514 *Macromolecules* **1996,** *29,* 514−518

Synthesis of Polymers Containing Pseudohalide Groups by Cationic Polymerization. 14.[†] Functionalizing "Living" Polymerization of 2-Methylpropene Initiated by the System 1,4-Bis(1-azido-1-methylethyl)benzene/Diethylaluminum Chloride

Berhooz Rajabalitabar and Hung Anh Nguyen

Laboratoire de Synthèse Macromoléculaire associé au CNRS (URA 24),
Université P. et M. Curie, 4 Place Jussieu, 75252 Paris, France

Hervé Cheradame*

Université d'Evry, LPCB−CNRS, 2 rue H. Dunant, 94320 Thiais, France

Received January 31, 1995; Revised Manuscript Received September 26, 1995[⊗]

ABSTRACT: The polymerizations of 2-methylpropene (MP) via "all monomer in" (AMI) and "incremental monomer addition" (IMA) techniques initiated by the system 1,4-bis(1-azido-1-methylethyl)benzene (DAMEB)/$AlEt_2Cl/CH_2Cl_2$ behave like a functionalizing "living" system in the range of $\bar{M}_n$ < 50 000 without the assistance of an electron donor. This is demonstrated by the azide F_{N_3} and aromatic ring F_Φ functionalities close to the theoretical values of 2 and of 1, respectively, for a specific functionalization, by the linearity of the $\bar{M}_n$ versus weight of polymers (W_p) plot without intercept, and by the constant chain number N close to the theoretical N_0. It is also shown that a poly(2-methylpropene) α,ω-diazide (PMP) used in combination with $AlEt_2Cl$ is able to reinitiate the polymerization of MP. The final polymer presents the same functionalities F_{N_3} and F_Φ as the starting polymer used as initiator, and the increase of $\bar{M}_n$ corresponds to the amount of MP introduced. The monomodal SEC chromatograms of the starting and of the final PMP show that the whole azide chain ends are efficient in this experiment of reinitiation of polymerization from the functionalized PMP. The Mayo $1/\overline{DP}$ versus $1/\overline{DP}_0$ plot gives a straight line, the intercept of which corresponds to the ratio $k_{trM}/k_p = 2 \times 10^{-5}$, indicating that a possible transfer reaction to monomer could proceed at a very low rate, only detectable in the range of high $\bar{M}_n$ > 50 000.

Introduction

Years ago, we reported that organic pseudohalide/Lewis acid combinations can initiate the electrophilic chain polymerization of olefins and give polymers functionalized by a pseudohalide group.[1−3] Recently, research focused on the polymerization of 2-methylpropene (MP) initiated by 1,4-bis(1-azido-1-methylethyl)-benzene (DAMEB)/Lewis acid (LA) systems. With $TiCl_4$, the poly(2-methylpropene) (PMP) showed various terminal functions such as *tert*-butyl, tertiary chlorine, azide, and terminal unsaturations (di- and trisubstituted).[4] Depending on experimental conditions, their relative percentages changed; more particularly, unsaturations could be increased to the detriment of azide. It was shown that an excess of $TiCl_4$ was necessary to observe polymerization but in the meantime the Lewis acid was acting as a catalyst in the initiation of side reactions like dehydroazidation and/or dehydrochlorination on the polymer chain ends.[4] With BCl_3, the same terminal functions mentioned above were found but the relative content could change with temperature.[5] It was assumed that this LA could also induce the dehydroazidation of DAMEB, leading to the in-situ formation of an α-methylstyrene derivative able to copolymerize with MP.[5] In this case, the azide F_{N_3} and aromatic ring F_Φ functionalities of PMPs were higher than the respective theoretical values of 2 and 1 for a specific functionalization. These results indicated that the nature of LA has a great influence on the functionalizing polymerization of MP. It was worth noting that BCl_3 and $TiCl_4$ are strong Lewis acids, and we concluded that a "living" polymerization cannot be obtained in these conditions.[4,5] According to Kaszas et al. the role of an electron donor is to stabilize the active species under the form of carbenium ions and thus to eliminate undesirable side reactions.[6] This assumption was consistent with the results obtained in our laboratory in the case of the DAMEB/BCl_3/DMSO initiating system where the polymerization of MP was found to be "living" in the range of $\bar{M}_n$ < 50 000.[7] For higher $\bar{M}_n$, the Mayo 1/DP versus 1/DP_0 plot allowed us to calculate the ratio of constants k_{trM}/k_p about 4×10^{-5}. These results pointed to the importance of the strength of the acid used. Thus, the role of the electron donor, i.e. DMSO in the preceding example, was worth being discussed. Two possibilities are offered, since the role of the electron donor could be to weaken the strength of the Lewis acid as well as to interact with the active species, thus transforming a non-"living" system into a "living" one. In order to shed more light on this point, we investigated MP polymerization initiated by the DAMEB/$AlEt_2Cl$ system, i.e. with a weak Lewis acid ($AlEt_2Cl$), in order to determine whether the functionalizing polymerization could be "living" without any additive.

