

# Controlled Radical Polymerization of (Meth)acrylates by ATRP with NiBr<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> as Catalyst<sup>†</sup>

G. Moineau,<sup>‡</sup> M. Minet,<sup>‡</sup> Ph. Dubois,<sup>‡,⊥</sup> Ph. Teyssié,<sup>‡</sup> T. Senninger,<sup>§</sup> and R. Jérôme<sup>\*,‡</sup>

Center for Education and Research on Macromolecules (CERM), University of Liège, Sart-Tilman, B6, 4000 Liège, Belgium, and Service Polymères de Grande Diffusion et Catalyse, Groupement de Recherches de Lacq, R.N. 117, B.P. 34, 64170 Lacq, France

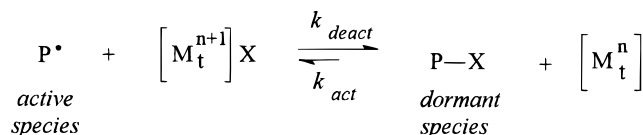
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**ABSTRACT:** NiBr<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> has been found to be an efficient catalyst for the ATRP of methyl methacrylate (MMA) and *n*-butyl acrylate (*n*-BuA) initiated by an alkyl halide in the absence of any activator (e.g., Lewis acid) at 85 °C. The molecular weight distribution of the poly(meth)acrylates is narrow ( $M_w/M_n = 1.1–1.4$ ). However, some side reactions (more likely coupling reactions) are observed at high monomer conversions in the case of *n*-BuA. An excess of PPh<sub>3</sub> has proved to increase the polymerization rate of MMA while preserving the control of the molecular parameters. When the catalyst/initiator molar ratio is too small (e.g., 0.05), the polymerization rate decreases, the polydispersity increases, and the initiation is less efficient.  $\alpha$ -Acid and  $\alpha$ -hydroxyl end groups have been successfully attached to the chains by using functional initiators, such as 2-bromo-2-methylpropionic acid and 2,2',2''-tribromoethanol. Reactivity ratios for the MMA/*n*-BuA comonomer pair have been measured and found to be close to the values observed for a conventional free-radical polymerization. Diethyl *meso*-2,5-dibromoadipate has been used as a difunctional initiator for the *n*-BuA polymerization, leading to  $\alpha,\omega$ -bromo-poly(*n*-BuA) of narrow molecular weight distribution. Finally, the thermal stability of PMMA is consistent with the lack of termination reactions, while  $T_g$  is as high as 125 °C.

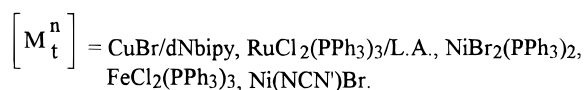
## Introduction

The concept of living polymerization pioneered by Szwarc<sup>1</sup> in 1956 in the case of anionic polymerization has been recently extended to free-radical polymerization. This remarkable progress started with the scientific contribution by Otsu et al. on the iniferter mechanism.<sup>2</sup> Rizzardo et al.<sup>3</sup> then introduced the concept of the stable free-radical polymerization (SFRP) by using permanent nitroxyl radicals, mainly TEMPO. This new mechanism proved high efficiency in the case of styrene<sup>4</sup> and derivatives,<sup>5</sup> whereas some other monomers, e.g., *n*-butyl acrylate, 4-vinylpyridine, and *N*-vinylcarbazole, were also polymerized<sup>6</sup> in a controlled way. Another strategy for the controlled radical polymerization is now intensively investigated: the atom transfer radical polymerization (ATRP) (Scheme 1), which is a direct extension to polymers of the Kharasch reaction well-known for low molecular weight compounds.<sup>7</sup> Sawamoto et al.<sup>8</sup> and Matyjaszewski et al.<sup>9</sup> were the first to report on ATRP, by using a catalytic complex containing ruthenium and copper, respectively. It must be noted that the ruthenium-based system proposed by Sawamoto et al. required the addition of a Lewis acid (LA), i.e., MeAl(*o,o'*-di-*tert*-butyl phenoxide)<sub>2</sub><sup>8</sup> or Al(*O-i*-Pr)<sub>3</sub><sup>10</sup> for being active. A steadily increasing attention is paid now to the ATRP.<sup>11</sup> For example, Granel et al.<sup>12</sup> described the use of a nickel-based catalyst, (*o,o'*-Me<sub>2</sub>N-CH<sub>2</sub>)-C<sub>6</sub>H<sub>3</sub>-NiBr or Ni(NCN')Br, able to control the radical polymerization of MMA at 80 °C, without any

## Scheme 1



with X = Cl, Br, ...



activator. This catalyst is very efficient in the controlled radical polymerization of methacrylates, the chain polydispersity being very narrow ( $M_w/M_n < 1.2$ ).

In 1997, Sawamoto et al. reported on two new catalysts for the ATRP of MMA, i.e., FeCl<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub><sup>13</sup> and NiBr<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>.<sup>14</sup> Similarly to RuCl<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub>, the NiBr<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> catalyst required the addition of a Lewis acid to be activated, even though some polymerization data collected in the absence of Lewis acid were also published.<sup>14</sup> The polymerization remains apparently controlled, although the polydispersity becomes broader at high monomer conversion. This broadening effect might however result from the slow thermal decomposition of the NiBr<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> complex as mentioned by the authors.<sup>14</sup> This slow decomposition could be avoided (or at least reduced) by increasing the monomer concentration, thus decreasing the reaction time compared to the catalyst decomposition. The aim of this paper is to report on the controlled ATRP of MMA and *n*-BuA catalyzed by NiBr<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> in the absence of Lewis acid. The random copolymerization of MMA and *n*-BuA will also be analyzed and the reactivity ratios determined. Finally, an activated dibromide, diethyl *meso*-2,5-dibromoadipate, will be tested as a potential difunctional

<sup>†</sup> Part of this work has been presented at the Symposium "Advances in Living and Controlled Radical Polymerization" held in Geleen (DSM Research), The Netherlands, April 22, 1998.

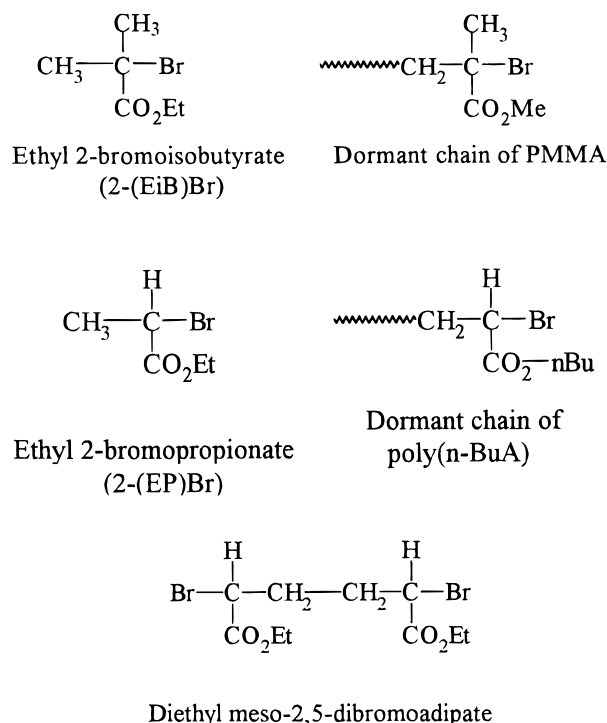
<sup>‡</sup> University of Liège.

<sup>§</sup> Groupement de Recherches de Lacq.

