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Aluminate and Magnesiate Complexes as Propagating Species in the Anionic Polymerization of Styrene and Dienes

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Summary: The influence of MgR_2 and AlR_3 additives on alkyllithium initiators in the anionic polymerization of butadiene has been investigated in non polar solvents. A strong decrease of the diene polymerization rate in the presence of the two Lewis acids was observed, similarly to that observed in the retarded anionic polymerisation of styrene. With n,s-Bu_2Mg, the percentage of 1,2 vinyl units increases with the [Mg]/[Li] ratio. This behavior is specific to magnesium derivatives bearing secondary alkyl groups and likely results from the additional complexation of lithium species by free dialkylmagnesium and/or a 1,4- to 1,2- chain end isomerization process during chain exchanges between polybutadienyl active chains and dormant ones attached to magnesium species. These reversible exchanges also lead to the formation of one supplementary chain by initial dialkyl magnesium which acts as reversible chain transfer agent. On the contrary with the R_3Al/RLi systems the number of chains is only determined by the concentration of initial alkyllithium and no modification of the polybutadiene microstructure compared to lithium initiators (1,4 units = 80%) is noticed.

Dialkyl magnesiate complexes with alkali metal derivatives (i.e. alkoxide) are also able to influence the stereochemistry of the styrene insertion during the propagation reaction. Polystyrenes with different tacticities ranging from predominantly isotactic (85% triad iso) to syndiotactic (80% triad syndio) can be obtained with these initiators.

Keywords: aluminate and magnesiate complex; anionic polymerization; diene; stereochemistry; styrene

Introduction

We have recently reported the use of dialkylmagnesium (R_2Mg, $0 < r = [Mg]/[Li] \leq 20$) and of trialkylaluminum (R_3Al, $0 < r = [Al]/[Li] < 1$) as retarders of the styrene anionic polymerization

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initiated by alkyllithium derivatives at elevated temperature[1-3]. The formation of “ate” heterocomplexes between PSLi and the organometallic additives is the key for the kinetic retardation and the stabilization of active species at high temperature. However, the mechanism of monomer insertion and the nature of the propagating species has not been yet completely clarified. To get further informations on these elementary reactions, a study of the influence of the added Lewis acids on the stereochemistry of both the butadiene and styrene polymerizations has been conducted. These results are reported and discussed in term of polymerization mechanism.

Experimental

Materials: s-Butyllithium (1.3 M in cyclohexane from SAFC, France), ether-free n,s-dibutylmagnesium (n,s-Bu_2Mg ; 1.0 M in heptane from SAFC, France), triisobutylaluminum (*i*-Bu_3Al ; 1.0 M in cyclohexane from SAFC, France), lithium *tert*-butoxide (1.0M in hexane from SAFC, France), sodium *tert*-butoxide (powder 97% from SAFC, France) and potassium *tert*-butoxide (powder 95% from SAFC, France) were used as received. Cyclohexane and methylcyclohexane (99.5% from SAFC, France) were degassed over freshly crushed CaH_2, stored over polystyryllithium oligomers and distilled before use. Styrene (99% from SAFC, France) was degassed over freshly crushed CaH_2, stored over n,s-dibutylmagnesium and distilled before use. 1,3-butadiene (99% from SAFC, France) was purified one night over *s*-BuLi (1.3 M) at –30°C and distilled before use.

Polymerization: Polymerizations of 1,3-butadiene were carried out under dry nitrogen in cyclohexane at 40°C in glass flasks equipped with a quartz cell and fitted with PTFE stopcocks. PBLi seeds ([PBLi]= 5-8 10^{-3} M) were used as polymerization initiators. They were prepared by addition of 1,3-butadiene to a solution of s-BuLi in cyclohexane. A known amount of R_2Mg or *i*-Bu_3Al was then added to PBLi seed solutions to obtain the appropriate ratio [Mg]/[Li] ([Mg]/[Li] = 0 to 10) or [Al]/[Li] ([Al]/[Li] = 0 to 1). After addition of 1,3-butadiene, the polymerization kinetics were followed by dilatometry. The polybutadienes were then recovered by precipitation of the polymerization media into acidified methanol and their microstructure was determined by ^1H and ^{13}C NMR.