Experimental Section

Reactants. Reactants were purified and dried by following the technique used in our laboratory. CH_2Cl_2 was distilled over H_2Ca and vacuum distilled over P_2O_5 before use. MP was distilled through columns of $CaCl_2$ and BaO and condensed under vacuum before use. $AlEt_2Cl$ in CH_2Cl_2 solution (sure seal bottle 1 M, Aldrich) was used as received. The synthesis of DAMEB was published elsewhere.[4] (DAMEB characterization: IR 2100 and 1264 cm^{-1} of azide; ^{1}H NMR $\delta_{CH_3} = 1.99$ ppm, $\delta_\Phi = 7.56$ ppm; ^{13}C NMR $\delta_{CH_3} = 34.10$ ppm, $\delta_C = 69.1$ ppm, $\delta_{\Phi H} = 125.2$ ppm, and $\delta_{C\Phi} = 145.4$ ppm.)

---

* To whom correspondence should be addressed.

[†] Part 13: cf. ref 7.

[⊗] Abstract published in *Advance ACS Abstracts,* December 1, 1995.

0024-9297/96/2229-0514$12.00/0 © 1996 American Chemical Society

Table 1. Polymerization of MP Initiated by the System DAMEB/AlEt$_2$Cl/CH$_2$Cl$_2$ ([MP] = 1 M; t = 50 min)[a]

run	T, °C	10^{-2}[DAMEB], M	10^{-2}[AlEt$_2$Cl], M	conv, %	$\overline{M}_{n_{th}}$	$\overline{M}_{n_{exp}}$	F_{N_3}	F_Φ	[AlEt$_2$Cl]/[DAMEB]
1	−50	0	2	0					
2	−20	5	30	100	1360	1400	1.30	0.96	6
3	−40	5	30	98	1350	1400	1.60	0.93	6
4	−50	1	2	15	1080	4000			2
5	−50	2	13	89	2740	2150	1.85	0.99	6
6	−50	3	25	98	2080	2500	2.10	1.09	8
7	−50	2	18	98	3000	3350	2.10	1.03	8
8[b]	−50	4	35	98	3000	2750	2.03	1.20	8

[a] F_{N_3} = functionality of azide determined by FTIR. F_Φ = functionality of aromatic ring determined by ^{1}H NMR. $\overline{M}_{n_{th}}$ calculated from M_{DAMEB} + [([MP] × conversion × 56)/[DAMEB]]. $\overline{M}_{n_{exp}}$ determined by SEC. [b] Experimental carried out with [MP] = 2M

Polymerization. Polymerizations were carried out under vacuum in a reactor equipped with a magnetic stirrer and a rubber septum. DAMEB, CH$_2$Cl$_2$, and MP were introduced in this order, and at the desired temperature AlEt$_2$Cl was added through a syringe. Polymerization was quenched by methanol addition.

Characterization. $\bar{M}_n$ was determined by size exclusion chromatography (Waters, μ Styragel, solvent THF, polystyrene standard).

$\bar{M}_{n_{th}}$ was determined from the relation

$$\bar{M}_{n_{th}} = M_{DAMEB} + [(56 \times [MP] \times \text{conversion})/[DAMEB]]$$

The azide content was determined by FT IR according to ref 3. The determination of $F_{N_3} = (\bar{X}\,\bar{M}_n)/42$ was carried out via IR calibration of mixtures of 2-azido-2,4,4-trimethylpentane with unfunctionalized PMP (various compositions) assuming that ϵ_{N_3} has the same value in the mixture as in PMP−N$_3$: $\bar{X}$ = average weight fraction of azide in polymer = N$_3$ (g)/PMP (g).