<sup>⊥</sup> Current address: Service des Matériaux Polymères et Composites, Université de Mons-Hainaut, Place du Parc, 20, 7000 Mons, Belgium.

\* To whom correspondence should be addressed.

Scheme 2



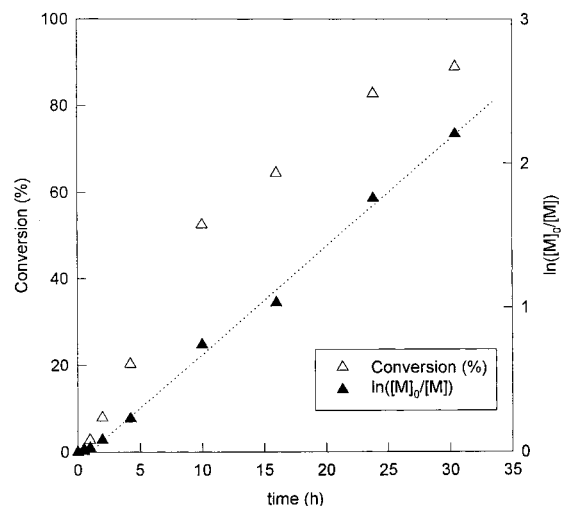
initiator, which is essential for the two-step synthesis of triblock copolymers and telechelic polymers.

### Experimental Section

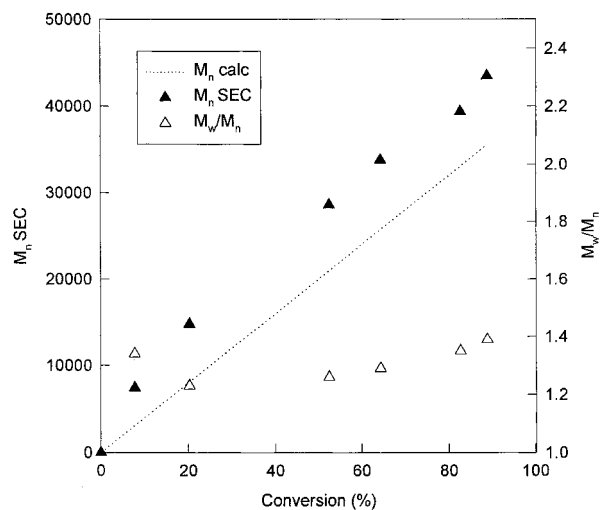
**Materials.** NiBr<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (99%), ethyl 2-bromoisobutyrate (2-(EiB)Br) (98%), 2,2'-dichloroacetophenone (97%), ethyl 2-bromopropionate (2-(EP)Br) (99%), 2-bromo-2-methylpropionic acid (98%), 2,2',2''-tribromoethanol (97%), and diethyl meso-2,5-dibromoadipate (98%) were purchased from Aldrich and used without any purification. 2,2'-Azobis(isobutyronitrile) (AIBN) (98%) was used as received from Acros. Monomers (Aldrich) were dried over CaH<sub>2</sub> and distilled under reduced pressure to remove the stabilizing agents and stored under N<sub>2</sub> at -20 °C. NiBr<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> was stored under nitrogen but was weighed in the open air prior to polymerization.<sup>15</sup>

**Polymerization.** All experiments were conducted according to the Schlenk method. In a typical experiment, the solid ingredients and a magnetic bar were introduced in a glass tube, which was then closed by a three-way stopcock and placed under nitrogen by repeating three times a vacuum/nitrogen cycle. The liquid reagents were then added under nitrogen with a syringe in the following order: solvent, monomer, initiator. When high temperature and/or long reaction time were required, the tubes were sealed under vacuum. MMA conversion was determined from the amount of PMMA precipitated in heptane. However, when small volumes of MMA polymerization medium were picked out, solvent and residual monomer were distilled off under vacuum. The same procedure was used in the case of the *n*-BuA polymerization. The recovered polymer was weighed after drying at 80 °C for 24 h under high vacuum. The catalyst residue was taken into account in the calculation of the monomer conversion.

**Characterization.** Molecular weight distribution was analyzed by SEC in THF at 40 °C using a Hewlett-Packard 1090 liquid chromatograph equipped with a Hewlett-Packard 1037A refractive index detector. PMMA standards (Polymer Laboratories) were used for calibration. Before SEC or NMR analysis, the polymer was purified by passing solutions through an Al<sub>2</sub>O<sub>3</sub>-filled column. <sup>1</sup>H NMR spectra were recorded at room temperature in CDCl<sub>3</sub> with TMS internal reference by using a Bruker AM 400 apparatus. DSC analysis was carried out with a Dupont 9000 apparatus under nitrogen (calibration with indium; heating rate 10 °C/min). TGA measurements



**Figure 1.** Plots of the conversion and of  $\ln([M]_0/[M])$  vs time (h) for MMA polymerization in toluene at 85 °C. Conditions:  $[\text{MMA}]_0 = 7.55 \text{ M}$ ,  $[\text{NiBr}_2(\text{PPh}_3)_2]_0 = 9.6 \text{ mM}$ ,  $[\text{2-(EiB)Br}]_0 = 19.2 \text{ mM}$ .



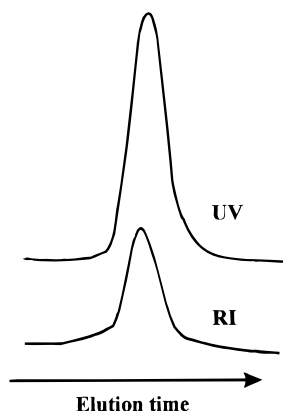
**Figure 2.** Conversion dependence of  $M_n$  and  $M_w/M_n$  for MMA polymerization. Conditions: at 85 °C in toluene,  $[\text{MMA}]_0 = 7.55 \text{ M}$ ,  $[\text{NiBr}_2(\text{PPh}_3)_2]_0 = 9.6 \text{ mM}$ ,  $[\text{2-(EiB)Br}]_0 = 19.2 \text{ mM}$ .

were carried out under nitrogen flow by using a Dupont TGA 51 thermogravimetric analyzer.

### Results and Discussion

**Controlled Polymerization of MMA.** MMA was polymerized at high concentration (7.55 M) in toluene at 85 °C (without any activator as a Lewis acid). 2-Ethylbromoisobutyrate (2-(EiB)Br) was used as an initiator because of a structure quite comparable to the dormant species of PMMA chains (Scheme 2).<sup>16</sup>

The linear time dependence of  $\ln([M]_0/[M])$  (Figure 1) is consistent with a controlled polymerization that is first order in monomer. Although the origin for the short induction period which is observed is not clear yet, it might be related to the formation of the actual initiating species as result of an interaction between the catalyst and the initiator.<sup>17a</sup> An alternative explanation might be found in residual oxygen consistent with a recent report by Matyjaszewski et al.<sup>17b</sup> The dependence of molecular weight and polydispersity on the MMA conversion is illustrated in Figure 2. The linear dependence observed for  $M_n$  is in agreement with a controlled process with a constant number of growing chains.