Styrene polymerizations were carried out under vacuum or argon atmosphere in cyclohexane (at 20°C) in glass flasks equipped with a quartz cell and fitted with PTFE stopcocks. The same kind of polymerizations were also carried out in methylcyclohexane (for temperatures below 5°C), but in sealed flasks. The initiating species n,s-Bu_2Mg / t-BuOMt (Mt = Li, Na, K) were prepared under argon by addition of the magnesium derivative and the alkoxide in the appropriate solvent and at the given temperature. The reactions were finally quenched by addition of degassed methanol in excess.

UV-Visible spectroscopy: The absorption spectra of the PBLi/R_2Mg and PBLi/i-Bu_3Al solutions were recorded on a UV-Vis spectrometer, Varian-Cary 3E, using a quartz cell (0.01 cm path-length) attached to the glass reactor ; $\varepsilon_{PBLi} = 8300$ $L.mol^{-1}.cm^{-1}$ at 275 nm.

Polymer characterizations: The average molar masses and the molar mass distributions of polystyrene and polybutadienes were determined by size exclusion chromatography (SEC) on a Varian apparatus equipped with a JASCO HPLC pump, type 880-PU, refractive index/UV detectors and TSK Gel columns calibrated with polystyrene standards. According to this calibration, a corrective factor has been applied for the polybutadienes experimental $\overline{M}_n$'s[12].
The stereochemistry of the polystyrene was determined in *d*-chloroform by ^{13}C NMR on Brüker AC 250 and DPX 200 on the aromatic quaternary carbon. Calculation of tacticity was carried out by deconvolution of the signal between 145.5 and 147 ppm using the "WINNMR1D" software.
Fractionation attempts of the polystyrene samples into highly tactic (insoluble) and atactic (soluble) fractions were performed by solubilization in methylethyl ketone at 80°C. All of our samples were completely soluble under these conditions.

Results and Discussion

Butadiene polymerization

In terms of kinetics, copolymer structure, and stereochemistry, the random anionic copolymerization of styrene and 1,3-butadiene is highly dependent on the nature of the anionic initiator and on the polymerization conditions. In hydrocarbon media, alkyllithium used in very low concentration compare to monomer gives polydienes exhibiting a high cis-1,4 microstructure[4]. Conversely, in polar media or in the presence of polar additives or complexing agents, as well as with alkali metal counter-ions other than lithium, polydienes with higher amount of 1,2-vinyl structure are obtained. Only very limited work has dealt with the influence of Lewis acids additives[5] on the stereochemistry of polybutadiene initiated by alkyllithium in hydrocarbons. We investigate in the first part of this paper the role of R_2Mg, ($0 < r = [Mg]/[Li] \leq 20$) and of *i*-$Bu_3Al$ ($0 < r = [Al]/[Li] < 1$) as additives in alkyllithium-initiated butadiene polymerization.

The UV-visible absorption spectra of polybutadienyllithium (PBLi) seeds in the presence of increasing amounts of *n,s*-Bu_2Mg and *i*-Bu_3Al are presented in Figures 1 and 2. The incremental addition of Lewis acids leads to a hypsochromic shift of the polybutadienyl band maximum (λ = 275 nm) to 259 nm for *n,s*-Bu_2Mg and 240 nm for *i*-Bu_3Al at r of about 1. These results are in agreement with the quantitative formation of 1:1 Lewis acid:PBLi complexes, see Scheme 1, as already reported for PSLi.

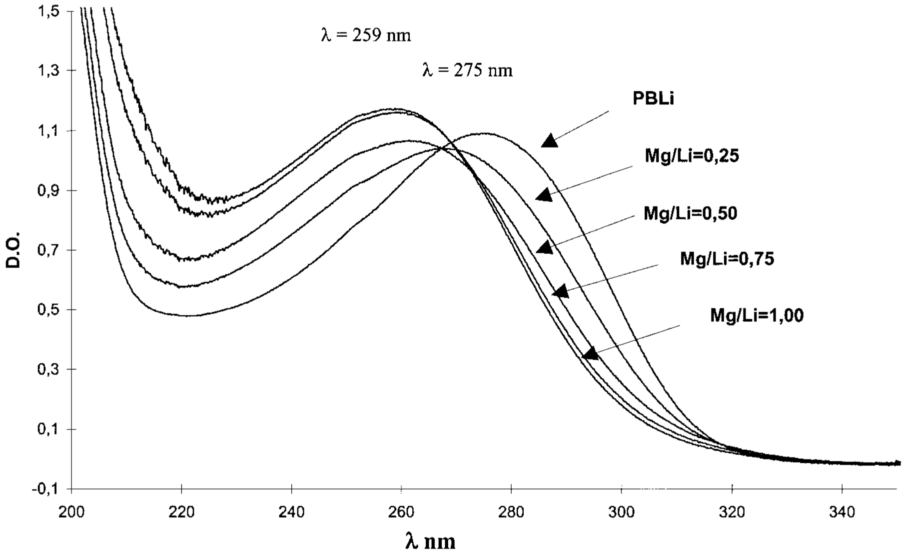


Figure 1. Influence of increasing amounts of n,s-Bu_2Mg on PBLi UV-visible spectrum ($[Mg]/[Li] \leq 1$, T = 25°C, cyclohexane).