X is given by the following relations (O.D. meaning optical density):

$$Y_1 = 27.24X_1 - 0.008 = \text{O.D. at } 2100\ \text{cm}^{-1}/\text{O.D. at } 1474\ \text{cm}^{-1}$$

$$Y_2 = 26.95X_2 - 0.021 = \text{O.D. at } 2100\ \text{cm}^{-1}/\text{O.D. at } 1369\ \text{cm}^{-1}$$

$$Y_3 = 17.77X_3 - 0.008 = \text{O.D. at } 2100\ \text{cm}^{-1}/\text{O.D. at } 1367\ \text{cm}^{-1}$$

Polymers were analyzed by FT IR (Bruker IFS 45) and by ^{1}H NMR (Bruker WP 100).

Results and Discussion

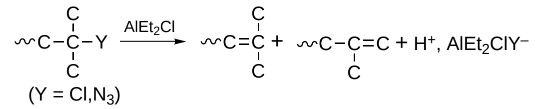
Influence of the Temperature and the Ratio *R* = [AlEt$_2$Cl]/[DAMEB]. Table 1 presents the results of MP polymerization at different temperatures and with various values of the ratio R = [AlEt$_2$Cl]/[DAMEB]. It is worth noting that, in the absence of DAMEB, polymerization of MP did not occur (run 1), and this indicates that DAMEB is the true initiator of MP polymerization. For a ratio R = 2 (run 4; stoichiometric ratio) at −50 °C, the polymerization yield was low, and runs 6 and 7 clearly indicated that an excess of AlEt$_2$Cl was needed for a quantitative polymerization. In the range of polymerization temperature −20 to −50 °C, the polymerization yield was not affected by temperature changes (run 2, 3, 5, ...). Similarly, the functionality of the aromatic ring F_Φ, which was close to the theoretical value of 1, did not change appreciably. Figure 1 is a typical FT IR spectrum of PMP (run 2) where peaks at 2100 cm^{-1}, corresponding to azide, and peaks at 1642 cm^{-1}, corresponding to unsaturations, are visible. The ^{1}H NMR spectrum of the same polymer (Figure 2) showed peaks at 0.99 ppm assigned to *tert*-butyl, at 4.63 and 4.83 ppm due to terminal disubstituted unsaturation (T-D), 5.15 ppm due to terminal trisubstituted unsaturation (T-T), 1.32 ppm assigned to CH$_3$(α)N$_3$, 1.58 ppm due to CH$_2$(β)N$_3$, 1.82 ppm assigned to CH$_2$(β)Cl, and 1.36 ppm assigned to CH$_3$(α)Cl. The existence of these end groups has been discussed, and their presence corresponds to the reaction scheme shown below.

−protonic initiation processes where H$_2$O comes from adventitious moisture, HN$_3$ comes from the dehydroazidation reaction, and HCl comes from Lewis acid hydrolysis or from dehydrochlorination

$$\begin{aligned} &H_2O + AlEt_2Cl \rightarrow H^+,AlEt_2ClOH^- \\ &HN_3 + AlEt_2Cl \rightarrow H^+,AlEt_2ClN_3^- \qquad (1) \\ &HCl + AlEt_2Cl \rightarrow H^+,AlEt_2Cl_2^- \end{aligned}$$

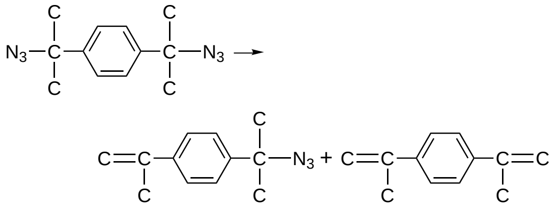
In fact, only H$_2$O or HN$_3$/MX combinations can initiate the polymerization of MP whereas HCl/MX$_n$ probably does not at low temperatures.[8]

−dehydroazidation and dehydrochlorination reactions leading to the formation of unsaturations (di- or trisubstituted) on the polymer (for the sake of clarity, only carbon atoms are shown in this scheme)



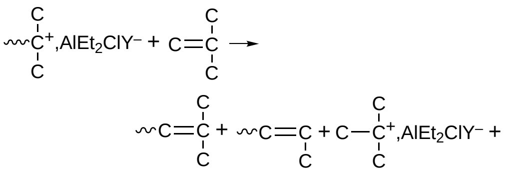
(2)

and on DAMEB


IIIa IIIb

(3)