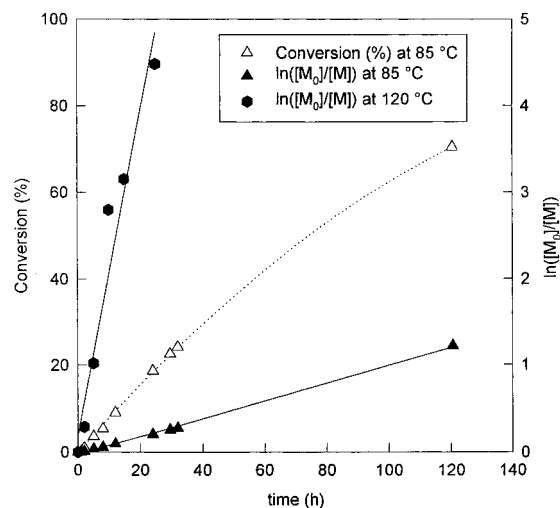


**Figure 3.** Comparison of the SEC chromatograms recorded with UV and RI detectors for PMMA initiated by 2,2'-dichloroacetophenone. Conditions:  $T = 85\text{ }^{\circ}\text{C}$  in toluene,  $[\text{MMA}]_0 = 6.23\text{ M}$ ;  $[\text{NiBr}_2(\text{PPh}_3)_2]_0 = 0.247\text{ M}$ ;  $[\text{2,2'-dichloroacetophenone}]_0 = 0.338\text{ M}$ . Reaction time = 16 h and yield = 85%.

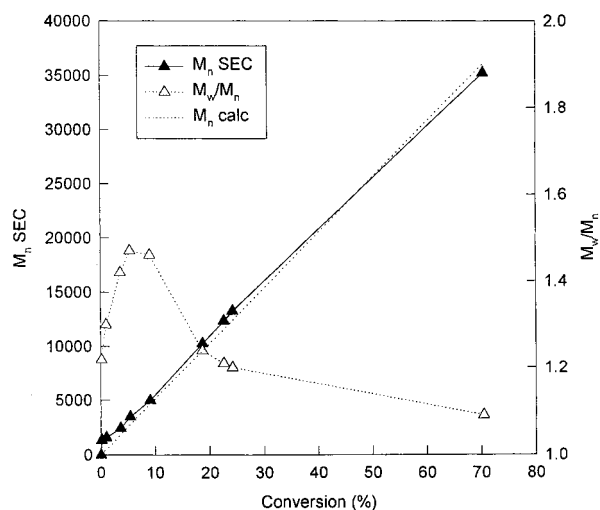
However, a slight broadening of the polydispersity is observed beyond 70% conversion. The dramatic increase of viscosity and final vitrification of the polymerization medium at high conversion are expected to change the rate of exchange between active and dormant species and accordingly increase the polydispersity. From the experimental  $M_n$  (SEC analysis) compared to the calculated one,<sup>18</sup> an initiation efficiency ( $f$ ) of 0.75 ( $f = M_n^{\text{calc}}/M_n^{\text{SEC}}$ ) has been calculated, which is quite similar to the value reported by Sawamoto et al.<sup>14</sup> It may be concluded that increasing the MMA concentration (from 2 to 7.55 M) is a way to preserve the polymerization control although no Lewis acid activator is used anymore.

The PMMA end groups have been analyzed by  $^1\text{H}$  NMR spectroscopy, and the observations are in line with the previous study by Sawamoto et al.<sup>14</sup> Furthermore, comparison of the SEC chromatograms recorded with dual refractive index and UV (at 254 nm) detectors, in the case of an aromatic initiator (i.e., 2,2'-dichloroacetophenone), confirms that the PMMA chains are essentially initiated by the halide compound (Figure 3).  $M_n$  has also been calculated by  $^1\text{H}$  NMR, from the signals typical of the methyl ester groups at 3.59 ppm and the  $\omega$ -ester end group at 3.77 ppm.  $M_n^{\text{NMR}} = 2500$  agrees with  $M_n^{\text{SEC}} = 2900$ , which confirms that the halide compound is the actual initiator and that the halogen is the  $\omega$ -end group.

**Controlled Polymerization of *n*-BuA.** The controlled polymerization of *n*-BuA has been reported in the case of SFRP systems.<sup>6a</sup> However, the TEMPO-mediated systems are such that the polymerization of MMA is out of control and do not allow block copolymers of MMA and *n*-BuA to be synthesized.<sup>19</sup> Radical polymerization catalyzed by organocobalt porphyrin complexes has the same limitations.<sup>20</sup> Interestingly enough, Matyjaszewski et al. have polymerized *n*-BuA in a controlled way according to the so-called degenerative transfer<sup>21</sup> and by ATRP catalyzed by a copper complex.<sup>22</sup> Very recently, Matyjaszewski et al. have reported a detailed study about the polymerization of *n*-BuA with CuBr and bipyridine or dNbipy.<sup>22d</sup> Polymerization is controlled in the case of bulk polymerization catalyzed by substituted bipyridine and when nonsubstituted bipyridine is used in ethylene carbonate, this solvent being beneficial to the polymerization kinetics. Most of the reported poly(*n*-BuA) samples are however of low  $M_n$  (below 5000)



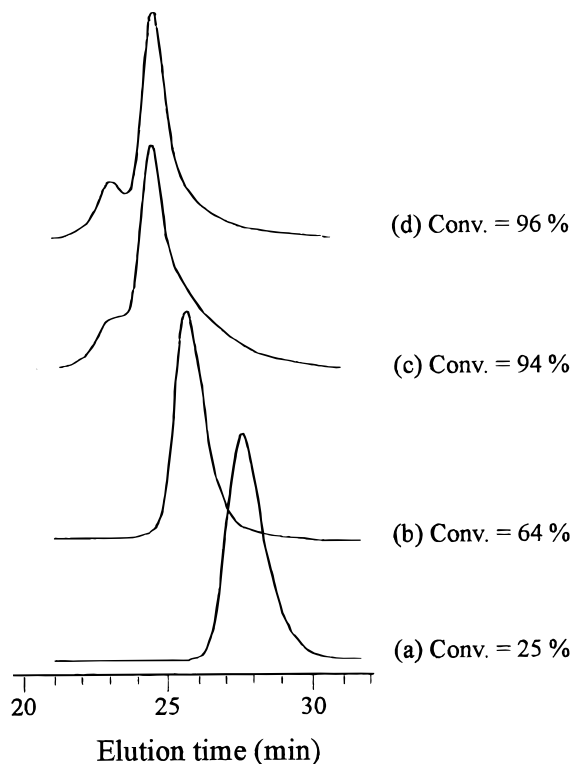
**Figure 4.** Kinetic plots for *n*-BuA polymerization in toluene at 85 and 120  $^{\circ}\text{C}$ . Conditions: (a) at 85  $^{\circ}\text{C}$ ,  $[\textit{n}\text{-BuA}]_0 = 5.94\text{ M}$ ,  $[\text{NiBr}_2(\text{PPh}_3)_2]_0 = 7.37\text{ mM}$ ,  $[\text{2-(EP)Br}]_0 = 14.9\text{ mM}$ ; (b) at 120  $^{\circ}\text{C}$ ,  $[\textit{n}\text{-BuA}]_0 = 6.64\text{ M}$ ,  $[\text{NiBr}_2(\text{PPh}_3)_2]_0 = 22\text{ mM}$ ,  $[\text{2-(EP)Br}]_0 = 22\text{ mM}$ .



**Figure 5.** Conversion dependence of  $M_n$  and  $M_w/M_n$  for *n*-BuA polymerization. Conditions: at 85  $^{\circ}\text{C}$ ,  $[\textit{n}\text{-BuA}]_0 = 5.94\text{ M}$ ,  $[\text{NiBr}_2(\text{PPh}_3)_2]_0 = 7.37\text{ mM}$ ,  $[\text{2-(EP)Br}]_0 = 14.9\text{ mM}$ .

with polydispersity of 1.1 in the case of dNbipy and in the 1.3–1.4 range when nonsubstituted bipyridine is used.

