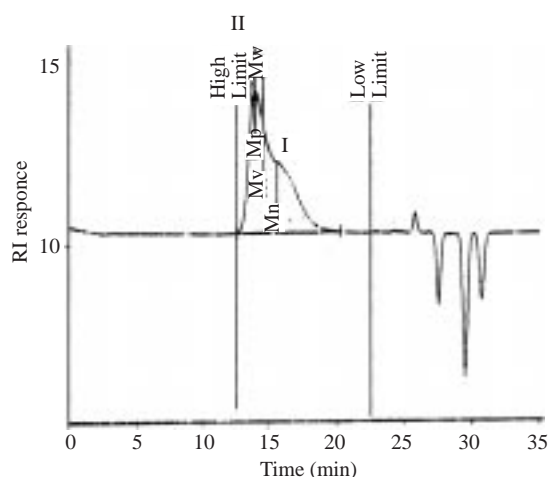


Figure 2. SEC chromatogram of PMMA sample 6.

In view of the fact that side termination reactions are not likely to be involved during the propagation of MMA in the first addition where MWD is narrow, the formation of bimodal molecular weight distribution in the second step is most probably due to the unstable PMMA chain-end/pyridazyllithium complex.

MMA polymerization was also carried out in toluene using the n-BuLi/pyridazine initiator system (Table 3).

Table 3. Polymerization of MMA in toluene using n-BuLi/pyridazine complex initiator system.

No	T(°C)	M_n $\times 10^{-3}$	HI ^a	Conv. %
9	-18	58	2.8	66
10	0	62	2.0	59

a: heterogeneity index

The low yield and very high molecular weight of the polymers may be attributed to the highly aggregated polar moieties of the initiator system in toluene whatever the temperature is.

¹H NMR analyses show that the PMMA chains formed in THF at temperatures exceeding -45 °C with alkoxide additives are rich in syndiotactic content. The stereochemistry of the polymer backbone was calculated by considering the peaks from backbone methyl groups: syndiotactic triad, 0.84 ppm; heterotactic triad, 1.01 ppm; isotactic triad, 1.18 ppm, as shown in Figure 3.

The syndiotacticity observed for PMMA synthesized in THF in the presence of LiOEM ligand clearly demonstrates that the lithium is coordinatively saturated by preventing its coordination with the penultimate ester group of the chain. Therefore the monomers approach in a sterically more favorable syndiotactic-like mode⁴. Moreover, the presence of pyridazine at the chain end does not disturb the expected tacticity in these conditions. It is well known that as the syndiotactic content of the PMMA increases the glass-transition temperature (T_g) increases. In our case, PMMA samples with high syndiotactic content have T_g values ranging from 135.6 to 143.6 °C (Table 4).

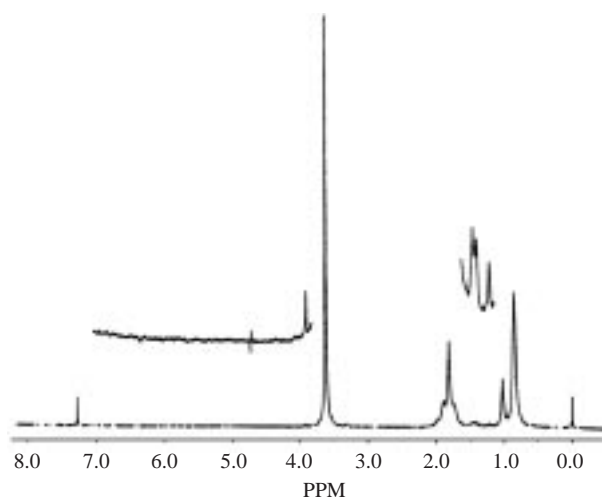


Figure 3. ^1H NMR spectrum of PMMA sample 4.

Table 4. Characterization of PMMA initiated by n-BuLi/pyridazine the presence of polyetheralkoxide.

No	T(°C)	Tacticity			T_g (°C)
		mm	rm	rr	
2	-33	4.9	28.6	66.5	135.6
3	-45	1.7	17.4	80.9	141.3
4	-33	0	20.9	79.1	143.6
5	0	1.3	23.3	75.4	141.5
6	0	1.2	24.5	74.3	140.7
8	20	4.7	26.3	69.0	139.6

Conclusions

It is evident that the anionic polymerization of MMA either in THF or a toluene solvents can be carried out by using n-BuLi/pyridazine complex as an initiator. When a polyetheralkoxide ligand was used as a complexation agent, an increase in polymer conversion was achieved. Although quantitative conversions and monomodal molecular weight distributions exist, the bimodal distribution obtained from monomer resumption experiments indicates that the propagating polymer does not have a living character. The produced PMMA samples still have a high percentage of syndiotactic content with high T_g 's.

Acknowledgments

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