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NEW σ-μ LIGANDS FOR THE ANIONIC POLYMERIZATION OF METHACRYLATES IN APOLAR MEDIUM

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Abstract : Poly(methyl methacrylate) (PMMA) has been anionically synthesized at high temperature and in apolar media, using diphenylhexyllithium (DPHLi) as initiator and a novel σ-μ chelating ligand to curb the side reactions. It has been indeed found that lithium 2-(dimethylamino-)ethoxide is a very efficient σ-μ ligand that prevents the anionic polymerization of methyl methacrylate (MMA) from being disrupted by significant secondary termination reactions. Ligand/initiator molar ratio, solvent polarity, temperature, monomer and active center concentrations are proved to be key parameters in the control of the polymerization process.

INTRODUCTION

Wiles and Bywater showed that the anionic polymerization of MMA by lithiated initiators in pure toluene is a very slow reaction that leads to broad multimodal molar mass distributions (MMD) [1]. Aluminium alkyls [2] and alkali alkoxides [3] are two μ-type ligands that were successfuly used to generate samples exhibiting unimodal and narrower MMD's in

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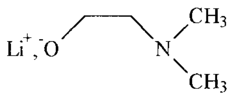
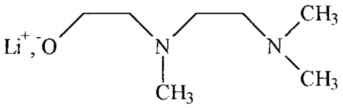
apolar media and at fairly low temperatures. Recently, Teyssié and coll. [4] developed the concept of dual σ and μ ligands that were actually oligomers of polyether fitted with a terminal lithium alkoxide. When modified by these ligands, lithium-containing ion pairs were found to be very efficient in promoting the controlled polymerization of MMA and of some primary acrylates, giving rise at the same time to samples with high syndiotactic content.

Compounds that form strong σ-type ligands with lithium are also good candidates to prevent the side reactions that usually occur in anionic polymerization of methacrylates [5]. The fact that bidentate tertiary diamines have better σ-cation binding capability than the corresponding bidentate oligoethers prompted us to check the effect of σ/μ ligands that would contain both lithium-based alkoxide and one or two tertiary amines.

In this respect, we recently demonstrated that lithium aminoalkoxides of type 1 and 2 afford the controlled anionic polymerization of methyl methacrylate (MMA) [6, 7]. Indeed, this controlled polymerization of MMA was achieved at temperatures as high as 70°C, in pure toluene in the presence of lithium 2-(dimethylamino-)ethoxide (1).



(1)



(2)

With these ligands, the polymerization goes to completion within a wide range of temperature. Multimodal distribution of molar masses are observed at low temperatures indicating that ligated species of different structure and thus different reactivity exist and slowly exchange. As the temperature is raised, the interconversion between the various species occurs at higher rates and, as witnessed in the SEC eluograms, the various peaks merge to give eventually a unimodal distribution. A further increase of the temperature results in the loss of the control of the polymerization. Similar behaviors are also observed in THF, in toluene and in the mixture of the two solvents. As the polarity of the medium decreases, the temperature window that affords controlled polymerization of MMA actually moves to higher temperatures.

In order to get more insight into the mechanism of polymerization in the presence of these ligands, a series of experiments was carried out in a flow tube reactor. Kinetic experiments using DPHLi as initiator and lithium 2-(dimethylamino-)ethoxide (1) as ligand were performed in various solvents, at temperatures between 0°C and 60°C.

EXPERIMENTAL PART

1. Purification of reactants and additives

MMA (Aldrich) was first vacuum-distilled over calcium hydride. Then, it was added to a 10 wt% triethylaluminium / toluene solution until a yellowish color developed [8]. The monomer was redistilled under reduced pressure just prior to polymerization. THF and toluene were first purified by refluxing over fresh sodium-benzophenone complex. Then, they were dried with a living carbanionic solution and distilled prior to use. Octane used as internal standard (Aldrich) was stirred over Na/K alloy, degased and distilled under high vacuum. Sec-butyllithium (Aldrich : 1,3 M solution in cyclohexane/hexane, 92/8) was used as received and handled under dry nitrogen. For the determination of its actual concentration, it was resorted to diphenylmethane / acetanilide-based double titration, prior to use. 1,1-diphenylethylene (DPE) (Aldrich) was distilled over calcium hydride under reduced pressure. The initiator was prepared by reacting a known amount of sec-BuLi with a slight excess of DPE in the polymerization medium at -40°C (when THF was present) or at +40°C during 4 hours (for polymerization in pure toluene). Then, the concentration of DPHLi ($[DPHLi]_0$) was determined by double titration. Lithium 2-(dimethylamino-)ethoxide was prepared in the polymerization medium and under nitrogen by reaction of 2-(dimethylamino-)ethanol (Aldrich) with DPHLi.