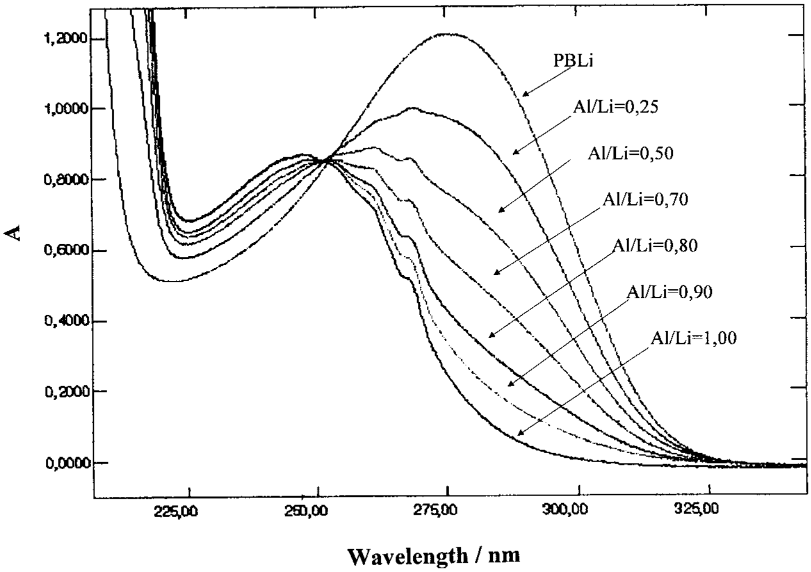
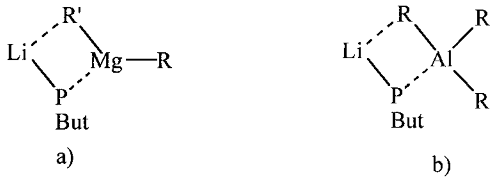


Figure 2. Influence of increasing amounts of i-Bu_3Al on PBLi UV-visible spectrum (T = 25°C, cyclohexane).



Scheme 1. Schematic representation of 1:1 Lewis acid:PBLi complexes.

The kinetics of 1,3-butadiene polymerization initiated by PBLi seeds in the presence of Lewis acid additives were investigated in cyclohexane at 40°C using the dilatometry technique. Since the aggregation state of Lewis acid:PBLi species is unknown, only apparent propagation rate constants have been determined using the kinetic equation

$$R_p = k_{p_{app}} [\text{"Li"}][\text{But}], \qquad (1)$$

where ["Li"], the concentration of active PBLi species, is assumed equal to initial *s*-BuLi.

Both the initial butadiene and *s*-BuLi concentrations were kept approximately constant for the whole series of kinetic experiments. For the (n,s-Bu_2Mg)$_x$:PBuLi systems, results collected in Table 1 show that the polymerization rate and apparent propagation rate constant decrease drastically with increasing r (factor 270 from r = 0 to 4). The experimental PB molar masses also decrease with increasing r, as previously reported for styrene. This is in agreement with coinitiation, or reversible chain transfer, involving n,s-Bu_2Mg. At low [Mg]/[Li] ratios one supplementary PB chain is formed by n,s-Bu_2Mg molecule, in addition to the one formed from PBLi seeds. However, at higher Mg/Li ratio the average number of PB chains per magnesium atom decreases suggesting incomplete coinitiation or reversible transfer processes with n,s-Bu_2Mg moieties when present in large excess.

For triisobutylaluminum systems butadiene polymerization rate and apparent propagation rate constant, Table 2, also decrease drastically with increasing proportion of i-Bu_3Al (factor 320 from r = 0 to 0.85) and no butadiene polymerization is observed for r equal or higher than one, as already described for styrene[2]. Experimental PB molar masses agree in this case with an initiation involving all the initial PBLi species, independently of r, whereas the contribution of the aluminum derivative to the formation of new PS chains is not observed.