−transfer reaction to monomer


(4)

−dimerization reaction of oligomers bearing disubstituted unsaturations

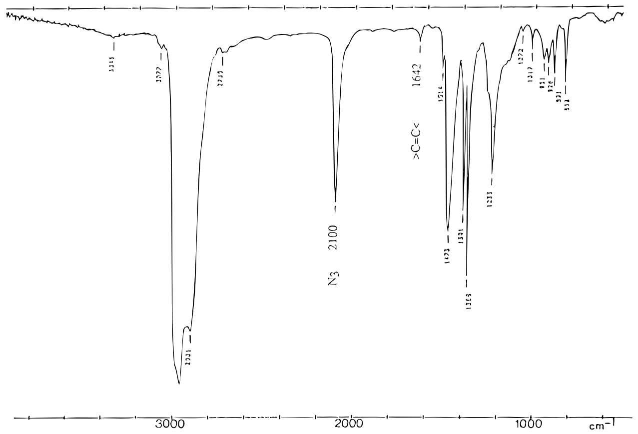


Figure 1. FT IR spectrum of poly(2-methylpropene) (experiment no. 2, Table 1). $T = 20$ °C; [AlEt$_2$Cl]/[DAMEB] = 6; [MP] = 1 M; [DAMEB] = 5×10^{-2} M.

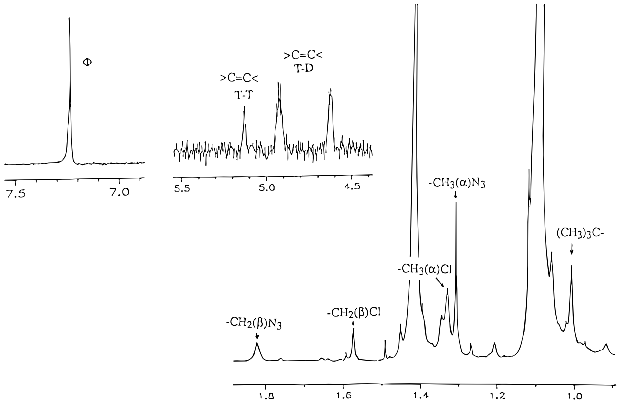
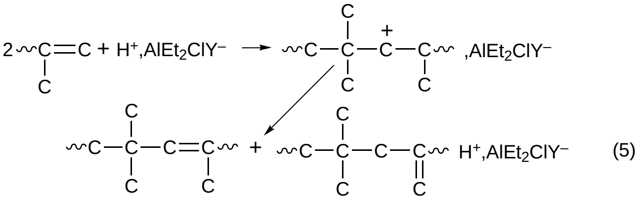


Figure 2. ^{1}H NMR spectrum of poly(2-methylpropene) (experiment no. 2, Table 1). $T = 20$ °C; [AlEt$_2$Cl]/[DAMEB] = 6; [MP] = 1 M; [DAMEB] = 5×10^{-2} M.


(5)

—copolymerization reaction

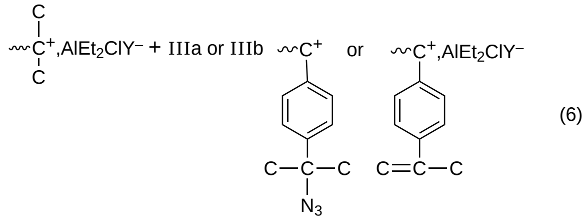

(6)

Table 2. Influence of the Polymerization Temperature on the Terminal Functions Content of Polymer Chains Determined by ^{1}H NMR[a]

run	T, °C	F_{N_3}[b] 10^4 g/mol	(T-D) 10^4 g/mol	(T-T) 10^4 g/mol	*tert*-butyl 10^4 g/mol	F_{N_3}[c] 10^4 g/mol
2	−20	9.4	3.9	0.5	0.13	9.3
3	−40	11.9	0.8	0.4	0.12	11.4
5	−50	8.9	ϵ	ϵ		8.6

[a] ϵ = amount too small to be detected. (T-D) = terminal disubstituted unsaturation. (T-T) = terminal trisubstituted unsaturation. [b] Functionality of azide determined by ^{1}H NMR. [c] Functionality of azide determined by FT IR.