In this work, ethyl 2-bromopropionate has been used as an initiator because of a molecular structure similar to the dormant species (see Scheme 2). Figures 4 and 5 show the time dependence of  $\ln([M]_0/[M])$  and the dependence of both the number-average molecular weight and polydispersity on the *n*-BuA conversion, the polymerization being conducted at 85  $^{\circ}\text{C}$  and high monomer concentration (ca. 6 M). Although the polymerization is slower compared to MMA (Figure 1), the molecular parameters of poly(*n*-BuA), including the chain polydispersity ( $M_w/M_n < 1.2$ ), are very well controlled. A slower kinetics indicates that either the propagation rate constant is smaller or the equilibrium is more displaced toward the dormant species (see Scheme 1). At very high *n*-BuA conversion, a shoulder is observed on the SEC chromatograms on the high MW side, although the polydispersity index remains low. The molecular weight of the chains associated with the new peak is ca. twice as high as the main chains population,



**Figure 6.** Evolution of the SEC chromatograms with conversion for *n*-BuA polymerization at 120 °C. Conditions: at 120 °C in toluene,  $[n\text{-BuA}]_0 = 6.64$  M,  $[\text{NiBr}_2(\text{PPh}_3)_2]_0 = 22$  mM,  $[\text{2-(EP)Br}]_0 = 22$  mM.

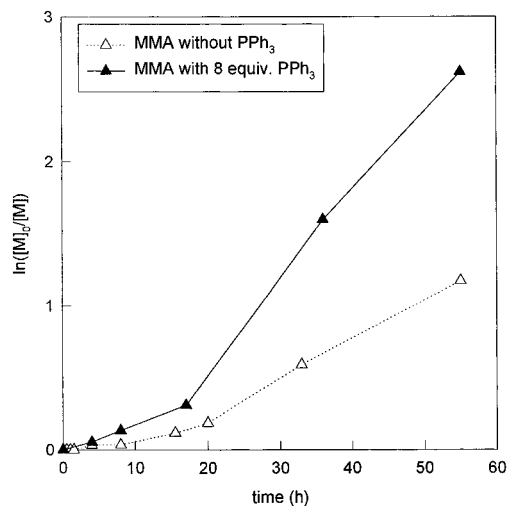
**Table 1. Comparison of  $[\text{P}^*]/[\text{P}_{\text{total}}]$  in the Case of MMA and *n*-BuA Polymerization**

	$k_p^{\text{PLP}} \times 10^{-2}$ $\text{mol}^{-1} \text{L s}^{-1}$	$k_p^{\text{app}} \times 10^5$ $\text{s}^{-1}$	$[\text{P}^*] \times 10^8$ $\text{mol L}^{-1}$	$[\text{P}^*]/[\text{P}_{\text{total}}]$ $\times 10^8$
MMA (85 °C) <sup>a</sup>	13.84	2.038	1.47	102.0
<i>n</i> -BuA (85 °C) <sup>b</sup>	503.42	0.281	0.00557	0.37
<i>n</i> -BuA (120 °C) <sup>c</sup>	840.07	5.564	0.0662	3.01

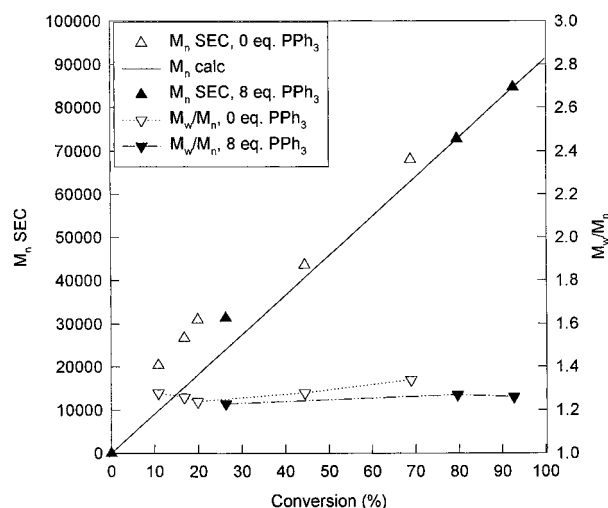
<sup>a</sup>  $[\text{MMA}]_0 = 7.55$  M,  $[\text{NiBr}_2(\text{PPh}_3)_2]_0 = 9.6$  mM,  $[\text{2-(EtB)Br}]_0 = 19.2$  mM. <sup>b</sup>  $[n\text{-BuA}]_0 = 5.94$  M,  $[\text{NiBr}_2(\text{PPh}_3)_2]_0 = 7.37$  mM,  $[\text{2-(EP)Br}]_0 = 14.9$  mM. <sup>c</sup>  $[n\text{-BuA}]_0 = 6.64$  M,  $[\text{NiBr}_2(\text{PPh}_3)_2]_0 = 22$  mM,  $[\text{2-(EP)Br}]_0 = 22$  mM.

which suggests the occurrence of a coupling reaction. These coupling reactions have also been detected by Matyjaszewski et al. for the copper catalyst.<sup>22d</sup> They are also more pronounced when the *n*-BuA polymerization is conducted at higher temperature (120 °C). Although the polymerization remains well-controlled, Figure 6 clearly shows the coupling peak that emerges at high *n*-BuA conversion and increases with time.

**Comparison of the Equilibrium between Active and Dormant Species in MMA and *n*-BuA Polymerization.** The apparent propagation rate constant ( $k_p^{\text{app}} = k_p[\text{P}^*]$ ) can be calculated from the plot of  $\ln([\text{M}]_0/[\text{M}])$  (Figures 1 and 4).  $[\text{P}^*]$ , i.e., the actual concentration of the growing chains, has been extracted from  $k_p^{\text{app}}$  assuming that  $k_p$  measured by the "pulsed laser polymerization" method (for free-radical polymerization) is applicable to controlled radical polymerization.<sup>23</sup> Then, the molar percent of active species (i.e.,  $[\text{P}^*]/[\text{P}_{\text{total}}]$ , where  $[\text{P}_{\text{total}}]$  is the initiator concentration corrected for the initiation efficiency (*f*) has been estimated as reported in Table 1 for polymerization of both MMA and *n*-BuA. The equilibrium is clearly shifted toward the dormant species in the case of *n*-BuA compared to MMA, in qualitative agreement with the



**Figure 7.** Time dependence of  $\ln([\text{M}]_0/[\text{M}])$  for the polymerization of MMA in the presence or not of an excess  $\text{PPh}_3$ . Conditions: at 82 °C in toluene,  $[\text{MMA}]_0 = 7.48$  M,  $[\text{NiBr}_2(\text{PPh}_3)_2]_0 = 4.1$  mM,  $[\text{2-(EtB)Br}]_0 = 8.2$  mM +  $[\text{PPh}_3]_0 = 32.8$  mM for the experience with excess of triphenylphosphine.



**Figure 8.** Effect of  $\text{PPh}_3$  on the MW and polydispersity of PMMA. Conditions:  $T = 82$  °C, solvent toluene,  $[\text{MMA}]_0 = 7.48$  M,  $[\text{NiBr}_2(\text{PPh}_3)_2]_0 = 4.1$  mM,  $[\text{EtBr}]_0 = 8.2$  mM and  $[\text{PPh}_3]_0 = 32.8$  mM for the case with excess of  $\text{PPh}_3$ .

difference in stability for the radicals formed in the two polymerization reactions. The PMMA propagating species is indeed a tertiary radical which is more stable than the secondary radical associated with the growing poly(*n*-BuA) chains.

