Macromol. Symp. ***157**, 151–160 (2000)*

Towards the Control of the Reactivity in High Temperature Anionic polymerization of Styrene : Retarded Anionic Polymerization

3 – Influence of triisobutylaluminum on the reactivity of polystyryllithium species.

Philippe Desbois[1,2], Michel Fontanille*[,1], Alain Deffieux[1], Volker Warzelhan[2], Christian Schade[2]

[1] Laboratoire de Chimie des Polymères Organiques, UMR ENSCPB - Université Bordeaux-1 - CNRS, BP 108, 33402 Talence-CEDEX, France
[2] BASF Aktiengesellschaft, Polymer Laboratory, 67056 Ludwigshafen, Germany

SUMMARY: the addition of triisobutylaluminum to a lithiated-based anionic polymerization of styrene leads to the formation of aluminate complexes and provokes a drastic reduction of the styrene polymerizability in relation with the Al/Li ratio used. The reaction is first order in monomer and active species and is stopped for $iBu_3Al/PSLi > 1$. From U.V. spectrometry, kinetic studies and viscometric measurements, it was possible to suggest the presence of various mixed complexes of different stoichiometries. The strong increase in the thermal stability of the new propagating species together with their much lower reactivity permits the controlled bulk polymerization of styrene at high temperature.

Introduction

For long time and until a recent period, polymer chemists tried to increase the reactivity of active centers propagating chain polymerizations in order to obtain a better productivity of the corresponding processes. This trend has found limitations where industrial chemists encountered severe heat transfer problems. In such instances, they are trying to improve the control of the processes by reducing the overall reactivity.

In previous papers[1-3] it was shown that the anionic polymerization of styrene initiated by an alkyllithium in hydrocarbon solution can be strongly retarded by addition of dialkylmagnesium to the system. The reduction of the polymerizability is due to the formation of "ate" complexes between magnesium and lithium species, which provokes a strong decrease of the reactivity of propagating centers.

Thus, it is possible to perform anionic polymerizations at temperatures higher than 100°C while keeping the process under control. The persistence of propagating centers is strongly increased simultaneously to the reactivity reduction, even though the ratio k_p/k_t decreases slightly with raising temperatures. The bulk retarded anionic polymerization of styrene thus

CCC 1022-1360/00/$ 17.50+.50/0

becomes possible at temperatures higher than T_g and an important new process for the production of polystyrene could be derived from Li/Mg-based systems as initiators.

In the light of the present knowledges and techniques and with the same objectives, it was tempting to revisit the system described by Welch[4] in 1960. This author had shown that addition of small amounts of aluminum alkyls to lithium alkyls ($[Al]/[Li] < 1$) leads to systems able to polymerize styrene but with a rate of polymerization lower than that observed with alkyllithium alone. Welch was considering that the decrease of the overall polymerization rate was due to the formation of a 1:1 RLi/AlR_3 inactive complex which was lowering the concentration of the reactive "free" RLi.

A rate reduction of the alkyllithium initiated polymerizations by addition of Al derivatives has been obtained and studied comprehensively in the case of polar monomers like methacrylates[5-8]. The presence of Al derivatives yields better kinetic control and (in addition, in several cases) a stereoregulation of the propagation process.

The present study was performed in order to demonstrate that mixed lithium/aluminum-based systems could be useful initiators for styrene anionic polymerization performed at relatively high temperatures. The main interest is to establish that the corresponding initiating systems preserve a living character for the polymerizations as for those performed at much lower temperatures.

In the aim to perform the polymerization in experimental conditions leading to a behavior close to that observed in bulk, experiments were realized in cyclohexane solution. Indeed, this solvent plays only the role of diluent and does not interfere on the intrinsic reactivity of the propagating centers. In such conditions the established data could be easily adapted to the bulk polymerization.

Results and Discussion

a) U.V.-Visible Study of Active Species

Addition of triisobutylaluminium ($i\text{-}Bu_3Al$) to polystyryllithium (PSLi) seeds in cyclohexane solution ($\lambda_{max} = 326$ nm) leads to the formation of a new peak located at 280-288 nm depending on the value of $r = [Al]/[Li]$. Simultaneously, the signal of PSLi decreases and disappears totally for $r = 1$ (Fig.1). For higher values of r, the U.V-Vis. absorption spectrum does not change and such a behavior is quite different of that observed with magnesiate complexes[1,2]. The modification of the U.V. spectrum is consistent with the formation of a 1/1 complex as suggested by Welch[4].

