

On the Polymerization of Alkyl Methacrylates with the Achiral Dimethylzirconocene Precursor Cp_2ZrMe_2

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ABSTRACT: Polymerization of methyl methacrylate (MMA) by the three component catalytic system $\text{Cp}_2\text{ZrMe}_2/\text{B}(\text{C}_6\text{F}_5)_3/\text{ZnEt}_2$ (**1**), in toluene, under thoroughly purified conditions, was found to produce polymers of high molecular weights ($M_w > 60 \times 10^3$), low polydispersities ($M_w/M_n = 1.12\text{--}1.22$) and almost quantitative yields. The polymerization process is characterized by a pronounced induction period followed by a rapid and constant rate of polymerization. The molecular weight of PMMA increases by increasing the conversion and is proportional to the ratio of $[\text{MMA}]_0/[\text{Zr}]_0$, while M_w/M_n remains intact, meaning that the present polymerization proceeds in a well-controlled fashion. Evidence for effects of $[\text{ZnEt}_2]$ and temperature in the molecular characteristics of the final products are also presented in this study. Moreover, the catalytic system **1** was found to catalyze the polymerization of other alkyl methacrylates (alkyl = *n*-butyl, *n*-hexyl) to high molecular weight syndiotactic materials, with narrow molecular weight distribution, in very high conversion. Well-controlled copolymerization of MMA with *n*-hexyl methacrylate was successful by the effective catalytic action of **1**, leading to multiblock polymeric structures. Copolymerization of MMA with stearyl methacrylate was also achieved, with the above-mentioned catalytic system. Evidence for the aggregation of the polymeric products in THF and toluene solutions was found by static and dynamic light scattering. The comparison of the polymerization results of this work with other studies clearly shows that in order to obtain improved molecular characteristics, thorough purification protocols should be applied.

Introduction

Recently, the group 4A metallocenes have attracted the interest of several research groups. In the presence of methylaluminoxane (MAO) or fluoroarylborates (i.e., $\text{B}(\text{C}_6\text{F}_5)_3$) they give well-defined, single-site catalytic systems for the polymerization of hydrocarbon olefins.^{1–5} Despite the oxophilicity of tetravalent group 4 metal centers and the cationic nature of the propagating species, these compounds are effective catalysts for the polymerization of polar monomers, such as methyl methacrylate.⁶

The first efficient polymerization (monomer conversion approaching 100%) of methyl methacrylate (MMA) with metallocene catalysts was reported by Collins et al. in 1992.⁷ The combination of the neutral Cp_2ZrMe_2 with the cationic zirconocene $\text{Cp}_2\text{ZrMe}(\text{THF})^+\text{BPh}_4^-$ afforded a syndio-rich poly(methyl methacrylate) (PMMA) (ca. 80% r diads) with rather high molecular weights ($M_w = 50\text{--}200\text{K}$) and narrow molecular weight distribution ($I: M_w/M_n = 1.2\text{--}1.4$), at or below room temperature. Recently, the same group has suggested a bimetallic polymerization mechanism via neutral zirconocene enolate species.⁸

Later, Soga and co-workers carried out the polymerization of MMA by using a different protocol. The MMA monomer was preaged with ZnEt_2 before the addition of dimethylzirconocenes. The catalyst was combined with a stoichiometric amount of a boron containing cocatalyst such as $\text{B}(\text{C}_6\text{F}_5)_3$ or $\text{Ph}_3\text{C}^+\text{B}(\text{C}_6\text{F}_5)_4^-$.^{9a–9e} The polymers prepared possessed high molecular weights ($M_n = 200\text{--}600\text{K}$) and rather narrow molecular weight distributions ($M_w/M_n = 1.25\text{--}1.85$). The polymerization duration was 24 h, and the monomer conversion ($\leq 60\%$) was lower compared with that observed in Collins work. Finally, the dialkylzinc compound has been claimed to

have a double role, first as an internal scavenger and second as an activator in the initiation step.

More recently, Cameron and collaborators reported the polymerization of MMA using the same catalytic system with Soga's group but without adding ZnEt_2 .¹⁰ The polymer produced had narrow molecular weight distribution ($I = 1.2\text{--}1.6$) but the molecular weights were lower ($M_w \approx 50\text{K}$), than those given by Soga, due to the much higher catalyst concentrations that were used. Cameron also tried to clarify the role of ZnEt_2 . It was suggested that this Lewis acid protects the boron compound from being poisoned by the carbonyl oxygen of the monomer.