**Effect of the  $\text{PPh}_3$  Ligand.** Figure 7 illustrates the beneficial effect of an excess of triphenylphosphine on the MMA polymerization kinetics. Furthermore, this excess leads to a linear dependence of  $M_n^{\text{SEC}}$  on the monomer conversion (Figure 8), in contrast to what happens in the absence of  $\text{PPh}_3$ . It is not clear whether these effects are due to substantial modification of the structure of the active catalytic species or to a shift of the equilibrium between the active and the dormant species. Further investigation is required to understand better the role of  $\text{PPh}_3$ , which is usually ignored, e.g., in the classical scheme (Scheme 1) used to discuss the ATRP mechanism. This oversimplified scheme should be completed by a discussion of the occupancy of the coordination sphere of the transition metal not only by the ligand added on purpose but also by molecules liable to coordination, such as monomer and initiator.



**Table 2. Effect of the Catalyst/Initiator Molar Ratio (Conditions:  $T = 75\text{ }^\circ\text{C}$ , Solvent, Toluene)**

entry	$[\text{Ni}]_0/[\text{2-(EiB)Br}]_0$	$[\text{MMA}]_0$	$[\text{MMA}]_0/[\text{2-(EiB)Br}]_0$	time (h)	conv (%)	$M_n(\text{SEC})^a$ (g/mol)	$M_w/M_n$	$f^b$
1	1	6.32	94.6	27	100	12 600	1.23	0.74
2	0.5 <sup>c</sup>	7.55	392.0	30	90	45 300	1.40	0.80
3	0.05	7.42	178.0	120	81	30 700	1.46	0.47

<sup>a</sup> Using PMMA calibration. <sup>b</sup>  $f = M_n^{\text{calc}}/M_n^{\text{SEC}}$ . <sup>c</sup>  $T = 85\text{ }^\circ\text{C}$ .

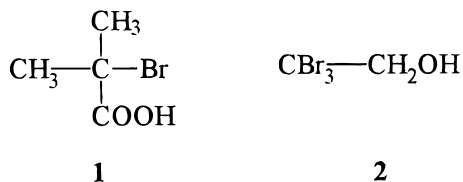
**Table 3. Synthesis of End-Functional PMMA and Poly(*n*-BuA)<sup>a</sup>**

entry	initiator	monomer	$[\text{monomer}]_0/[\text{initiator}]_0$	$T$ ( $^\circ\text{C}$ )	time (h)	conv (%)	$M_n^{\text{calc}}$ (g/mol)	$M_n^{\text{SEC}}$ (g/mol)	$M_w/M_n$
1	1	MMA	38	85	22	95	3 700	5 500	1.30
2	1	MMA	200	75	15	90	19 000	27 000	1.23
3	1	MMA	814	85	32	62	50 000	66 000	1.55
4	2	MMA	30	75	47	95	3 000	2 900	1.32
5	2	MMA	600	75	47	52	31 500	37 000	1.34
6	2	<i>n</i> -BuA	30	85	20	34	1 300	2 200	1.59
7	2	<i>n</i> -BuA	600	85	48	48	48 500	52 500	1.19

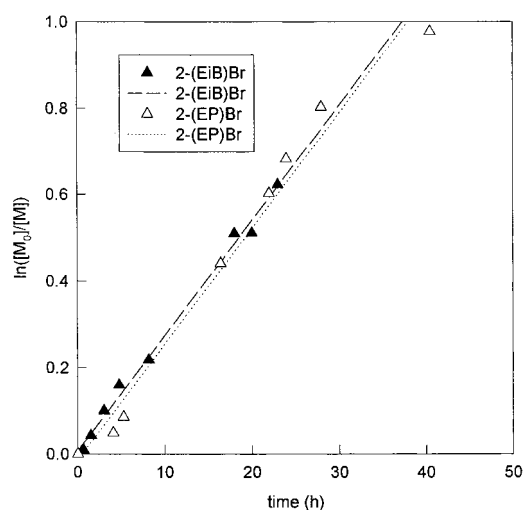
<sup>a</sup> Conditions:  $[\text{catalyst}]_0/[\text{initiator}]_0 = 0.5$ .  $[\text{Monomer}]_0 = 7.0\text{ M}$  for entry 1,  $8.0\text{ M}$  for entry 2,  $6.2\text{ M}$  for entries 3–5, and  $6.9\text{ M}$  for entries 6 and 7.

**Effect of the Catalyst/Initiator Molar Ratio.** The major drawback of ATRP is the large amount of catalyst which is usually required to promote the polymerization control.<sup>24</sup> Additional cost and metal residues in the final polymer may then be limitations for industrial applications. In Table 2, the catalyst/initiator molar ratio has been decreased from 1.0 to 0.05, which results in a slower polymerization, a larger polydispersity, and a smaller initiation efficiency. The decrease in  $f$  might be attributed to more frequent termination reactions during the early stage of the polymerization, thus before the persistent radical effect is effective and allows for the self-regulation of the radical polymerization.<sup>25</sup>

**End Functionalization of Polymers.** One of the main advantages of a controlled polymerization is the possibility to attach functional groups to the chain extremities. Carboxylic acid and alcohol are highly desirable end groups in the synthesis of  $\alpha(\omega)$ - and  $\omega,\omega$ -functional polymers. The use of a functional initiator is a straightforward way to  $\alpha$ -functional chains.<sup>26</sup> In this study, 2-bromo-2-methylpropionic acid (**1**) has been used as an initiator, with the purpose of synthesizing  $\alpha$ -carboxylic acid PMMA or poly(*n*-BuA). Similarly  $\alpha$ -hydroxyl PMMA or poly(*n*-BuA) should result from initiation by 2,2',2''-tribromoethanol (**2**). Results of the end functionalization of PMMA and poly(*n*-BuA) are listed in Table 3. The polymerization temperature being low ( $75\text{--}85\text{ }^\circ\text{C}$ ) the thermal initiation is negligible, so that a quasi-quantitative functionalization of the polymer may be expected, in contrast to the TEMPO-mediated polymerization which is usually perturbed by thermally induced polymerization.



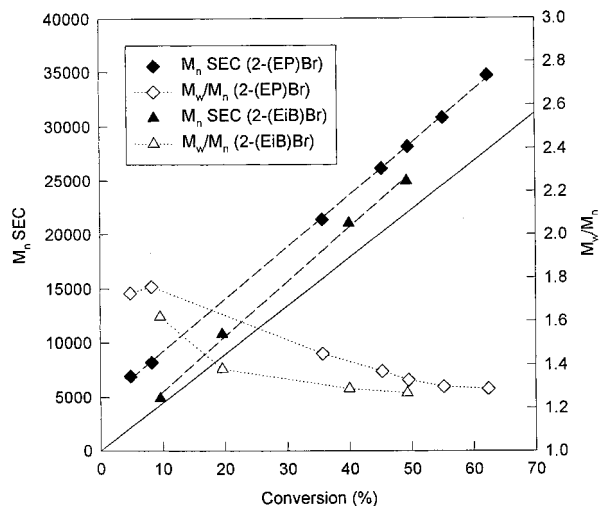
$M_n$  of  $\alpha$ -carboxylic acid PMMA has been measured by titration of the acid end groups by tetramethylammonium hydroxide (TMAH) in a 90/10 (v/v) toluene/MeOH mixture. A good agreement between  $M_n(\text{titration}) = 5200 \pm 6\%$  and  $M_n(\text{SEC}) = 5500$  is observed. It must be noted that the  $\alpha$ -hydroxyl polymers have been successfully used as macroinitiators for the ring-opening polymerization of  $\epsilon$ -caprolactone as reported elsewhere.<sup>27</sup>