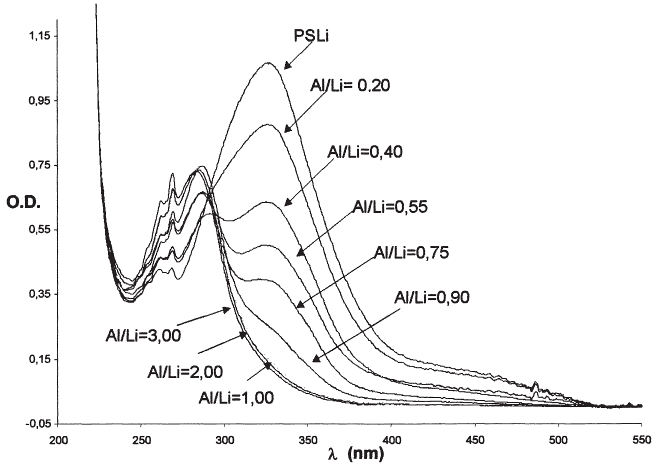


Fig. 1: Effect of addition of increasing amounts of i-Bu_3Al on U.V. spectrum of PSLi in cyclohexane ([PSLi] = 5.10^{-3} mol/L).

It is important to point out that for ratio close to 1 (Al/Li=0,8-1) the formation of the final spectrum needs several hours and proceeds in two stages (Fig. 2). The existence of an isosbestic point on the recorded spectra suggests the instantaneous formation of a "primary" complex between lithiated species and i-Bu_3Al (the "kinetic" complex) which rearranges into aλ more stable one (the "thermodynamic" complex).

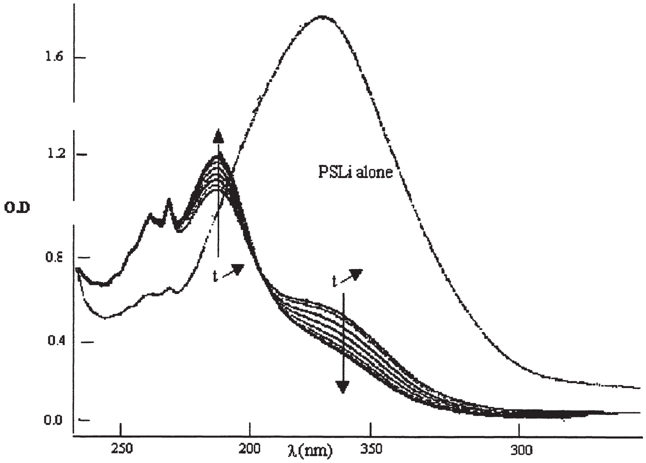


Fig. 2: Effect of aging on the U.V. spectrum of PSLi/i-Bu_3Al system. Interval of time between 2 spectra: 2 hours (r = 0.9 and T = 50°C).

Thus, the following steps and equilibria could be written:

$$2\,PSLi$$
$$\updownarrow$$
$$(PSLi)_2 + 2\,AlR_3 \rightleftharpoons \overset{\textbf{(a)}}{{}^{x}\!/_{n}\,[PSLi,AlR_3]_n} + \overset{\textbf{(b)}}{[(2-x)PSLi,(2r-x)AlR_3]} \qquad \text{and}$$

$$ {}^{x}\!/_{n}\,[PSLi,AlR_3]_n + [(2-x)PSLi,(2r-x)AlR_3] \rightleftharpoons \underset{\textbf{(a)}}{{}^{y}\!/_{n}\,[PSLi,AlR_3]_n} + \underset{\textbf{(b')}}{[(2-y)PSLi,(2r-y)AlR_3]}$$

The second equilibrium is reached after a period of time of about 15 hours at 50°C.

b) Kinetic Studies

Table 1. Kinetic data for styrene polymerizations performed at 50°C in cyclohexane solution and initiated with Li/Al-based systems; r = [Al]/[Li.]. (a)