Table 1. 1,3-Butadiene polymerization in the presence of n,s-Bu_2Mg/PBLi seeds at different [Mg]/[Li] ratios, cyclohexane, T = 40°C.

[n,s-Bu_2Mg] /[RLi]	**[PBLi] mol.L^{-1} ×10^3**	**Rp/[M] min^{-1} ×10^3**	$k_{p_{app}}$ $^{(a)}$ **L.mol^{-1}. min^{-1}**	$\overline{M}_n$ **th$^{(b)}$ Li**	$\overline{M}_n$ **th$^{(c)}$ Li+Mg**	$\overline{M}_n$ **(SEC)$^{(d)}$**	$\overline{M}_w / \overline{M}_n$
0	8.0	15	1.9	5 200	-	4 600	1.06
1	7.0	2.7	0.4	19 700	10 000	10 000	1.08
2	5.6	0.24	0.04	20 400	7 200	9 500	1.40
4	5.3	0.038	0.007	10 000	2 400	5 000	1.60

(a) $k_{p_{app}} = (R_p/M) / [PBLi]$

(b) theoretical molar masses (g.mol^{-1}) calculated assuming the contribution of [PBLi] alone

(c) theoretical molar masses (g.mol^{-1}) calculated assuming the contribution of [PBLi + R_2Mg]

(d) experimental molar masses (g.mol^{-1})

Table 2. 1,3-Butadiene polymerization in the presence of *i*-Bu_3Al/PBLi seeds at different [Al]/[Li] ratios, cyclohexane, T = 40°C.

[*i*-Bu_3Al] /[RLi]	**[PBLi] mol.L^{-1} ×10^3**	**Rp/[M] min^{-1} ×10^3**	$k_{p_{app}}$ $^{(a)}$ **L.mol^{-1}. min^{-1}**	$\overline{M_n}$ **th$^{(b)}$** **Li**	$\overline{M_n}$ **(SEC)$^{(c)}$**	$\overline{M_w}/\overline{M_n}$
0	8.0	15	1.9	5 200	4 600	1.06
0.70	6.2	0.51	0.08	14 400	13 500	1.16
0.85	6.1	0.034	0.006	6 400	6 600	1.18
1	6.0	0	0	-	-	-

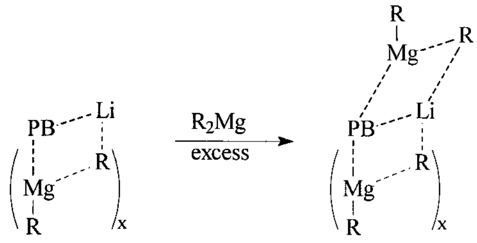
[a] $k_{p_{app}} = (R_p/M) / [PBLi]$
[b] theoretical molar masses (g.mol^{-1}) calculated assuming the contribution of [PBLi] alone
[c] experimental molar masses (g.mol^{-1})

Hsieh and Wang[5] have reported that the association of *n,s*-Bu_2Mg to alkyllithium initiators (r lower than 1) does not affect the stereochemistry of the diene polymerization. However, at higher [Mg]/[Li] ratios, Table 3, increasing proportions of *n,s*-Bu_2Mg induce an important and continuous increase of the 1,2- vinyl unit content in the polymer; whereas no significant change in the 1,4- cis/trans ratio is observed. At r = 1, only 13% of the butadiene units exhibit a vinylic 1,2- structure, but this is more than 50% at r = 10. This would suggest at first that 1,3-butadiene insertion proceeds into both uncomplexed PBLi and mixed Mg:Li complexes, and the proportion of the latter increases with r. However the quite quantitative formation of the 1:1 heterocomplex at r ≈ 1, supported both by UV-visible spectroscopy and kinetic data, should not yield a linear variation of the PB microstructure in the whole Mg:Li range examined (0 to 10). This indicates the contribution of a second reaction mechanism which could be the additional complexation of lithium species by free dialkylmagnesium (Scheme 2) and/or a 1,4- to 1,2- chain end isomerization process during chain exchanges between polybutadienyl active chains and dormant ones attached to magnesium species, as illustrated in Scheme 3. An isomerization of PBLi ends through chain exchanges inside aggregates has been already discussed by Bywater[4]. The presence of these secondary processes does not allow to use the observed PB microstructure as a probe of the structure of polymerization active species.