2. Kinetics

The kinetic experiments were carried out in a flow tube reactor (Feinwerktechnik) specially designed to monitor fast polymerizations. Monomer and premixed initiator/lithium aminoalkoxide solution were pre-cooled and mixed efficiently within less than 1 ms in a mixing jet and allowed to pass through a capillary tube (1 mm inner diameter). The particular residence time ($5 \text{ ms} \leq \tau \leq 2 \text{ s}$) of the polymerization solution was chosen by changing the flow rate and the capillary tube length ($4 \text{ cm} \leq l \leq 448 \text{ cm}$). The reaction mixture was terminated in a quenching jet at the end of the capillary tube with methanol containing a small amount of acetic acid. The temperature of the mixing jet, T_{mx}, and the quenching jet, T_q, were determined by using thermocouples. In all runs the flow rate was carefully chosen in order to maintain a turbulent flow throughout polymerization with a characteristic Reynolds number, $Re > 3000$. Experiments were carried out at T_{mx} = 0°C, 20°C, 25°C, 30°C and 60°C. The effective temperature (T_{eff}) of each run was higher than T_{mx}. The effective temperature of the each experiment was determined using the equation, $T_{eff} = T_{mx} + 0{,}55\Delta T$ [9]. Since the polymerization is very fast, heat transfer through the walls of the tube is negligible, leading to a nearly adiabatic behavior. Thus, data points corresponding to T_{eff} were recalculated to T_{mx} using equation (1) and the known activation energy, $E_a = 24 \text{ kJ.mol}^{-1}$, for the MMA polymerization with lithium as counterion [10],

$$\ln k_{app}(T_{mx}) = \ln k_{app}(T_{eff}) + \frac{E_a}{R}\left(\frac{1}{T_{eff}} - \frac{1}{T_{mx}}\right) \qquad (1)$$

3. Characterization

Monomer conversion was determined with GC using octane as an internal standard. Molar masses and molar mass distributions were determined using SEC equipped with refractive index / UV dual detection and TSK columns calibrated with PMMA standards. THF was used as eluent.

RESULTS AND DISCUSSION

For this series of polymerizations of MMA that were carried out in the presence of lithium 2-(dimethylamino-)ethoxide (1) and with DPHLi as initiator, the temperature window was chosen after a previous study [6] that established the conditions the most appropriate to obtain samples with unimodal MMD.

The results of the kinetic experiments that were performed in the flow tube reactor, using a mixture of toluene/THF as reaction medium are summarized in Tab. 1. The temperature of the reaction, the initial concentrations of initiator and of ligand were the parameters that were varied.

The $\ln([M]_0/[M])$ vs. time plots show a downward curvature irrespective of the concentration of initiator used (Fig. 1). The non linearity of the semilogarithmic time-conversion plot indicates that the apparent rate constant of propagation, k_{app}, decreases during polymerization because of the occurrence of termination reactions competing with propagation. The expression of the rate of polymerization for a chain process that is affected by unimolecular termination is given by the equation :

$$\ln\frac{[M]_o}{[M]_t} = \frac{k_{app}}{k_t}(1 - e^{-k_t \cdot t}) \qquad (2)$$

where $k_{app} = k_p.[P^*]$, the apparent rate constant of propagation, is the initial slope of the first order time-conversion plot, k_p and k_t being the rate constants of propagation and termination, respectively. $[P^*] = f.[DPHLi]_0$ is the actual concentration of active centers, f being the efficiency of the initiation step. The values of k_{app} and k_t were determined by using equation 2 and a least-square method that helps to fit all experimental points corresponding to a same experiment in a same curve. Despite the curvature observed, the values of the rate constant of termination estimated are rather low ; an increase of the ratio r of [ligand] to [DPHLi] actually helped to further curb the termination reactions yielding an almost linear time-conversion plot (Fig. 2).

As to $\overline{M}_n$ versus conversion plots their linearity shows that the polymerization is free of transfer reactions, the little deviation from the theoretical line being due to initiator efficiencies that are slightly lower than unity (Fig. 3).