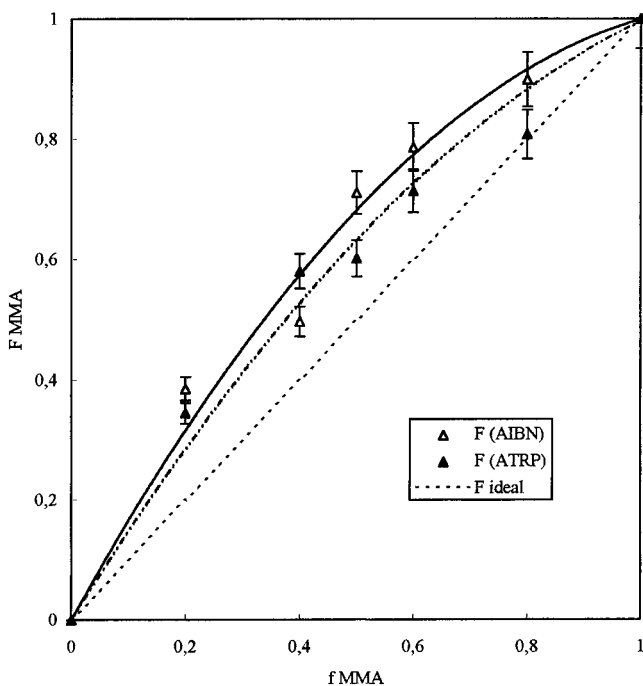
**Figure 9.** Time dependence of  $\ln([\text{M}]_0/[\text{M}])$  for the random copolymerization of MMA and *n*-BuA (50/50) initiated by 2-(EiB)Br or 2-(EP)Br at  $85\text{ }^\circ\text{C}$ . Conditions: at  $85\text{ }^\circ\text{C}$  in toluene:  $[\text{MMA}]_0 = 2.99\text{ M}$ ;  $[\textit{n}\text{-BuA}]_0 = 3.00\text{ M}$ ;  $[\text{2-(EiB)Br}]_0$  or  $[\text{2-(EP)Br}]_0 = 15.33\text{ mM}$ .

**Random Copolymerization and Reactivity Ratios.** The random copolymerization of MMA and *n*-BuA has been initiated by ethyl 2-bromoisobutyrate (2-(EiB)Br) and ethyl 2-bromopropionate (2-(EP)Br) and catalyzed by  $\text{NiBr}_2(\text{PPh}_3)_2$ . Figures 9 and 10 show the time dependence of  $\ln([\text{M}]_0/[\text{M}])$  and the dependence of  $M_n$  and polydispersity on the comonomer conversion. The experimental results are quite comparable for the two initiators, the initiation efficiency being slightly smaller for 2-(EP)Br compared to 2-(EiB)Br. Whatever the initiator, the polydispersity is narrow, and the molar ratio of MMA units incorporated into the copolymer (determined by  $^1\text{H NMR}$  analysis for  $0\% < \text{conversion} < 60\%$ ) is in the range of 65 mol %, the comonomer feed composition being 50 mol %.

Random copolymerization initiated by 2-(EiB)Br for different MMA and *n*-BuA molar ratios has been carried out with the purpose of determining the reactivity ratios. Parallel experiments have been conducted with 2,2'-azobis(isobutyronitrile) (AIBN) as initiator. Figure 11 shows the dependence of the molar fraction of MMA in the copolymer ( $F_{\text{MMA}}$ ) on the initial molar composition of the comonomer feed ( $f_{\text{MMA}}$ ). The reactivity ratios,  $r_{\text{MMA}}$  and  $r_{\textit{n}\text{-BuA}}$ , have been determined by using the error



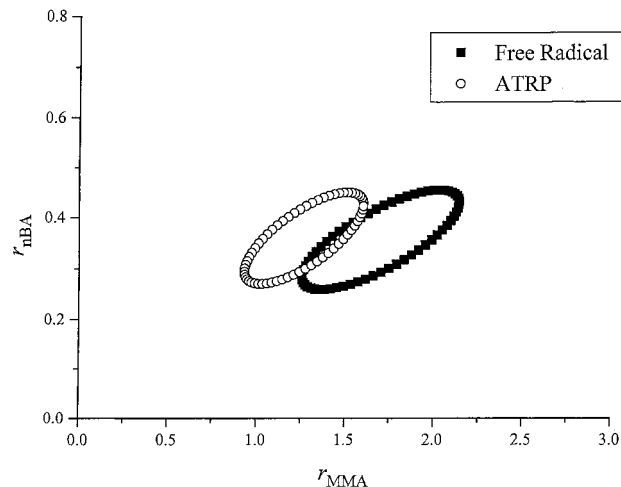
**Figure 10.** Conversion dependence of  $M_n$  and  $M_w/M_n$  for the copolymerization of MMA and *n*-BuA initiated by 2-(EiB)Br or 2-(EP)Br at 85 °C. Conditions: at 85 °C in toluene:  $[MMA]_0 = 2.99$  M;  $[n\text{-BuA}]_0 = 3.00$  M;  $[2\text{-(EiB)Br}]_0$  or  $[2\text{-(EP)Br}]_0 = 15.33$  mM.



**Figure 11.** Dependence of the copolymer composition ( $F$ ) on the comonomer feed composition ( $f$ ). Conversions are  $<5\%$ , and  $F$  is determined by  $^1\text{H}$  NMR.

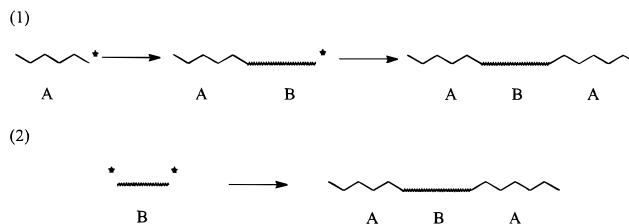
variable model (EVM),<sup>28</sup> and Figure 12 shows the 95% confidence contours for  $r_{\text{MMA}}$  and  $r_{n\text{-BuA}}$ . Although the contours for free-radical polymerization (FRP) and for ATRP do not coincide, their partial superposition strongly suggests that radicals are the actual growing species in ATRP. The difference observed in the reactivity ratios might indicate either some interaction between the metal and the growing species or the equilibrium between the dormant and the active species which is different for MMA and *n*-BuA at the same polymerization temperature. Would it be so, the propagating active species associated with one comonomer would be, for example, active for a longer period of time, so changing the reactivity ratios.

**Difunctional Initiation of *n*-BuA Polymerization.** Scheme 3 summarizes the two main routes for the

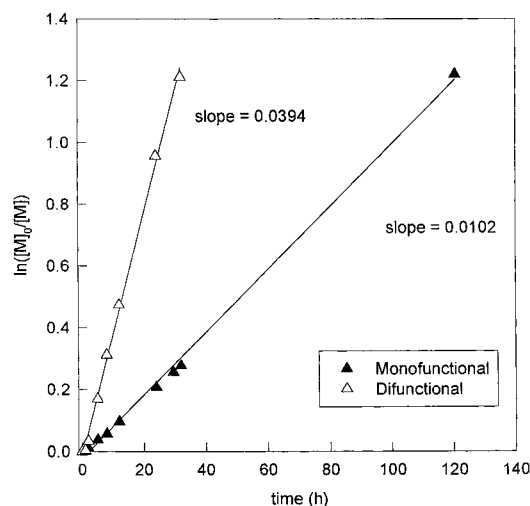


**Figure 12.** Determination of the MMA/*n*-BuA reactivity ratios by the EVM method for free radical polymerization and ATRP catalyzed by  $\text{NiBr}_2(\text{PPh}_3)_2$ .