For *i*-Bu_3Al/PBLi systems, both the 1,4- and 1,2- unit ratio (1,4- units = 87-90%) and the cis/trans ratio in 1,4- units (cis/trans = 0.76) remain constant and close to those found with s-BuLi, Table 3. A similar tendancy was reported by Arest-Yakubovitch in the case of AlR_3/sodium-based initiators[6]. Since no reversible chain exchanges between the two metals take place in *i*-Bu_3Al/PBLi systems, chain end isomerization, as in dialkylmagnesium based systems, is not possible. However, because the PB microstructures observed with *i*-Bu_3Al/PBLi systems is very close to those observed with PBLi alone, the question concerning butadiene insertion either directly into active AlR_3/PBLi complexes or into remaining uncomplexed PBLi, present in very low concentration, cannot be answered yet.

Table 3. Influence of [n,s-Bu_2Mg]/[Li] and [i-Bu_3Al]/[Li] ratios on the configuration of polybutadienes; polymerization solvent: cyclohexane; T = 40°C.

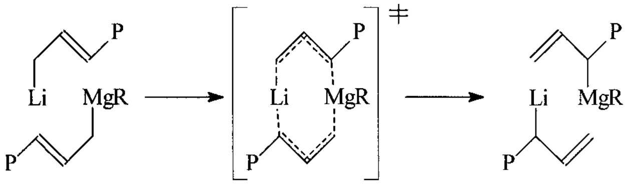
[n,s-Bu_2Mg] /[RLi]	**[i-Bu_3Al] /[RLi]**	**1,2 %**	**1,4 %**		**cis % / trans %**
			cis	**trans**	
0	0	10	38.5	51.5	0.75
-	0.5	9.5	39	51.5	0.76
-	0.7	10	39	51	0.76
-	0.9	13	36	51	0.70
1	-	13	37	50	0.75
2	-	20	35	45	0.76
4	-	31	29	40	0.73
10	-	49	20.5	30.5	0.67



$(MgR_2)_x$: PBLi complex

x= 1,2,...

Scheme 2. Possible representation of the additional complexation of lithium species by free dialkylmagnesium.



1,4 **1,2**

Scheme 3. Possible 1,4 to 1,2 isomerisation mechanism of polybutadienyl ends inside magnesiate complexes.

Stereoregulation in styrene anionic polymerization initiated by magnesiate complexes

Although alkali metal alkoxide as well as dialkylmagnesium are inactive alone in styrene polymerization, their combination yields an active initiating system, in agreement with the formation of alkali metal alkyl moieties through ligand exchanges in the complex[7]. Data concerning styrene polymerization initiated by alkali metal tert-butoxide/n,s-dibutylmagnesium "ate" complexes in hydrocarbon are given in Table 4. Besides the observed effect of temperature on both the reactivity and initiator efficiency, which both decrease when temperature goes down, magnesiate systems with different alkali metal yield polystyrene with different tacticities. At 20°C, with t-BuOLi/n,s-Bu_2Mg a PS with a predominantly syndiotactic microstructure, close to that observed with s-BuLi ($i=0.10$; $h = 0.25$; $s = 0.65$) is formed. No significant effect of the temperature on the syndioregulation is noticed. With the sodium cation the polystyrene shows an atactic structure. Conversely, a predominantly isotactic polymer is obtained with the potassium cation. The tacticity of polystyrenes prepared by the t-BuOK/n,s-Bu_2Mg system ($r=1$) in the range 20 to -40°C are given in Table 4.

As it may be seen, the isotactic character increases significantly when decreasing the temperature (85% of isotactic triads at –40°C) although in these conditions yields are low due in particular to a low initiation efficiency with respect to initial *t*-BuOK and the possibility of formation of alkylpotassium moieties. This can be explained by the insolubility of *t*-BuOK and the heterogeneous character of the polymerization system. These systems clearly differ from those described by Hogen-Esch[8],[9] and others[10],[11] obtained by the association of alkyllithium derivatives with lithium hydroxide as additive. No isotactic character is observed when lithium is used as alkali metal in the magnesiate complex. Fractionation of the highly isotactic PS into highly isotactic and atactic fractions could not be achieved in contrast to isotactic polystyrene obtained with alkyllithium/lithium hydroxide, suggesting one single type of propagating sites and the presence of stereodefects between isotactic polystyrene sequences.

Table 4. Polymerization of styrene initiated by the systems n,s-Bu_2Mg / t-BuOMt[(a)] (Mt = Li, Na, K ; Mg/Mt=1; cyclohexane ; 16 hours ; $\overline{Mn}_{th}$=10 000 $g.mol^{-1}$).