$\frac{[Bu_3Al]}{[RLi]}$	[PSLi] mol.L^{-1}	Rp/[M] min^{-1}	k_{app} mol$^{-0.5}$L$^{0.5}$min^{-1}	$\bar{M}_{n,th}$(Li)	$\bar{M}_{n,GPC}$	$I_p=\bar{M}_w/\bar{M}_n$
0	6.2.10^{-3}	0.13	1.6	10200	10900	1.05
0,50	6.5.10^{-3}	0.044	0.54	7250	12000	1.23
0,60	6.3.10^{-3}	0.021	0.26	7450	11000	1.28
0,75	7.7.10^{-3}	7.0.10^{-3}	0.08	6600	6700	1.30
0,95	4.8.10^{-3}	3.1.10^{-4}	0.004	13100	13600	1.08
1	5.1.10^{-3}	0	0	-	-	-

Data reported in Table 1 show that, whatever the values of r, the experimental number average molar masses are in satisfactory agreement with those calculated from initial [RLi] which exhibit the non-participation of i-Bu$_3$Al as chain carrier. Moreover, the polydispersity indexes I_p (Table 1) and the linearity of $\log_e[M_0]/[M]$ *vs* time (Fig. 3) indicate the absence of significant termination reactions. Similar results have been observed at higher temperature (T = 100°C).

The kinetic order with respect to active centers was calculated from these data. It equals to 0.98 and thus is considered as first order. This means that the proportion of actually active species is not affected by their concentration even if they are in equilibrium with other species with a different reactivity. The whole of this behavior is consistent with a living character of the process; thus, assuming the concentration of active species equal to that of RLi it is possible to deduce an apparent rate constant of propagation : $k_{app} = \dfrac{R_P}{[S]\,[PSLi]}$

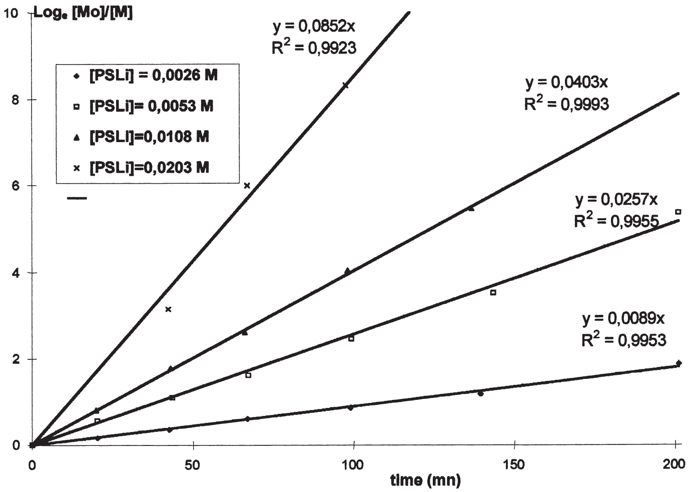


Fig. 3: Variation of $\log_e[M_0]/[M]$ *vs* time for different values of [Li]. r = 0.80; T = 100°C; cyclohexane.

At 50°C, k_{app} for r = 0.50 is 3 times lower than that measured for r = 0. With r = 0.95, the relative rate is further reduced to 1/400. Note that even for this ratio the number of PS chains formed is consistent with the contribution of the initial RLi species. The plot which represents the variation of $\log_e(k_{app})$ with r (Fig. 4) shows the drastic effect of [$i\text{-}Bu_3Al$] on the kinetics of propagation for values of r > 0.80. For r = 1, the system is unable to polymerize, suggesting the quantitative formation of a totally inactive 1/1 complex.

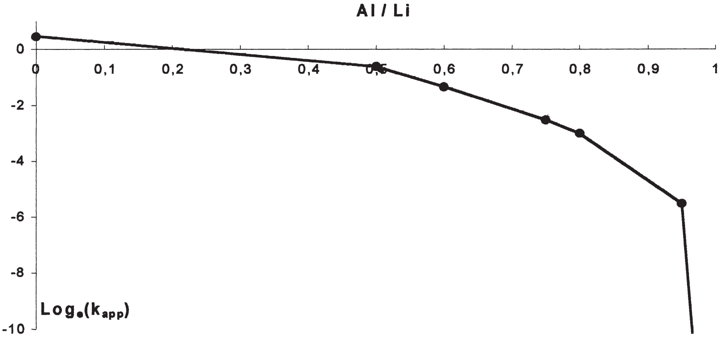


Fig. 4: Variation of $\log_e(k_{app})$ *vs* [Al]/[Li]; T = 50°C; cyclohexane.