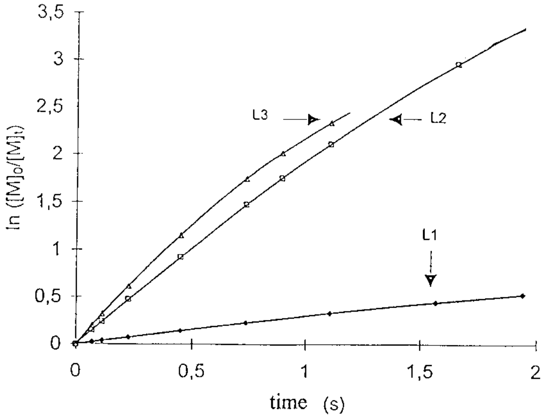


Fig. 1. First-order time conversion plots for polymerizations of MMA in toluene/THF (9/1) mixture in the presence of a 10-fold molar excess of lithium 2-(dimethylamino-)ethoxide with respect to initiator concentration and at 20°C.

$[MMA]_0$=0,20 mol/L, $[DPHLi]_0$ 0,75.10^{-3} (L1), 5.10^{-3} (L2) and 6,9.10^{-3} (L3) all in mol/L

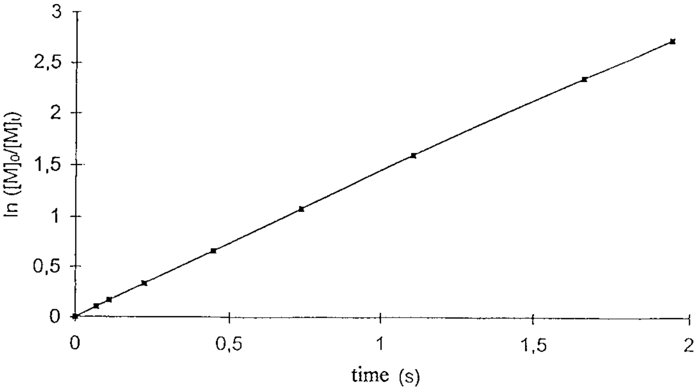


Fig. 2. First-order time conversion plots for polymerizations of MMA in toluene/THF (9/1) mixture in the presence of a 100-fold molar excess of lithium 2-(dimethylamino-)ethoxide with respect to initiator concentration and at 30°C.

$[MMA]_0$=0,20 mol/L, $[DPHLi]_0$ = 7,5.10^{-3} mol/L

Tab. 1. Kinetic data for polymerizations of MMA in the presence of (1) as chelating agent in toluene/THF (9/1) mixture using the flow tube reactor ($[MMA]_0$ = 0,20 mol/L)

Exp.	$[DPHLi]_0$ $.10^3$ (mol/L)	T_{eff} (°C)	$r_0^{(a)}$	$[P^*]^{(b)}$ $.10^3$ (mol/L)	$r^{(c)}$	$f^{(d)}$	k_{app} (s^{-1})	k_t (s^{-1})
L1	0,75	20	10	0,62	11,3	0,83	0,345	0,249
L2	5,00	20	10	4,40	12,1	0,88	2,188	0,255
L3	6,90	20	10	5,41	12,8	0,78	2,996	0,672
L4$^{(e)}$	3,00	25	10	2,38	12,6	0,79	3,306	0,974
L5$^{(e)}$	7,50	30	100	5,71	131,6	0,76	1,505	0,073
L6$^{(e)}$	2,00	30	10	1,51	13,2	0,75	4,212	1,410

(a) $r_0 = [(1)] / [DPHLi]_0$ (b) $[P^*] = f . [DPHLi]_0$ (c) $r = [(1)] / [P^*]$

(d) initiator efficiency, f, is obtained by taking the ratio of targeted values of $\overline{M}_n$ to those really measured.

(e) initiator efficiency, f, from only one value of $\overline{M}_{n,\ SEC}$.