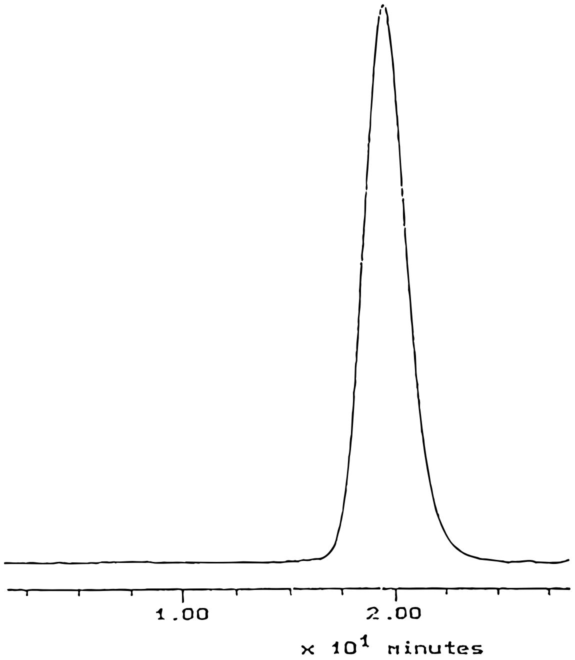


Figure 3. SEC chromatogram of poly(2-methylpropene) (experiment no. 5, Table 1). $T = 50$ °C; [AlEt$_2$Cl]/[DAMEB] = 6; [MP] = 1 M; [DAMEB] = 2×10^{-2} M.

With the experimental conditions $T = -50$ °C and $R = 8$ (runs 5−8), the azide F_{N_3} and the aromatic ring F_Φ functionalities were close to the theoretical values of 2 and 1, respectively. The corresponding PMPs presented exclusively azide end groups within experimental accuracy (tertiary chlorine, *tert*-butyl, and unsaturations being too low to be detected). $\bar{M}_{n_{exp}}$ was close to $\bar{M}_{n_{th}}$, indicating that the initiator efficiency is nearly quantitative. Another important point was that polymerization specificity, expressed in terms of functionalizations close to the theoretical values, did not depend on the absolute concentrations of [DAMEB] and of [AlEt$_2$Cl] but rather on their ratio R, at least in the present concentration range.

Table 2 shows the terminal azide and unsaturation functions content in the polymer determined by ^{1}H NMR for different polymerization temperatures. The N$_3$ content was increasing and the unsaturations content (terminal-disubstituted, T-D, and -trisubstituted, T-T) was decreasing with decreasing temperature. At −50 °C, PMPs presented only azide group chain ends. The interdependence between azide/unsaturation ends has been already observed when TiCl$_4$ was used.[3] SEC analysis of PMPs showed unimodal chromatograms with a polydispersity index of 1.2−1.3. An example of SEC is shown in Figure 3. These last results prompted us to examine in depth the details at −50 °C, the conditions at which the system could apparently be qualified as a "living" system.

"Living" Polymerization. Table 3 presents the results of MP polymerization via "all monomer in" (AMI) and "incremental monomer addition" (IMA) techniques. Whatever the technique used, the conversion is quantitative. PMP analyses by FT IR exhibited only a peak at 2100 cm^{-1} assigned to the azide function, peaks at 1640 and 890 cm^{-1} corresponding to unsaturations being absent. The ^{1}H NMR spectrum did not show any peak at 0.99 ppm attributed to *tert*-butyl and at 4.65, 4.85, and 5.10 ppm attributed to unsaturation functions; on the other hand, the peak at 7.28 ppm (aromatic ring) was detected. The PMP functionalities of azide (F_{N_3})

Table 3. AMI and IMA Polymerization of MP Inititated by the System $AlEt_2Cl/DAMEB/CH_2Cl_2$ (T = −50 °C; t = 50 min; V_t = 180 mL; [DAMEB] = 2.1×10^{-3} M; $[AlEt_2Cl] = 1.9 \times 10^{-2}$ M)[a]