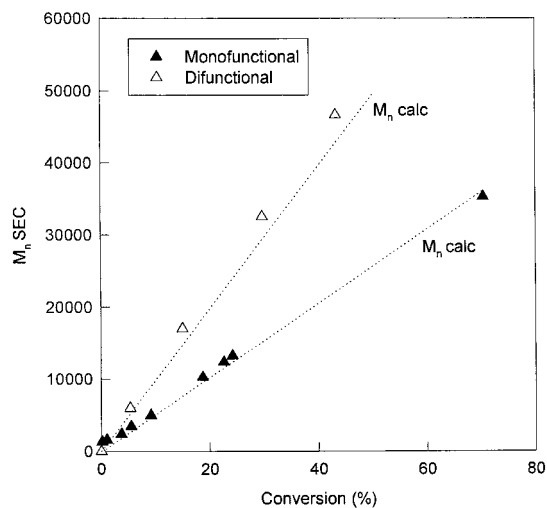
### Scheme 3



synthesis of symmetric A–B–A triblock copolymers. The first strategy consists of a three-step copolymerization, i.e., the sequential polymerization of the A and B comonomers, followed by either polymerization of A or addition of a difunctional coupling agent. As an alternative, a difunctional initiator could be used to sequentially copolymerize B and A, in a two-step process. The advantage of chains growing from each extremity is that they remain living and difunctional even in the case of side coupling reactions. Since ethyl 2-bromopropionate has proved to be an efficient monofunctional initiator for the polymerization of *n*-BuA, diethyl *meso*-2,5-dibromoadipate (Scheme 2) has been used as a difunctional initiator for the polymerization of *n*-BuA. The polymerization proved to be well controlled, except for some side reactions observed at high monomer conversions. The polydispersity index of the final polymer (when coupling reactions are not significant) is very low ( $M_w/M_n \sim 1.1$ ). Figure 13 compares the plot of  $\ln([M]_0/[M])$  vs time for the *n*-BuA polymerization initiated by the monobromo and dibromo derivative, while keeping the monomer/initiator and catalyst/Br molar ratios comparable.  $k_p^{\text{app}}$  is approximately 4 times higher in the case of the difunctional initiator, which may be explained as follows. The monomer/initiator molar ratio being the same for the two initiators, the content of alkyl bromide (the actual initiating species) is thus 2 times higher when the initiator is difunctional rather than monofunctional. Since the catalyst/Br molar ratio is also the same, 2 times more catalyst has been used in the case of the difunctional initiator. So,  $k_p^{\text{app}}$  for the polymerization initiated by the dibromo derivative has to be 4 times as high as  $k_{\text{app}}$  in the case of the monofunctional initiator, consistent with the first kinetic order in the alkyl halide initiator and in the catalyst, similar to the Cu(I)/Cu(II) system.<sup>11e</sup> This

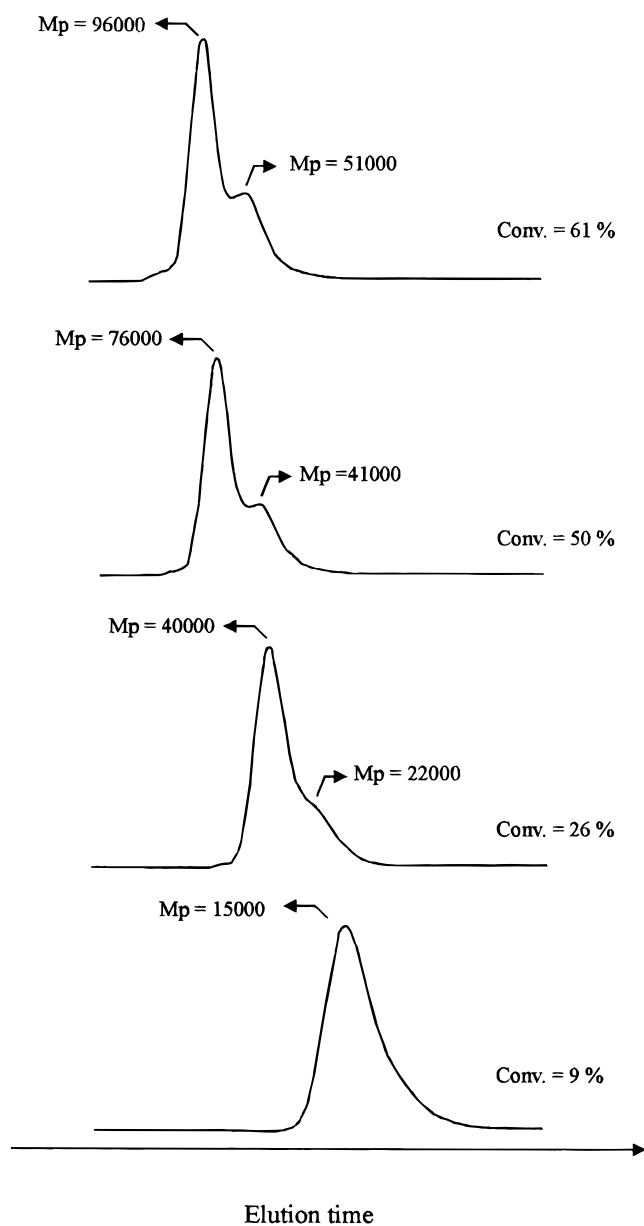


**Figure 13.** Comparative plots of  $\ln([M]_0/[M])$  vs time for the polymerization of *n*-BuA initiated by a monofunctional or a difunctional initiator. Conditions:  $T = 85^\circ\text{C}$  in toluene. (a) Monofunctional:  $[n\text{-BuA}]_0 = 5.94\text{ M}$ ,  $[\text{NiBr}_2(\text{PPh}_3)_2]_0 = 7.37\text{ mM}$ ,  $[2\text{-(EP)Br}]_0 = 14.9\text{ mM}$ . (b) Difunctional initiator:  $[n\text{-BuA}]_0 = 6.34\text{ M}$ ,  $[\text{NiBr}_2(\text{PPh}_3)_2]_0 = 13.5\text{ mM}$ ,  $[\text{diethyl } meso\text{-}2,5\text{-dibromoadipate}]_0 = 14\text{ mM}$ .