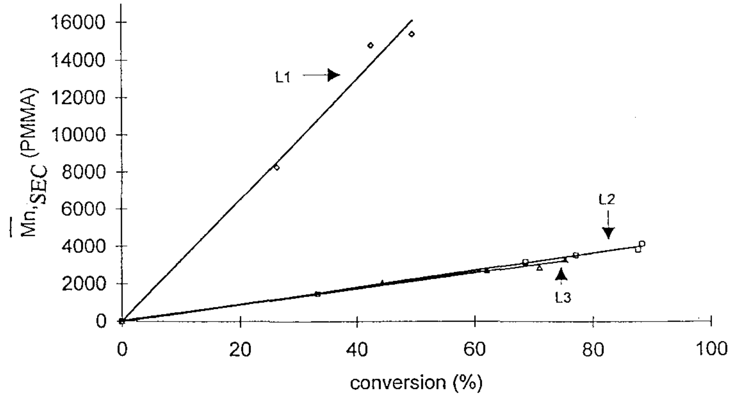
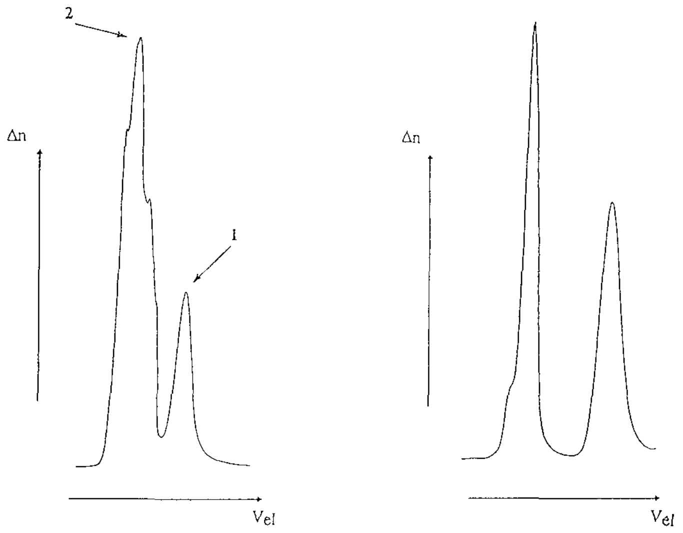


Fig. 3. Dependence of $\overline{M}_n$ with conversion for the polymerizations of MMA in toluene/THF (9/1) mixture in the presence of a 10-fold molar excess of lithium 2-(dimethylamino-)ethoxide with respect to initiator concentration and at 20°C.

$[MMA]_0$=0,20 mol/L, $[DPHLi]_0$ 0,75.10^{-3} (L1), 5.10^{-3} (L2) and 6,9.10^{-3} (L3) all in mol/L

In spite of the choice of a temperature that was supposedly appropriate to generate polymers with a unimodal distribution [6], samples obtained in the flow-tube reactor were found to exhibit a multimodal MMD. This feature is an indication that various active species with different reactivity are formed with this type of ligated initiator. For the calculation of the average molar masses of the samples, all the populations present in the SEC eluograms were taken into account (Fig. 4).



(a) (b)

Fig. 4. SEC eluograms of samples obtained at 20°C in toluene/THF (9/1) mixture at different monomer conversions. Experimental conditions : [MMA]$_0$*=0,20 mol/L,*
a) L1 (Tab. 1), residence time = 1,93 s, conversion = 49%
b) L2 (Tab. 1), residence time = 0,223 s, conversion = 32%

The difference in the modality of the MMD between samples prepared in a classical glass reactor vessel and in the flow tube reactor can be attributed to two factors. First, the overall concentration of the reaction medium is at least five times higher in the stirred glass tank than it is in the flow tube : species that exist at low concentrations may not exist at high concentrations and *vice-versa*. Secondly, the mixing rate in the glass vessel is certainly close to the polymerization rate favouring the formation of a monomodal envelope in which individual population could not be distinguished.

In order to understand the actual reasons for the formation of multiple, yet narrowly distributed populations when using the flow-tube reactor, we first checked the possible presence of aggregated species. The reaction order with respect to the concentration of active centers, [P*], was determined by plotting the bi-logarithamic variation of k_{app} versus [P*] ; the linear variation with a slope of 0,97 (Fig. 5) that is observed indicates the presence of non-aggregated active centers. Thus, multimodal distributions would not be due to the existence of slowly exchanging aggregates but to miscellaneous non-aggregated active species of different reactivity.