run	tech	[MP], M	W_p, g	$\overline{M}_{n_{th}}$	$\overline{M}_{n_{ex}}$	conv %	F_{N_3}	F_Φ	I	10^{-4} N
1	AMI	0.053	0.61	1390	1650	98	2.0	1.09	1.3	3.7
2	AMI	0.087	0.95	2280	2350	98	2.1	1.08	1.3	4.0
3	AMI	0.156	1.63	4080	4250	98	2.1	0.95	1.2	3.8
4	AMI	0.216	2.27	5770	5570	100	2.1	0.94	1.3	4.0
5[b]	AMI	0.53	5.05	14550	14100	93	2.1	1.06	1.3	3.5
6[b]	AMI	0.65	6.30	18250	18100	95	2.1	1.03	1.3	3.5
7[b]	AMI	0.84	8.38	24300	24300	98	2.0	1.00	1.3	3.4
8[b]	AMI	1.52	15.09	44000	40000	98	1.9	0.99	1.5	3.4
9	AMI	3.07	31.00	82000	74600	100			1.4	3.8
10	IMA	0.11	1.18	2880	3050	98	2.0	1.00	1.3	4.0
11	IMA	0.135	1.42	3530	3600	98	2.1	1.00	1.3	3.9
12	IMA	0.15	1.58	3890	4000	97	2.0	0.99	1.3	3.9

[a] $I = \overline{M}_w/\overline{M}_n$. $\overline{M}_{n_{th}}$ calculated from m_{DAMEB} + ([MP] × 56.1 × conversion)/[DAMEB]. $\overline{M}_{n_{ex}}$ determined by SEC. F_Φ = functionality of aromatic ring determined by ^1H NMR. F_{N_3} = functionality of azide determined by FT IR. N = chain number of PMP calculated from $W_p/\overline{M}_n$. W_p = weight (g) of PMP. [b] [DAMEB] = 1.9×10^{-3} M.

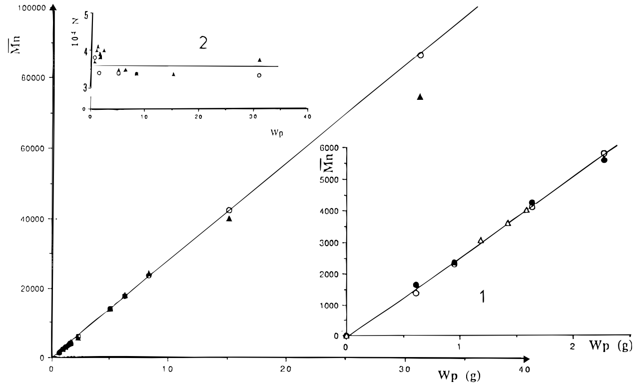


Figure 4. Molecular weight $\bar{M}_{n_{exp}}$ versus weight of polymer W_p (g) plot: (○) theoretical; (▲) experimental (*Inset 1*) Low $\bar{M}_{n_{exp}}$ range ($\bar{M}_n$ < 6000): (○) theoretical; (●) AMI; (△) IMA. (*Inset 2*) Chain number N versus weight of polymer W_P (g) plot: (○) theoretical; (▲) experimental. The horizontal line is simply an indication of the average of the theoretical values.

and of the aromatic ring (F_Φ) were close to the theoretical values of 2 and of 1, respectively, for a specific functionalization. This indicates a high initiation efficiency of DAMEB and the only presence of azide as end group in the polymer chains. Molecular weights $\bar{M}_{n_{exp}}$ determined by SEC were also close to the theoretical values with a rather narrow molecular polydispersity index (1.3−1.5). The $\bar{M}_{n_{exp}}$ versus weight of PMP (W_P) plot (Figure 4) is a straight line without intercept. Inset 1 presents the same plot in the low-$\bar{M}_{n_{exp}}$ range, and the results by the AMI and IMA techniques fit well with the theoretical straight line. The chain number N = $W_P/(\bar{M}_n \times \text{conversion})$ is constant and is close to the theoretical N_0 = [DAMEB]V total (Figure 4, inset 2).

These results indicate a living behavior of the polymerizing system, except for high molecular weights were a slight deviation from the theoretical values can be noticed. Sigwalt has shown that the linearity of $\bar{M}_n$ against W_P does not exclude the existence of transfer and termination reactions, particularly in the range of low $\bar{M}_n$.[9] Penczek et al. have demonstrated that one can obtain a narrow molecular weight distribution in the presence of an important termination reaction.[10] Sigwalt[11] and recently Kennedy[12] have defined the criteria which can qualify a "living" polymerization.