MALDI TOF analysis of polystyrene samples obtained from $i\text{-}Bu_3Al$ and PSLi seeds initiated by n-hexyllithium shows only the presence of chains bearing hexyl moieties (Fig. 5). This supports that monomer insertion proceeds only in R-Li bonds to the contrary of n,s-dibutyl magnesium-based binary systems[3].

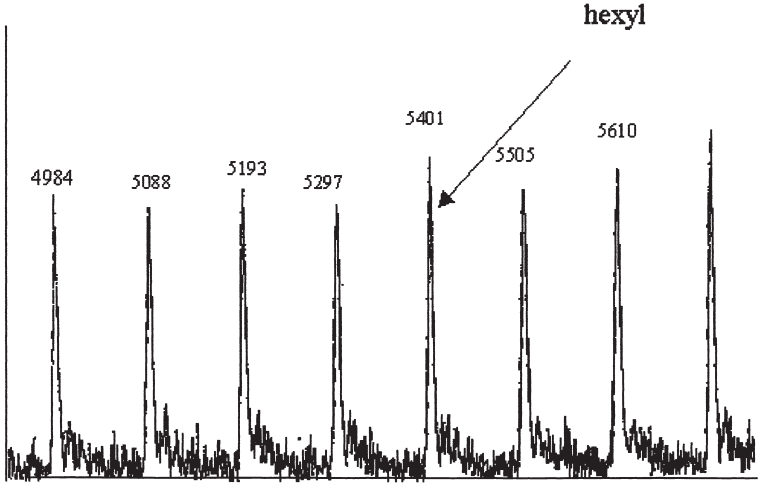
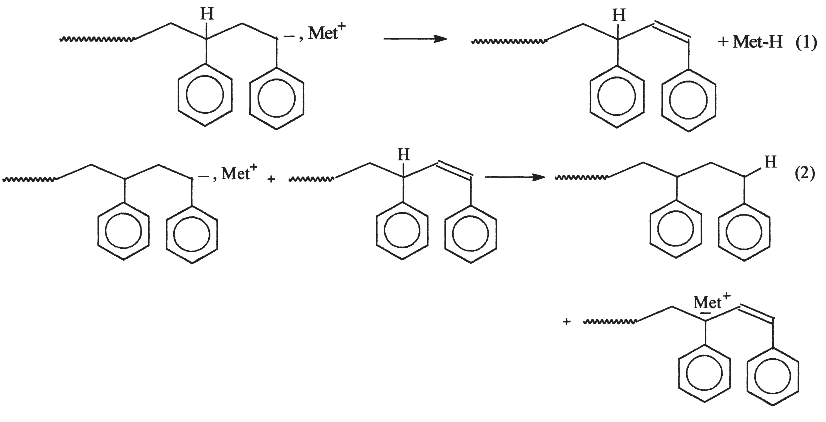


Fig.5: MALDI-TOF spectrogram corresponding to chains initiated by a hexyl moiety.

c) Persistence of Propagating Species

It is generally considered[10,11] that the thermal degradation of polystyryllithium in hydrocarbon solvents proceeds *via* the mechanism established by Szwarc and coll.[12] for polystyrylsodium in THF:



The rate of the degradation process can be determined from the disappearance of the initial U.V. absorption peak in the range 320-340nm (step 1) and the appearance of the new absorption peak in the range 450-500 nm (step 2). The rate of degradation is highly dependent on the dielectric constant of the medium. For example, the reaction is almost instantaneous for PS$^-$, Na$^+$ in hexamethylphosphortriamide (HMPA) at room temperature[12] whereas the half-life time of PSLi in cyclohexane at 100°C is around 3 hours.