Related work on lanthanocenes has been reported by Yasuda and co-workers,^{11a–c} at about the same time as Collins. Very narrow molecular weight distributions ($I < 1.05$) have been achieved using initiators such as $[\text{Cp}^*_2\text{SmH}]_2$ or $[\text{Cp}^*_2\text{LnMe}(\text{THF})]$ [$\text{Ln} = \text{Sm}, \text{Yb}, \text{or Lu}$]. The polymerization was quantitative producing highly syndiotactic poly(MMA) (up to 90% r diads, increasing with the decrease of temperature) with high molecular weights ($M_n > 100\text{K}$). The polymerization seems to be promoted in a "living" way since the M_n is proportional to the yield and the molecular weight distribution is very narrow. In this case, the presence of a Lewis acid was not necessary, since the organosamarium center can serve as initiator (insertion) and catalyst (monomer activation) simultaneously.

To gain additional insight into the polymerization of methyl methacrylate by zirconocenes and moreover to study the degree of control that this polymerization procedure tolerates, it was decided to investigate the zirconocene-initiated polymerization of alkyl methacrylates. One of the objectives of the present work was to record the evolution of the polymerization procedure with time for the catalytic system $\text{Cp}_2\text{ZrMe}_2/\text{B}(\text{C}_6\text{F}_5)_3/$

ZnEt₂ (**1**). Furthermore, the homopolymerization of other methacrylates and their copolymerization with MMA were also investigated.

Experimental Section

Materials. All manipulations were performed using high vacuum and/or Schlenk techniques. Cp₂ZrMe₂ was purchased from Aldrich or synthesized according to the literature.¹² [NEt₃H⁺][BPh₄⁻] and [N(*n*-Butyl)₃H⁺][BPh₄⁻] were synthesized according to the procedure of Witting et al.¹³ Tris(pentafluorophenyl)borane (B(C₆F₅)₃) was prepared according to literature procedures.¹⁴ Diethyl zinc (ZnEt₂, 97%) was purchased from Fluka. Dichloromethane (CH₂Cl₂, Aldrich) was dried and distilled from calcium hydride (CaH₂) or P₂O₅, under a slow continuous stream of nitrogen. Toluene (Aldrich) was dried and vacuum distilled from calcium hydride (CaH₂) and metallic sodium, subsequently. Methyl methacrylate (MMA, Merck), *n*-butyl methacrylate (*n*-BuMA, Polylab), *tert*-butyl methacrylate (*t*-BuMA, Polylab) and *n*-hexyl methacrylate (HMA, Polylab) were vacuum distilled from calcium hydride and triethyl aluminum (AlEt₃) or trioctyl aluminum (Al(octyl)₃). Stearyl methacrylate (SMA, Merck) was recrystallized three times in dry hexane at -20 °C and then dried in high vacuum at room temperature.

Polymerization Procedure. Polymerization of Alkyl Methacrylates with the Catalytic System Cp₂ZrMe₂/B(C₆F₅)₃/ZnEt₂ (1**).** The polymerization procedure was carried out at 0 °C in a 0.5 dm³ Schlenk type reaction flask. A typical polymerization process is as follows: in the reaction flask, toluene (30 mL) and MMA (5 mL, 47 mmol) were added. The mixture was stirred in an 2-propanol bath, which was kept at 0 °C. Then ZnEt₂ (97%, 1.2 mL, 12 mmol) was injected, and the reaction mixture was left under stirring at this reduced temperature for 1 h. After the aging period, 3.0 mL of a metallocene Cp₂ZrMe₂ solution in toluene (26.6 mM) and finally 3.3 mL of a cocatalyst B(C₆F₅)₃ solution in toluene (26.6 mM) were introduced to initiate the polymerization. The polymerization was quenched after 24 h by addition of HCl/methanol solution and the polymer was precipitated in methanol. The polymer produced was washed with methanol, filtered, and dried in a high vacuum at room temperature.

The polymers were further purified by ultracentrifugation and passage through columns of silica to remove inorganic compounds (zinc oxides, catalyst, etc.).

