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STEREOREGULAR POLYMERIZATION OF METHYL METHACRYLATE INITIATED BY DIALKYLMAGNESIUM-QUATERNARY AMMONIUM SALT ADDUCTS

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Abstract: The anionic polymerization of methyl methacrylate was carried out in the presence of Bu_2Mg/quaternary ammonium salts in toluene at 0°C. It was found that the bulkiness and shape of the salt strongly affect the polydispersity and tacticity of the resulting polymers. Molecular weight distribution is in the range $1.3 < M_w/M_n < 4.7$. Tetrahexylammonium chloride causes the most drastic change in the tacticity. The structure of R_4NX, as well as the nature of the metal and the t-BuOLi ligands produce a radical effect on the polymer properties. These initiator components perform their role by changing the microenvironment of the ligated and aggregated growing chains. The results clearly reveal the great potential of the mixed associate or mixed base as strong stereospecific initiator systems.

INTRODUCTION

The anionic polymerization (AP) of methyl methacrylate (MMA) is the most intensively studied polymerization of polar vinyl monomers which can produce polymers with a wide range of stereoregularity. The mechanism of steric control over the tacticity of the polymer which substantially depends on the structure of the active centres (AC) remains equivocal. The steric structure and the association state of the initiator along with the mode of coordination of the monomer might be very important. For industrial application it is desirable

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to carry out AP of MMA in hydrocarbon solvents such as toluene at elevated temperature and obtain a highly syndiotactic PMMA with low polydispersity and controlled molecular characteristics. Therefore we focus our attention on finding out modified initiating systems effective for AP of MMA in nonpolar solvents.

Organomagnesium initiators have been widely used. The tacticity of the PMMA prepared is controllable within a wide range (Ref. 1). The polydispersity (MWD) is usually broad or bimodal. The propagation mechanism involves multiple active species which possess different reactivities and stereospecifities. As a result the tacticity and MWD are dominated by the relative amount of these active species (Ref. 2). The formation of multiple active species has been discussed in terms of the Schlenk equilibrium with exchange between RMgX and R_2Mg (Ref. 3). The results of Hatada (Ref. 4) and Matsuzaki (Ref. 5) clearly indicate that "RMgBr" gives a highly isotactic PMMA whereas "R_2Mg" gives predominantly a syndiotactic polymer. Isotactic polymerization has never been observed with dialkylmagnesium initiators except for dibenzylmagnesium prepared from dibenzylmercury (Ref. 6).

In our previous investigations on the AP of MMA two quite different types of initiators have been used: ethyl-α-lithioisobutyrate (α-LiEtIB) and t-BuOK (Refs. 7,8). It has been established that their combination with quaternary ammonium salts (QAS) provides us with a new type of initiating systems, producing PMMA whose microstructure and polydispersity strongly depend on the shape and structure of the quaternary ammonium ion (Q^+) (Ref. 9). Usually quaternary ammonium ions with one or two very long alkyl groups ($>C_{12}$) and other methyl substituents promote the isotactic placement in contrast to QAS with four bulky substituents, which favour syndiotactic placement as a result of the steric hindrance.

In this work we have studied the polymerization of MMA initiated by Bu_2Mg/QAS adducts under various reaction conditions in an attempt to clarify the role of the QAS structure on the mechanism of formation of highly syndiotactic and highly isotactic PMMA with narrow MWD.

EXPERIMENTAL PART

MMA was purified by distillation, and then distilled twice over calcium dihydride under high vacuum just before use. Toluene was purified in the usual manner and then distilled under high vacuum after treatment with nBuLi.

QAS (Fluka and Aldrich) were purified by "freeze-drying" their benzene solutions in the reaction vessel, directly before the polymerization.

Dibutylmagnesium, 1.0M solution in heptane was purchased by Aldrich. The organomagnesium compound was distributed in small volumes in glove-box under argon. With the aid of high-vacuum line technique heptane was evaporated and the initiator was dissolved in toluene. The concentration of Bu_2Mg was determined by hydrolysis in excess of 0.1 N HCl and titrated with 0.1 N NaOH using phenolphtalein as indicator.

The polymerization was carried out, using a high vacuum line technique (10^{-6} mbar) in a reaction vessel described earlier (Ref. 10). MMA (0.5 mol.l^{-1}) was introduced in toluene solution containing Bu_2Mg and QAS in a mole ratio 1:1. The polymerizations were carried out at 0°C for 6 hrs. The polymerization was terminated by adding methanol containing HCl equivalent to the Mg^{2+}. The polymer was precipitated in methanol, and after filtration washed with methanol and dried in vacuum.

The number-average molecular weight and the polydispersity of the polymers were determined by SEC in THF at 45 °C on Waters 840 Instrument, equipped with Waters Styragel columns, calibrated with polystyrene standards. The stereoregularity of the polymers was estimated from the ^1H NMR spectra, using a Bruker WM 250 NMR spectrometer in $CHCl_3$.