Addition of R_2 Mg or R'_3Al to the living system increases strongly the persistence of the species (Fig. 6). Moreover, the absence of any U.V. signal in the 450-500nm range indicates that if the β-elimination of a hydride is possible (1st step), "ate" species are apparently unable to attack the acidic phenylallyl hydrogen generated in this step. This corroborates the lack of detectable "free" PSLi in equilibrium with the "ate" complex and the much lower reactivity of the "ate" complex propagating species than that of "free" PSLi.

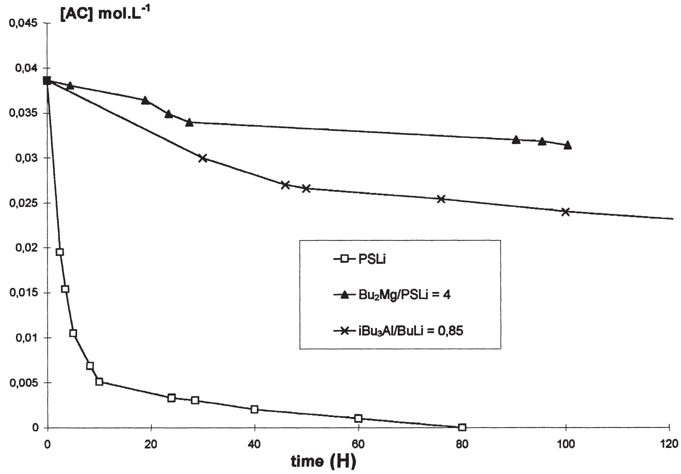


Fig 6: Variation of the concentration in active centers (AC) against time for different PSLi at 100°C and in cyclohexane.

d) Viscometric Studies

In order to obtain more information about the active "ate" complexes, the evaluation of the average number of polystyryl chains forming these complexes was obtained from viscometric measurements on dilute solutions. The degree of aggregation n can be derived from the ratio of the viscosity of active species to that of deactivated ones. It is given by the relation

$$n = (\eta_{act}/\eta_{deact})^2$$

η_{act} and η_{deact} being the relative viscosity of active and deactivated cyclohexane solutions, respectively.

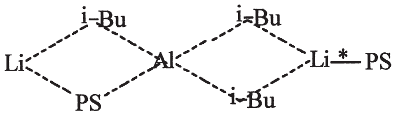
From Table 2 it can be seen that η_{exp} varies from 1.80 to 1.05 for r varying from 0 to 1. This might indicate that the main part of the new species generated by addition of i-Bu_3Al form 1:1 complex. The formation of a 2:1 complex in small proportion (with 2 polystyryl chains) and of lower stability, in equilibrium with the 1:1 complex remains however possible.

Table 2: Determination of the aggregation state from viscosity measurements. $M_{n\,PSLi}$ = 5000g/mol; T = 35°C; solvent: cyclohexane.

System	$n = (\eta_{act}/\eta_{deact})^2$
PSLi alone	1.80
PSLi + i-Bu_3Al (r = 0.25)	1.65
PSLi + i-Bu_3Al (r = 0.50)	1.43
PSLi + i-Bu_3Al (r = 0.75)	1.26
PSLi + i-Bu_3Al (r = 0.90)	1.11
PSLi + i-Bu_3Al (r = 1.00)	1.05

e) Nature of Propagating Species and Equilibria Involved

For r=1, all data point to the formation of the well known lithium tetraalkylaluminate complex, Li[Al(iBu)$_3$PS]. For values of r < 1 the kinetic behavior cannot be explained only by the progressive formation of the inactive 1/1 complex. The existence of equilibria between complexes with different stoichiometries (each having their own reactivity) in rapid exchange, is suggested. For example :



(corresponding to compounds b or b')