**Figure 14.** Dependence of  $M_n$  SEC on the *n*-BuA conversion for monofunctional and difunctional initiators. Conditions:  $T = 85^\circ\text{C}$  in toluene. (a) Monofunctional:  $[n\text{-BuA}]_0 = 5.94\text{ M}$ ,  $[\text{NiBr}_2(\text{PPh}_3)_2]_0 = 7.37\text{ mM}$ ,  $[2\text{-(EP)Br}]_0 = 14.9\text{ mM}$ . (b) Difunctional:  $[n\text{-BuA}]_0 = 6.96\text{ M}$ ,  $[\text{NiBr}_2(\text{PPh}_3)_2]_0 = 8.65\text{ mM}$ ,  $[\text{diethyl } meso\text{-}2,5\text{-dibromoadipate}]_0 = 9.04\text{ mM}$ .

observation might indicate that the Ni(III) concentration is the same although the Ni(II) concentration is different. A deeper analysis of the dependence of the Ni(III) on the initial Ni(II) is however required before drawing a reliable conclusion. Figure 14 shows how  $M_n$  increases with the monomer conversion for both the monofunctional and the difunctional initiators, when the monomer/Br molar ratio is kept constant. The initiation efficiency is close to unity for the two initiators. As additional evidence for the difunctional initiation by the dihalide, *n*-BuA polymerization has been initiated by an equimolar mixture of monohalide and dihalide. Indeed, the SEC chromatograms show two elution peaks that are as better resolved as the monomer conversion is high (Figure 15). Molecular weights at the peak maxima are approximately in a 2/1 ratio. Therefore, combination of diethyl *meso*-2,5-dibromoadipate with  $\text{NiBr}_2(\text{PPh}_3)_2$  allows for the controlled synthesis of difunctional poly(*n*-

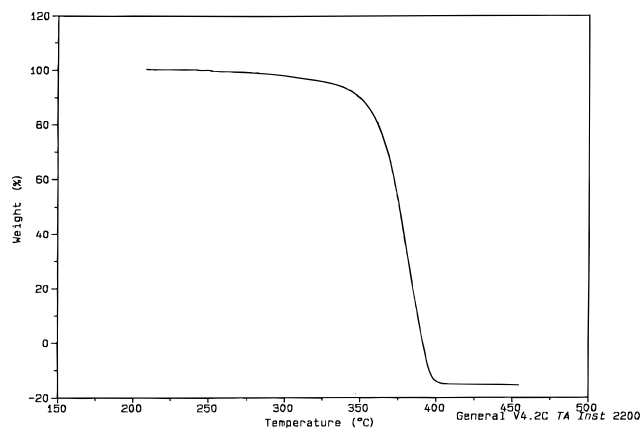


**Figure 15.** Dependence of the SEC chromatograms on the *n*-BuA conversion, in the case of ATRP initiated by an equimolar mixture of mono- and difunctional initiators. Conditions: at  $85^\circ\text{C}$  in toluene:  $[n\text{-BuA}]_0 = 6.59\text{ M}$ ,  $[\text{NiBr}_2(\text{PPh}_3)_2]_0 = 8.2\text{ mM}$ ,  $[2\text{-(EP)Br}]_0 = 5.5\text{ mM}$ ,  $[\text{diethyl } meso\text{-}2,5\text{-dibromoadipate}]_0 = 5.5\text{ mM}$ .

BuA) of at least 100 000 molecular weight with a narrow MWD ( $M_w/M_n < 1.2$ ).

These difunctional polymers can be used as macro-initiators for the "controlled" polymerization of MMA leading to the formation of poly(methyl methacrylate)-*b*-poly(*n*-butyl acrylate)-*b*-poly(methyl methacrylate) copolymers which are potential thermoplastic elastomers. Synthesis and properties of these triblocks will be the topic of a forthcoming paper.

**Thermal Stability of PMMA.** No information on the thermal properties of PMMA synthesized by ATRP has been reported until now. DSC analysis of PMMA prepared by 2-(EiB)Br in combination with  $\text{NiBr}_2(\text{PPh}_3)_2$  shows a  $T_g$  at  $125^\circ\text{C}$ , compared to  $115^\circ\text{C}$  for PMMA synthesized by traditional free-radical polymerization.<sup>29</sup> This difference in  $T_g$  should be compared to the polymer tacticity which is however comparable since rr:rm:mm



**Figure 16.** TGA analysis of a PMMA synthesized by  $\text{NiBr}_2\text{-(PPh}_3)_2\text{-}2\text{-(EtI)Br}$  system at 75 °C. Conditions: the PMMA sample ( $M_n = 39\,000$ ,  $M_w/M_n = 1.26$ ) was precipitated from heptane. TGA was performed under nitrogen flow at a heating rate of 10 °C/min.

= 61:32:7 for the PMMA synthesized with the Ni catalyst at 75 °C and 56:38:6 in case of initiation by AIBN at the same temperature (PMMA<sub>ATRP</sub>:  $M_n = 39\,000$  and  $M_w/M_n = 1.26$ ; PMMA<sub>AIBN</sub>:  $M_n = 130\,000$  and  $M_w/M_n = 2.2$ ). The fraction of low molecular weight chains in PMMA synthesized by FRP might have a plasticization effect and account for a lower  $T_g$ .

The thermal stability of PMMA synthesized by controlled radical polymerization has been analyzed by TGA by Granel et al.,<sup>12b</sup> Müllen et al.,<sup>30a</sup> and Colombani et al.<sup>30b</sup> in the case of ATRP catalyzed by  $\text{Ni}(\text{NCN})\text{Br}$  and when tetrathiofulvalene (TTF) and 1,3,5,5-tetraphenyl- $\Delta^3$ -1,2,4-triazonyl-2-yl were used as "counter-radical", respectively. Compared to PMMA synthesized by conventional free-radical polymerization, a better thermal stability was observed by Granel et al. and by Müllen et al., whereas the reverse observation was reported by Colombani et al.

The absence of degradation until 300 °C (Figure 16) indicates that the coupling and disproportionation reactions which are usually responsible for degradation at 160 and 270 °C, respectively,<sup>31</sup> have a minor role if any. Thermal degradation actually occurs at ca. 360 °C, as result of random chain scissions. Furthermore, when PMMA prepared by ATRP is heated at 250 °C for 6 h,<sup>32</sup> the isothermal TGA shows a very limited weight loss (<5 wt %), and SEC analysis emphasizes only a slight broadening of the polydispersity (from 1.3 to 1.4). The remarkable thermal stability of PMMA is an indirect confirmation of the living/controlled character of the ATRP of MMA catalyzed by  $\text{NiBr}_2(\text{PPh}_3)_2$ .

## Conclusion

Control of radical polymerization usually relies upon an equilibrium between active and dormant species, which has the characteristic feature of decreasing the instantaneous concentration of free radicals and thus the relative extent of bimolecular termination reactions compared to the propagation step. At very low concentration of the active species, the overall polymerization rate may become small enough for side reactions to occur at the expense of the polymerization control. A way to increase the polymerization rate while keeping the actual radical concentration low is to increase the monomer concentration. The efficiency of this strategy has been confirmed in this study and thus for the ATRP of MMA and *n*-BuA catalyzed by  $\text{NiBr}_2(\text{PPh}_3)_2$ . The

beneficial effect is such that no activator, e.g., a Lewis acid, is required anymore.

The reactivity ratios of MMA and *n*-BuA have been determined and are close to the values found for the free-radical copolymerization at the same temperature. A difference in the equilibrium constant between active and dormant species for the two monomers might be an explanation for the slight deviation observed. It could also result from some interaction between the radicals and the metal complex during propagation. The catalyst/initiator molar ratio can be decreased down to 0.05, although the polymerization rate and the initiation efficiency become smaller and the MWD broader. PMMA and poly(*n*-BuA) end-capped by a carboxylic acid and a hydroxyl group have been successfully synthesized and  $\alpha,\omega$ -bromo-poly(*n*-BuA) as well. An excess of  $\text{PPh}_3$  accelerates the MMA polymerization which remains controlled. Finally, the high thermal stability of PMMA synthesized by ATRP with the  $\text{NiBr}_2(\text{PPh}_3)_2$  catalyst confirms the lack of vinylidene end groups. Polymerizability of other (meth)acrylic monomers and synthesis and properties of poly(MMA)-*b*-poly(*n*-BuA)-*b*-poly(MMA) copolymers are currently investigated.

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