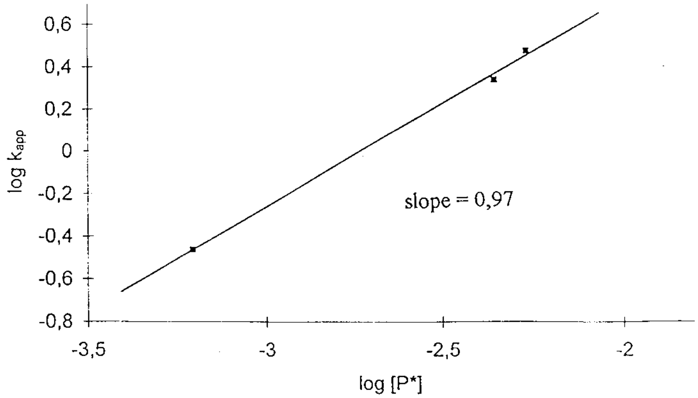


Fig. 5. Reaction order with respect to initiator concentration for the polymerization of MMA with lithium 2-(dimethylamino) ethoxide as ligand, in toluene/THF (9/1) mixture and at 20°C.

The second series of experiments was aimed at checking whether a similar behavior also occurs when the polarity of the reaction medium is varied. Kinetic experiments whose results are summarized in Tab. 2 were then carried out in pure toluene and in pure THF.

Tab. 2. Kinetic results for the polymerizations of MMA in the presence of (1) as chelating agent in THF (L7 and L8) and in toluene (L9), using the flow tube reactor ($[MMA]_0$ = 0,20 mol/L)

Exp.	$[DPHLi]_0$ $.10^3$ (mol/L)	T_{eff} (°C)	$r_0^{(a)}$	$[P^*]^{(b)}$ $.10^3$ (mol/L)	$r^{(c)}$	$f^{(d)}$	k_{app} (s^{-1})	k_t (s^{-1})
L7$^{(e)}$	2,50	0	10	2,11	11,7	0,85	2,521	0,257
L8$^{(e)}$	0,50	0	10	0,42	11,9	0,84	0,423	0,105
L9$^{(e)}$	0,80	60	100	0,68	117,6	0,85	1,851	-

(a) $r_0 = [(1)] / [DPHLi]_0$

(b) $[P^*] = f . [DPHLi]_0$

(c) $r = [(1)] / [P^*]$

(d) same as (d) in table 1

(e) same as (e) in table 1

Whatever the nature of the polymerization solvent (pure THF, pure toluene or toluene/THF mixture), two main peaks were observed in the SEC eluogram.

In such a case, even though the kinetic order with respect to active centers is unity, k_{app} cannot be written as $k_{app}=k_p.[P^*]$. Assuming that the two main peaks observed in the SEC eluogram are due to two growing species of different reactivity, k_{app} can be expressed as :

$$k_{app} = k_{p,1} \,.\, [P^*]_1 + k_{p,2} \,.\, [P^*]_2 \qquad \text{with } [P^*]_1 + [P^*]_2 = [P^*] \qquad (3)$$

To get access to the values of $k_{p,1}$, $k_{p,2}$, $[P^*]_1$ et $[P^*]_2$, we followed the below described rationale : let us define $d\upsilon_1$ as the number of monomer units consumed by the growing species 1 during the time dt :

$$d\upsilon_1 \,.\, [P^*]_1 = k_{p,1} \,.\, [M] \,.\, dt \qquad (4)$$

similarly, for the growing species 2, one obtains :

$$d\upsilon_2 \,.\, [P^*]_2 = k_{p,2} \,.\, [M] \,.\, dt \qquad (5)$$

As $d\upsilon_1$ and $d\upsilon_2$ can be assimilated to $\overline{DP}_{n,1}$ and $\overline{DP}_{n,2}$, the degrees of polymerization corresponding to the peaks 1 and 2, the following equation can be written :

$$\frac{(4)}{(5)} = \frac{\overline{DP}_{n,1}}{\overline{DP}_{n,2}} \frac{[P^*]_1}{[P^*]_2} = \frac{k_{p,1}}{k_{p,2}} \qquad (6)$$

As to $[P^*]_1$ and $[P^*]_2$, they can be estimated by the following way :

$$d[M]_1 = k_{p,1} \,.\, [M] \,.\, [P^*]_1 \,.\, dt$$
$$d[M]_2 = k_{p,2} \,.\, [M] \,.\, [P^*]_2 \,.\, dt$$