RESULTS AND DISCUSSION

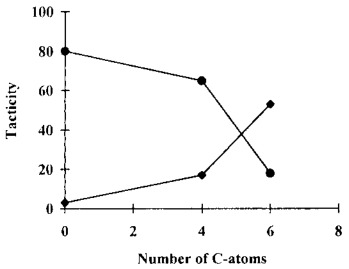
Effect of QAS adducts with α-LiEtIB, t-BuOLi and t-BuOK

In our previous study we found that the interaction between the growing esterenolate species (AC) and QAS in toluene does not proceed as a pure cation exchange reaction (Ref. 9):

$$P^-,Mt^+ + X^-,N^+R_4 \rightleftarrows P^-,N^+R_4 + Mt^+,X^-$$

The presence of metal salts in the solution as a part of the active species affects the mechanism of the polymerization process. In other words the esterenolate anion is not "naked" as was traditionally termed in phase transfer catalysis reactions. The anions and cations of QAS and AC are tightly bound to each other via the formation of mixed associates.

This type of interaction provides a possibility to change the microenvironment of the growing species, which depends on the structure of the bulkier substituents of the quaternary ammonium ions. The longer fatty alkyl chains participate in the formation of the first solvation shell, thus greatly affecting the mode of monomer addition. In the case of tetraalkylammonium ions with four equal substituents the AC penetrate into the inner sphere of Q^+. The influence of the alkyl chain length of the R_4NX additive on the PMMA tacticity when using α-LiEtIB and t-BuOK is shown on Fig. 1 and Fig. 2.



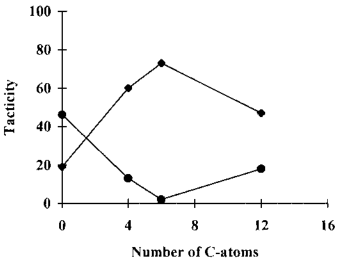


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Fig.1.Role of the alkyl chain length of R_4NX on PMMA tacticity, initiator α-LiEtIB, toluene, -60°C (Ref. 7)

Fig.2. Role of the alkyl chain length of R_4NX on PMMA tacticity, initiator t-BuOK, toluene, -60°C (Ref. 8)

The results shown on Fig. 1 and Fig. 2 clearly indicate that the tacticity strongly depends on the size and shape of the QAS additive as a result of the different steric restrictions imposed on the metal atom approaching the monomer. Tetrahexylammonium chloride causes a drastic change in the tacticity in both cases. Tab. 1 summarizes the effect of $(C_6)_4NCl$ in AP of MMA, initiated by 5 different types of organometallic compounds. The syndiotactic placement is enhanced in the following order:

t-BuOK > Bu_2Mg > α-LiEtIB > t-BuOLi > Bu_2Mg.t-BuOLi

t-BuOLi makes the tacticity of PMMA remarkably insensitive to the presence of QAS additives. Addition of t-BuOLi only usually increases the isotactic content. Most probably this is due to the strong association of t-BuOLi species with the growing chain end. In this way they compete with QAS and prevail in the process of formation of the solvation shell in the vicinity of the AC species (shielding effect). Each time the addition of $(C_6)_4NCl$ or t-BuOLi leads to a substantial decrease of the polydispersity of the polymer.

Tab. 1. Effect of $(C_6)_4NCl$ and t-BuOLi as additives in AP of MMA in toluene

Initiator	Time	T	Yield	$\overline{M}_w/$	Eff.	Tacticity		
	in min	in °C	in %	$\overline{M}_n$		mm	mr	rr
t-BuOLi	1440	20	10	2.0	0.005	0.78	0.15	0.07
+$(C_{12})_2Me_2NBr$	1440	20	20	1.8	0.005	0.76	0.15	0.09
+$(C_{12})_4NBr$	1440	20	20	1.6	0.005	0.79	0.13	0.08
α-LiEtIB	15	-60	85	7.0	0.150	0.80	0.17	0.03
+$(C_6)_4NCl$	5	-60	85	1.9	0.080	0.16	0.28	0.56
t-BuOK	60	-60	7	2.7	0.007	0.48	0.33	0.19
+$(C_6)_4NCl$	60	-60	90	1.9	0.047	0.02	0.25	0.73
Bu_2Mg	360	0	32	12.0	0.050	0.51	0.20	0.29
+$(C_6)_4NCl$	360	0	85	1.9	0.060	0.03	0.24	0.73
+t-BuOLi	360	0	15	1.7	0.020	0.70	0.17	0.13
+t-BuOLi/$(C_6)_4NCl$	360	0	90	1.3	0.050	0.59	0.17	0.24

Effect of QAS adducts with Bu_2Mg

The influence of QAS as additives on the AP of MMA in toluene can be traced using the results presented in Tab. 2 and Fig. 3.

t-Bu_2Mg alone is an extremely slow initiator of the polymerization of MMA, and after 6 hrs at 0°C the conversion of the monomer was 32 %. From the M_n of the polymer formed, one may conclude that the number of AC corresponds to only 9% of the initiator. The polydispersity is very broad and multimodal, due to the presence of different independent growth centres which maintain their identity throughout the reaction (Ref. 11).