Polymerization of MMA with the Catalytic Systems Cp₂ZrMe₂/[NEt₃H⁺][BPh₄⁻] (2A**) and Cp₂ZrMe₂/[N(*n*-Butyl)₃H⁺][BPh₄⁻] (**2B**).** The polymerization procedure was carried out at 0 °C in a 0.5 dm³ Schlenk type reaction flask. A typical polymerization process is as follows: in the reaction flask, CH₂Cl₂ (30 mL) was added, followed by the addition of the appropriate amount of catalyst, Cp₂ZrMe₂ (3.0 mL of a 26.6 mM solution in CH₂Cl₂) and cocatalyst, [NEt₃H⁺][BPh₄⁻] or [N(*n*-Butyl)₃H⁺][BPh₄⁻] (3.3 mL of a 26.6 mM solution in CH₂Cl₂). Finally, the monomer (MMA) was added (5 mL, 47 mmol), and the polymerization was quenched after 24 h by addition of HCl/methanol solution and the polymer was precipitated in methanol. The polymer produced was washed with methanol, filtered, and dried in high vacuum at room temperature.

Kinetic Experiments. The kinetic experiments were carried out following two different protocols. According to the first, appropriate samples were taken from the reaction mixture via syringe utilizing standard Schlenk techniques, at specific periods of time. The aliquots were quenched immediately in the appropriate amount of MeOH/HCl. The precipitated polymer was filtered, rinsed with methanol, and dried in a high vacuum until constant weight. In the second protocol, independent experiments were conducted under the same conditions. Termination of the polymerization reaction took place at the determined time followed by precipitation, filtration, rinsing, and drying of the resulting polymer.

Both protocols were utilized in order to record the polymerization time evolution (experiment series **A** and **B**). The experimental results of the above-mentioned protocols did not show any significant differentiation, in all cases.

Characterization Techniques. Size exclusion chromatography (SEC) experiments were carried out using a modular instrument consisting of a Waters model 510 pump, a Waters model U6K sample injector, a Waters model 401 differential refractometer, and a set of four μ -Styragel columns with a continuous porosity range from 10⁶ to 10³ Å. The columns were housed in an oven thermostated at 40 °C. THF was the carrier solvent at a flow rate of 1 mL/min. The instrument was calibrated with PMMA standards.

Static light scattering measurements were performed in THF or dimethylformamide (DMF). THF was refluxed over Na metal, whereas DMF was stirred overnight over anhydrous MgSO₄ and refluxed over KOH. Both solvents were distilled just prior their use. A Chromatix KMX-6 low angle laser light scattering (LALLS) photometer at 25 °C equipped with a 2 mW He-Ne laser operating at λ = 633 nm was used. Stock solutions were prepared, followed by dilution with solvent to obtain solutions with lower concentrations. All the solutions were optically clarified by filtering through 0.22 or 0.45 μ m pore size nylon filters directly into the scattering cell.

Dynamic light scattering measurements were performed in THF and toluene. The purification procedure for THF was described above. Toluene was refluxed over CaH₂ and then distilled just prior its use. The measurements were conducted with a series 4700 Malvern system composed of a PCS5101 goniometer with a PCS stepper motor controller, a Cyonics variable power Ar⁺ laser operating at 488 nm, a PCS8 temperature control unit, a RR98 pump/filtering unit, and a 192-channel correlator for the accumulation of the data. The correlation functions were analyzed by the cumulant method and the CONTIN software.

The measurements of the refractive index increments (dn/dc) were performed in THF at 25 °C. A Chromatix KMX-16 refractometer operating at 633 nm and calibrated with aqueous NaCl solutions, was used.

Polymer composition and tacticities were determined from ¹H NMR and ¹³C NMR spectra, which were recorded in chloroform-*d* at 30 °C with a Varian Unity Plus 300/54 NMR spectrometer. The tacticity of poly methacrylates was calculated using the signals of the methyl and carbonyl groups of the ¹³C NMR spectrum.

Polymers melting points (T_m) and glass transition (T_g) temperatures were obtained by differential scanning calorimetry (DSC) using a 2910 modulated DSC model from TA Instruments. The samples were heated or cooled at a rate of 10 °C/min.