In this complex, the PS*-Li bond would be the only active part, as suggested by Arest-Yakubovitch for an Al/Na complexes[9]. The formation of the 2:1 complex of reduced reactivity would fit to the strong reactivity reduction at r > 0.5. In this range, the equilibrium

$$Li[Al(iBu)_3PS'] + Li_2[Al(iBu)_3(PS)_2] \rightleftarrows Li_2[Al(iBu)_3(PS)(PS')] + Li[Al(iBu)_3PS]$$

would support the living character and the kinetic behavior of the polymerization. The aging process might involve the formation of the 2:1 complex from the mixture 1:1 complex and PSLi. Thus, we suggest the following scheme :

$$\begin{tikzcd}
2\,\mathrm{PSLi} \arrow[d, shift right] \arrow[d, leftarrow, shift left] & \\
(\mathrm{PSLi})_2 + 2r\,\mathrm{AlR_3} \arrow[r, leftarrow, shift left, "\text{fast equilibrium}"] \arrow[r, shift right] & 2r\,[\mathrm{PSLi,AlR_3}] + 2(1\text{-}r)\,\mathrm{PSLi} \arrow[d, shift right] \arrow[d, leftarrow, shift left, "\text{slow equilibrium}"'] \\
 & 2(1\text{-}r)\,[\mathrm{AlR_3,2PSLi}] + 2(2r\text{-}1)\,[\mathrm{AlR_3,PSLi}]
\end{tikzcd}$$

Experimental

Materials, techniques of polymerization and of characterization have already been described in the previous papers[1-3]. Additionally, triisobutylaluminium (ether-free, 1.0M in hexanes from Aldrich) was used as received. MALDI-TOF measurements were performed on a BIFLEX III (Bruker-Franzen Analytik GmbH) in reflection mode using a dithranol matrix in THF and silver trifluoroacetate. Viscosimetric measurements were performed in a Ubbelhode viscosimeter. The apparatus was placed inside a thermostated oven and a capillary (l = 10cm, d = 1mm) attached to the glass reactor was used.

Conclusion

The use of trialkylaluminium derivatives as an additive in the styrene anionic polymerization initiated by lithium derivatives allows a strong reduction of the reactivity of propagating active species in hydrocarbon media. The rate decrease depends upon the ratio [Al]/[Li] and a concomitant stability increase of the active species is observed. The living character of the polymerization, especially the control of molar masses is preserved over the entire range [Al]/[Li] studied. The elementary mechanisms involved in {triisobutylaluminium/polystyryllithium} styrene polymerization implies the formation of different mixed aggregates in rapid interchange, the final 1:1 one being inactive. Evolution of the [Al]/[Li] ratio varies the proportion of these species and allows to modulate the reactivity from a common lithiated polymerization to a completely dormant system. The exact nature of these species cannot yet be elucidated. We suggest a rapid equilibrium among inactive 1:1 and reactive 1:2 species. More detailed kinetic study is in progress.

The possibility to use these systems in styrene bulk polymerization will be presented in following papers.

References

1. P. Desbois,M. Fontanille, A. Deffieux, V. Warzelhan, S. Lätsch, C. Schade, *Macromol. Chem. Phys.*, **200**, 621 (1999)
2. P. Desbois, M. Fontanille, A. Deffieux, V.Warzelhan, S. Lätsch, C. Schade, *Ionic Polymerizations and RelatedProcesses*, Kluwer Academic Publishers, 223-237 (1999)
3. P. Desbois, M. Fontanille, A. Deffieux, V. Warzelhan, S. Lätsch, C. Schade, to be published
4. F. J. Welch, *J. Am. Chem. Soc.*, **81**, 1345 (1959)
5. C.B. Tsvetanov, D.T. Petrova, P.H. Li, M. Panayotov, *Eur.Pol.J.,* **14**, 25 (1978)
6. D.G.H. Ballard, R.J. Bowles, D.M. Haddelton, S.N. Richards, R. Sellens, D.L. Twose, *Macromolecules,* **25**, 5907 (1992)
7. K. Ute, T. Asada; Y. Nabeshima, K. Hatada, *Polym.Bull.*, **30**, 171 (1993)
8. H. Schlaad, A.H.E. Müller, *Macromol.Symp.*, **95**, 13 (1995)
9. A.A. Arest-Yakubovich, *Chem. Reviews*, **19**(4), 1-72 (1994)
10. M.D. Glasse, *Prog. Pol. Sci.* **9**, 133 (1983)
11. F. Schué, P. Nicol, R. Aznar, *Macromol. Chem., Macrom. Symp.* **67**, 213, (1993)
12. M. Fontanille, unpublished results