Apparently the isotactic content of PMMA is reduced when QAS are added. In all cases the formation of a stereospecific AC is only a minor component of the reactions which occur during the initiation step since the concentration of the growth centres is much lower than that of the residual Bu_2Mg (low efficiency).

Tab. 2. Results from the polymerization of MMA in toluene initiated by Bu_2Mg/QAS adducts [a)]

Additive	Yield	$\overline{M}_n$	$\overline{M}_w$/	Eff.	Tacticity		
	in %	x10^3	$\overline{M}_n$		mm	mr	rr
	32	11	12.0	0.090	0.51	0.20	0.29
$C_{18}Me_3NBr$	27	48	2.8	0.020	0.22	0.27	0.51
$(C_{16})_2Me_2NBr$	22	23	2.9	0.040	0.31	0.24	0.45
$(C_1)_4NBr$	10	29	2.2	0.004	0.51	0.14	0.35
$(C_4)_4NBr$	17	22	1.8	0.030	0.11	0.27	0.62
$(C_6)_4NCl$	85	22	1.9	0.060	0.03	0.24.	0.73
$(C_{12})_4NBr$	29	22	4.3	0.040	0.19	0.27	0.54
$(C_{16})_4NBr$	38	25	4.7	0.050	0.46	0.18	0.36
Bu_3Al	15	20	7.3	0.040	0.64	0.11	0.25
Bu_3Al/t-BuOLi	70	79	1.5	0.020	0.05	0.24	0.71

[a)] Polym. time-6 hrs, polym. temp.-0°C, [In]=0.015-0.030 M, [M]=0.5 M, [Add]/[In]=1-2

The addition of the R_4NX additive brings about a substantial change in the polymer tacticity. A certain similarity in behaviour (Fig. 3) is observed by the experiments with α-LiEtIB (Fig.1) and t-BuOK (Fig. 2). The PMMA tacticity reverses by adding $(C_4)_4NBr$ as the most syndiospecific system is $Bu_2Mg.(C_6)_4NCl$. The polymerization in the presence of $(C_{12})_4NBr$ leads to a lower syndiotacticity. A second reversion was observed by using the $Bu_2Mg/(C_{16})_4NBr$ initiating system. In view of this the tacticity of PMMA obtained resembles the tacticity obtained when using pure Bu_2Mg initiator. Obviously the mode and depth of penetration of the growing esterenolate anion into the void spaces between the alkyl chains depends on the length of the alkyl substituents (Ref. 9). The different PMMA tacticity observed with $(C_6)_4NX$ and $(C_{16})_4NX$ (Fig. 3) implies the importance of the following two parameters : distance of closest approach between the nitrogen centre of QAS and the AC and the distance between the centre of the penetrating esterenolate anion and the outer boundary of Q^+.

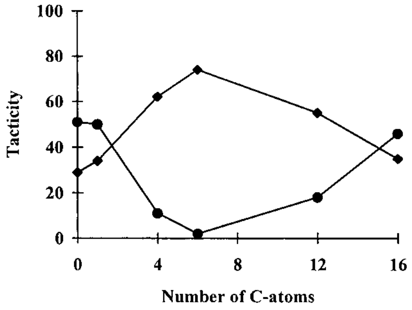

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Fig. 3. Role of the alkyl chain length of R_4NX on PMMA tacticity, initiator Bu_2Mg, toluene 0°C

The addition of a quite different type of additive namely Bu_3Al.t-BuOLi aggregates to Bu_2Mg (1:1:1) generates a new initiating system that produces PMMA with almost the same characteristics as the one obtained with $Bu_2Mg.(C_6)_4NCl$ as initiator. This result clearly reveals the great potential of mixed associates or mixed bases as strong stereospecific intiation systems.

CONCLUSIONS

The polymerization of MMA initiated by Bu_2Mg/QAS in toluene proceeds through different stereomechanisms depending on the structure of QAS. The detailed structures of the AC/QAS mixed associates remain elusive. However some speculations can be laid down. The properties of PMMA obtained with α-LiEtIB/QAS, Bu_2Mg/QAS, t-BuOK/QAS and t-BuOLi/QAS are different. The most reasonable explanation suggests that each of the counterions Li, Mg and K acts in a specific way as a part of the ligated chiral growth centre.

Some similarity in the action of R_4NX as additives should be also mentioned; namely the inversion of the tacticity of PMMA depending on the length of the alkyl substituents as well as the much lower polydispersity and the unimodal MWD. This observation reveals the importance of the shape and size of QAS in the process of AC deaggregation as well as of the mode of AC penetration into the void spaces of QAS.

Contrary to other initiator systems the addition of QAS to t-BuOLi does not change the tacticity of the polymer obviously due to the strong association ability of t-BuOLi molecules which successfully compete with QAS for the coordination sites of the growing species.

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