It could be argued that our system is a chain-transfer polymerization, i.e. a process in which the assumed transfer agent (here DAMEB) concentration controls the molecular weight. This point cannot be accepted. DAMEB is the initiator, since in its absence polymerization cannot be observed. In agreement with our interpretation, reinitiation from an azido-terminated PIB could not be observed in a chain-transfer polymerization, as will be shown in the next section below.

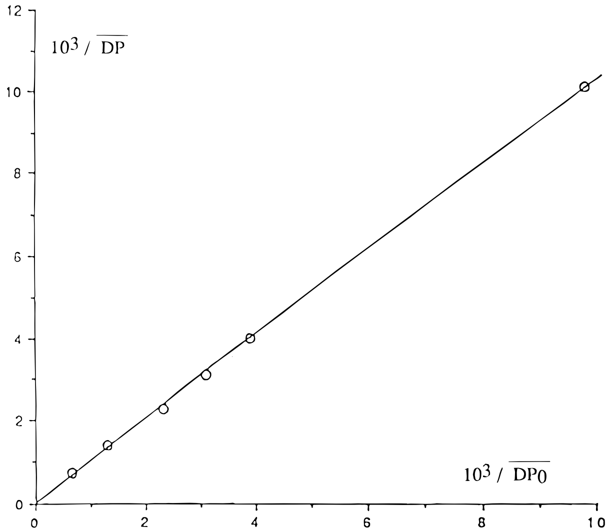


Figure 5. Mayo $1/\overline{DP}$ versus $1/\overline{DP}_0$ plot in the range of high $\bar{M}_n$.

Thus, in the range of high $\bar{M}_n$, the Mayo $1/\overline{DP}$ versus $1/\overline{DP}_0$ plot (Figure 5) gives a straight line, the intercept of which gives the ratio of constants:

$$k_{trM}/k_P = 2 \times 10^{-5}$$

The low value of this ratio shows that the transfer reaction to monomer proceeds at a very low rate but can be detected for $\bar{M}_n$ > 50 000. From the above result, we can deduce that the system is apparently limited to molecular weights lower than $56k_P/k_{trM} = 2.8 \times 10^6$ which shows the quality of our system. The "livingness" is clearly demonstrated, at least when the polymer molecular weight is lower than 50 000.

Polymerization by Reinitiation. The "living" behavior and the specific functionalization of azide were confirmed by an experiment where a PMP α,ω-diazide was used to initiate the polymerization of MP in combination with $AlEt_2Cl$. The experimental conditions were [MP] = 1.4 M, $[N_3] = 2 \times 10^{-2}$ M, T = −50 °C, and t = 50 min. PMP obtained from run 1: $\bar{M}_n$ = 1650; F_{N_3} = 2.0; F_Φ = 1.09; I = 1.3.

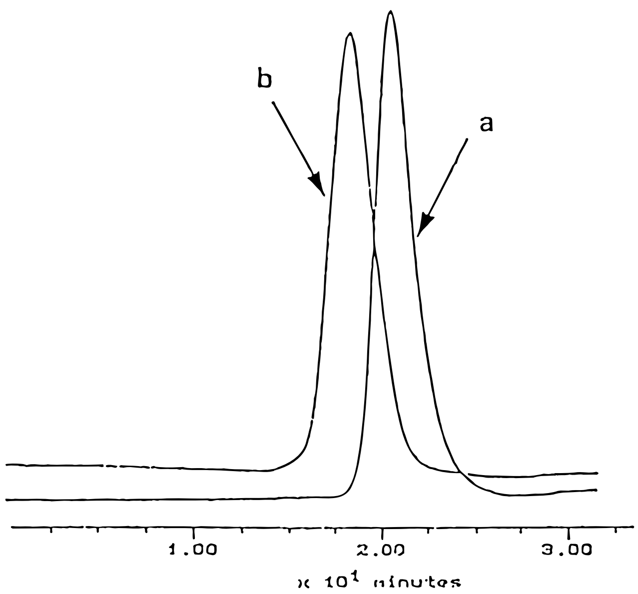


Figure 6. SEC chromatogramms of MP polymerization initiated by PMP α,ω-diazide/AlEt$_2$Cl: (a) PMP before polymerization; (b) PMP after polymerization.