As $d[M]_1$ and $d[M]_2$ correspond to the surface areas S_1 and S_2 of peaks 1 and 2, their ratio gives :

$$\frac{d[M]_1}{d[M]_2} = \frac{S_1}{S_2} = \frac{k_{p,1}[P^*]_1}{k_{p,2}[P^*]_2} = \frac{\overline{DP}_{n,1}[P^*]_1^2}{\overline{DP}_{n,2}[P^*]_2^2} \Rightarrow [P^*]_1 = [P^*]_2 \cdot \sqrt{\frac{S_1}{S_2} \cdot \frac{\overline{DP}_{n,2}}{\overline{DP}_{n,1}}} \qquad (7)$$

From equations (3) and (7), $[P^*]_1$ and $[P^*]_2$ can be easily deduced ; as to $k_{p,1}$ and $k_{p,2}$, they were calculated from the ratio of (4) to (5), using the value of $\overline{DP}_{n,1}$ and $\overline{DP}_{n,2}$ given by the SEC eluogram. The results of the calculation are summarized in Tab. 3.

Tab. 3. Respective concentrations and rate constants of propagation of the two active species that are formed in the polymerization of MMA in the presence of lithium 2-(dimethylamino) ethoxide, in toluene/THF (9/1) mixture.

Exp.	T_{eff} (°C)	r	[P*] .10^3 (mol/L)	% (1)$^{(a)}$	% (2)$^{(a)}$	$k_{p,1}$ (L.mol^{-1}.s^{-1})	$k_{p,2}$ (L.mol^{-1}.s^{-1})
L1	20	10	0,62	63	37	182	1200
L2	20	10	4,40	72	28	290	1030
L3	20	10	5,41	85	15	420	1300
L4	25	10	2,38	76	24	945	2810
L5	30	100	5,71	53	47	45	510
L6	30	10	1,51	61	39	756	6010
L7	0	10	2,11	46	54	440	1845
L8	0	10	0,42	55	45	410	1725
L9	60	100	0,68	49	51	235	5075

(a) percentage calculated with concentration values of the species 1 and 2 ($[P^*]_1$ et $[P^*]_2$ respectively) estimated from previous calculations.

Two species of quite different reactivity coexist in the reaction medium and grow at different paces : the rate constant of propagation of the species of lowest reactivity corresponds to that measured for lithium enolates σ-ligated by tertiary diamines [11]. As for the second type of species, its rate constant of polymerization is very high. The formation of species of enhanced reactivity might be due to the complexation of several ligand molecules to the lithium cation causing the loosening of the contact ion pairs and the generation of "ligand-separated" ion pairs with larger interionic distance. Another point of outmost importance which deserves to be underlined is the proportion of ligand defined by the ratio r : upon increasing the molar ratio of ligand to initiator from 10 to 100, the rate constants of propagation for both species decrease and the termination process is severly curbed as indicates the almost linear $\ln([M]_0/[M])$ versus time plot (Fig. 2).

As to the respective concentrations of the two species, it appears that the larger of the concentration of active centers, the higher the proportion of species of lower reactivity (L1 to L3). This observation bears out the results obtained with classical glass reactor in which much higher concentrations of active centers were used than those allowed in the flow-tube reactor : the only way to prepare samples of controlled size and unimodal MMD in the presence of aminoalkoxides is to resort to the traditional glass vessel that is able to accomodate quite high overall concentration of polymers. It must be stressed that the same behavior has also been observed in the case of alkoxyalkoxides mediated polymerizations [12].

CONCLUSION

This novel ligated system of polymerization offers a typical illustration of the differences between living and controlled polymerization as exposed by Matyjaszewski [13]. A living polymerization is generally defined as a chain process that occurs without irreversible transfer and termination ; however, its initiation can be slow in comparison with propagation as well as the exchange between species if the medium were to contain many kinds of them. Thus, a living system can produce polymers with broad polydispersities and degrees of polymerization much higher than the ratio given by $\Delta[M]/[I]_0$. On the other hand, transfer and termination are allowed in a controlled polymerization if their contribution is sufficiently small : through a proper choice of the reaction conditions polymers with predetermined molar masses and low polydispersity can result in.

In the presence of lithium aminoalkoxides and at temperatures as high as 20-30°C polymerization of MMA in apolar medium exhibits all the characteristics of "livingness" (see L5 and L9) ; however, it is requested to carry out the polymerizations at relatively high concentrations ($[MMA]_0 = 1$ mol/L) so as to obtain samples with predetermined size and unimodal MMD's.

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