Initiating system *t*-BuOMet / *n,s*-Bu_2Mg	T (°C)	Yield[(b)] (%)	$\overline{Mn}_{exp}$ (g/mol)	MMD	f[(c)] (%)	Tacticity[(d)] iso	hetero	syndio
Li	20	76	18 500	1.3	41	0.15	0.22	0.64
Li[(e)]	-40	8	4 000	1.1	20	0.16	0.26	0.59
Na	20	72	21 500	1.3	33	0.28	0.30	0.42
K	20	91	25 000	1.4	36	0.61	0.29	0.10
K[(e,f)]	0	84	105 000	1.5	8	0.63	0.28	0.09
K[(e,f)]	-20	5	16 600	1.3	3	0.72	0.22	0.06
K[(e,g)]	-40	5	6 300	1.4	8	0.85	0.14	0.01

[(a)] [Initiator] = 5.10^{-3} M, [styrene] = 0.48 M

[(b)] Polymer yield determined gravimetrically

[(c)] initiator efficiency; $f = (yield_{wt} . \overline{Mn}_{th}) / \overline{Mn}_{exp}$

[(d)] determined by ^{13}C NMR of quaternary carbon in $CDCl_3$ at room temperature

[(e)] solvent = methylcyclohexane

[(f)] reaction for 24h

[(g)] reaction for 48h

In conclusion, the differences observed with "ate" complexes compared to the general behavior of alkyllithium systems, for styrene and 1,3 butadiene copolymerization in hydrocarbons yield some support to polymerization mechanisms involving monomer insertion into R_2Mg:PBLi and *i*-Bu_3Al:PBLi heterocomplexes. However the situation is not completely clear so far.

For magnesiate systems, secondary processes such as chain end isomerization or additional complexation of "ate" complexes by MgR_2 can explain the continuous change observed on the PB microstructure with increasing the proportion of dialkylmagnesium in the system. The mechanism yielding isotactic rich polystyrene in the presence of potassium metal alkoxide/ dialkylmagnesium initiating systems is also not completely elucidated. Isoregulation through insertion into magnesiate complexes or involving the potassium cation can still be postulated.

For alkylaluminum systems, the microstructure of butadiene units does not change with r ($r < 1$) and remains similar to PBLi in absence of any additives. Since 1,4- configuration of butadiene units is not altered, these results suggest that 1,4- insertion does not necessarily requires a preliminary strong diene coordination on the active species before insertion. The very low ionic character of the active species, ionic in ate complexes, might be in this case the determining factor for 1,4-insertion. Other results given by the study of styrene and butadiene copolymerization, which will be published soon, tend to show significant differences between the "ates" complexes and alkyllithiums alone systems.

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[1] P. Desbois, M. Fontanille, A. Deffieux, V. Warzelhan, S. Lätsch, C. Schade, *Macromol. Chem. Phys.* **1999**, *200*, 621.

[2] P. Desbois, M. Fontanille, A. Deffieux, V. Warzelhan, C. Schade, *Macromol. Symp.* **2000**, *157*, 151.

[3] S. Ménoret, S. Carlotti, M. Fontanille, A. Deffieux, P. Desbois, C. Schade, W. Schrepp, V. Warzelhan, *Macromol. Chem. Phys.* **2001**, *202*, 3219.

[4] D.J. Worsfold, S. Bywater, *Macromolecules* **1978**, *11*, 582.

[5] H.L. Hsieh, I.W. Wang, *Macromolecules* **1986**, *19*, 299.

[6] a) A. Arest-Yakubovich, *Macromol. Symp.* **1994**, *85*, 279 ; b) A. Arest-Yakubovich, *Chem. Reviews* **1994**, *19(4)*, 1.

[7] S. Ménoret, M. Fontanille, A. Deffieux, P. Desbois, *Polymer* **2002**, *43*, 7077.

[8] T. Makino, T.E. Hogen-Esch, *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1997**, *38(1)*, 164.

[9] T. Makino, T.E. Hogen-Esch, *Macromolecules* **1999**, *32*, 5712.

[10] J.E.L. Roovers, S. Bywater, *Macromolecules* **1975**, *8*, 251.

[11] L. Cazzaniga, R.E. Cohen, *Macromolecules* **1991**, *24*, 5817.

[12] M.F.K. Takahashi, M. De Lima, W.L. Polito, *Polymer Bulletin* **1997**, *38*, 455.