The final product was a PMP with $\bar{M}_n = 5500$, $F_{N_3} = 2.07$, $F_\Phi = 1.05$, and $I = 1.3$. Taking into account that the conversion was 96%, the final $\bar{M}_{n_{th}}$ can be calculated:

$$\bar{M}_{n_{th}} = 1650 + [([MP]/[N_3]) \times 56.1 \text{ conversion}]$$

$$\bar{M}_{n_{th}} = 5400$$

The final $\bar{M}_{n_{exp}}$ determined by SEC is 5500, which fits well with $\bar{M}_{n_{th}}$. Figure 6 presents the SEC chromatograms of the starting (a) and the final (b) PMPs. The trace of the latter is monomodal. This indicates that all the azide chain ends participated in the reinitiaiton of MP polymerization, which is an improvement over the previous initiating system DAMEB/BCl$_3$/DMSO.[7]

Cocatalysis (reaction 1 above) cannot occur with a weak acid like AlEt$_2$Cl, since it was shown that this acid alone (moisture) does not initiate the polymerization of MP. Its weak acidic strength makes it unable to induce the side reactions of dehydroazidation and/or dehydrochlorination on the polymer chains at the end of polymerization (2) and on DAMEB (3), dimerization of oligomers (5), and copolymerization reaction (6) mentioned above. In terms of termination reactions, a competition between tertiary chlorine and azide ends is expected but it seems that AlEt$_2$Cl favors predominantly the recombination of the more nucleophilic moiety (N_3^-) coming from the counteranion with the carbenium. The reason why a high AlEt$_2$Cl/DAMEB molar ratio is needed to observe a living system is easily explained by the necessity of having a sufficiently large concentration of active species, given by the ionization of carbon−azide bonds, to obtain complete polymerization in our conditions in a time sufficiently short to keep side reactions at a negligible level.

In conclusion, the system DAMEB/AlEt$_2$Cl/CH$_2$Cl$_2$ gives a “living” polymerization of MP in the range of $\bar{M}_n < 50\,000$ where the presence of an electron donor like DMSO is not necessary. Our system also presents the advantage that a directly functionalizing polymerization with a reactive chain end function like the azide group is obtained and can be used for further chemistry such as chain extension.[13]

References and Notes

(1) Cheradame, H.; Habimana, J.; Chen, F. J.; Johnston, J. E. 9th International Symposium on Cationic Polymerization and Related Ionic Processes, Strasbourg, France, 1989; Preprints p 61.
(2) Nguyen, H. A.; Chen, F. J.; Johnston, J. E.; Cheradame, H. 9th International Symposium on Cationic Polymerization and Related Ionic Processes, Strasbourg, France, 1989; Preprints p 96.
(3) Cheradame, H.; Habimana, J.; Chen, F. J. *Makromol. Chem.* **1992**, *193*, 2647. This paper presents part of the results coming from the “Thèse de Doctorat de l'Institut National Polytechnique de Grenoble” presented by Jean de la Croix Habimana, Grenoble, France, 1989.
(4) Rajabalitabar, B.; Nguyen, H. A.; Chen, F. J.; Cheradame, H. *Eur. Polym. J.* **1995**, *31* (2), 173.
(5) Rajabalitabar, B.; Nguyen, H. A.; Cheradame, H. *Eur. Polym. J.* **1995**, *31* (3), 297. Copolymerization of the growing chain with the α-methylstyrene derivative coming from the in-situ dehydroazidation is deduced from the fact that the polymer presents a functionality of azide F_{N_3} and of aromatic ring F_Φ higher than the theoretical values of 2 and 1 for a specific functionalization.
(6) Kaszas, G.; Puskas, J.; Chen, C. C.; Kennedy, J. P. *Polym. Bull.* **1988**, *20*, 413.
(7) Rajabalitabar, B.; Nguyen, H. A.; Cheradame, H. *Macroml. Chem. Phys.*, submitted for publication.
(8) Pham, T. M. C. Thèse 3^e Cycle, University of Paris VI, Paris, 1973.
(9) Sigwalt, P. *Makromol. Chem., Makromol. Symp.* **1991**, *47*, 179.
(10) Penczek, S.; Kubisa, P.; Szymanski, R. *Makromol. Chem. Rapid Commun.* **1991**, *12*, 77.
(11) Sigwalt, P. *Polym. J.* **1985**, *17*, 57.
(12) Kennedy, J. P. *Makromol. Chem., Makromol. Symp.* **1991**, *47*, 55.
(13) Nguyen, H. A.; Cheradame, H.; Marechal, E. *Makromol. Chem.* **1992**, *193*, 2495.

MA950113G