Results and Discussion

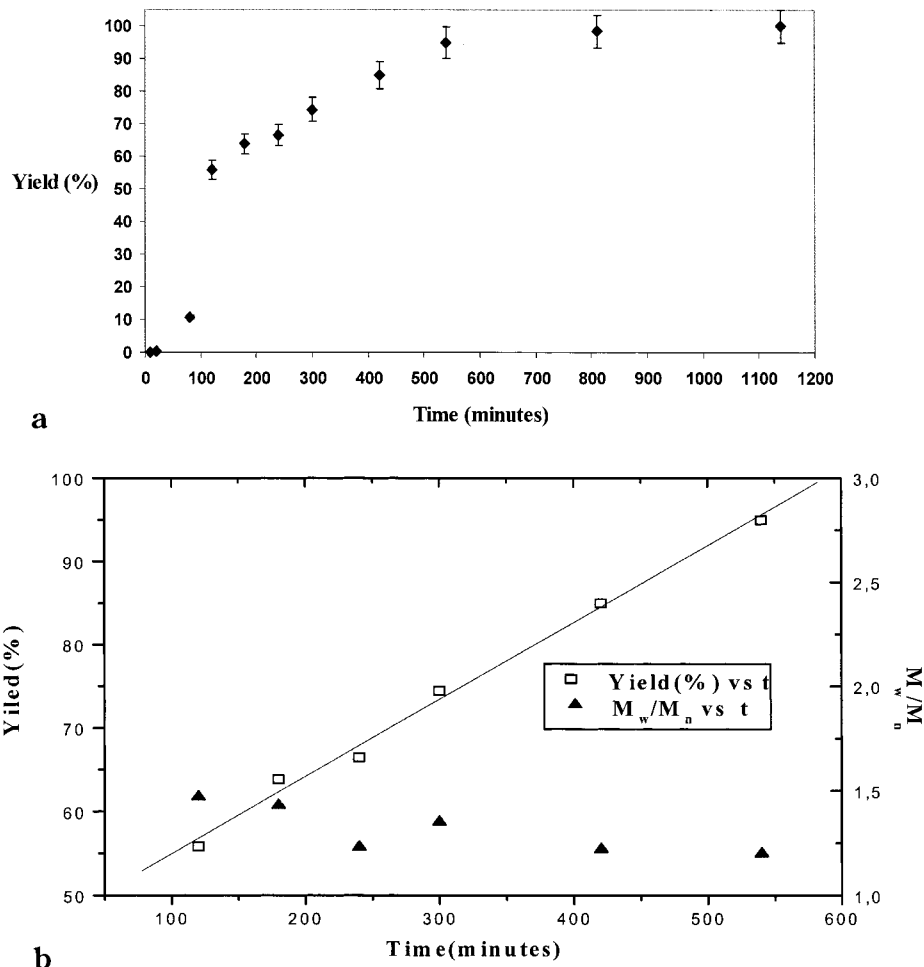
Polymerization Studies. The present work is focused on the behavior of catalytic systems based on the achiral metallocene precatalyst Cp₂ZrMe₂ toward MMA and other alkyl methacrylates. Initially, the catalytic systems Cp₂ZrMe₂/[NEt₃H⁺][BPh₄⁻] (**2A**) and Cp₂ZrMe₂/[N(*n*-Butyl)₃H⁺][BPh₄⁻] (**2B**), were studied (entries 1 and 2, respectively, in Table 1). Unfortunately, the efforts to polymerize MMA utilizing the catalytic system **2A** proved unsuccessful, resulting only in traces of polymeric product (PMMA). On the other hand polymerization experiments based on the catalytic system **2B** led to PMMA with reasonably narrow molecular polydispersity, but in very small yield (<10%). These results are probably due to the presence of the noninnocent tetraphenylborate counteranion (BPh₄⁻) and/or the Et₃N or (*n*-Butyl)₃N byproducts binding to the active site.¹⁰

Experiments have been conducted to thoroughly investigate the polymerization procedure of MMA in the presence of the catalytic system **1**. Two sets of kinetics experiments were conducted using different concentration ranges for the catalytic system. The first set of experiments utilized rather low concentrations (representative values for experiment series **A**: [Zr]₀ = [B(C₆F₅)₃] = 0.400–0.700 mM, [MMA] = 500–700 mM,

Table 1. Representative Experimental Results for the Polymerization of Alkyl Methacrylates with Catalytic Precursor $\text{Cp}_2\text{ZrMe}_2^a$

run	cocatalyst	activator	monomer	[Zr] ^b (mM)	[B] ^c (mM)	[monomer] (M)	T _p (°C)	yield (%)	M _n ^h (× 10 ³)	M _w /M _n ^g	M _{n,theor} ^h (× 10 ³)	N/[Zr] ⁱ (%)	A/ × 10 ³
1 ^e	[Et ₃ NH] ⁺ [BPh ₄] ⁻		MMA	5.0	2.5	3.0	0–20	traces					
2 ^e	[(<i>n</i> -But) ₃ NH] ⁺ [BPh ₄] ⁻		MMA	5.0	2.5	3.0	0	≤6	25	1.32		≤2.2	<0.04
3 ^f	B(C ₆ F ₅) ₃	ZnEt ₂	MMA	0.10	0.10	0.30	0	≥90	750	1.17	300	40 ^m	10
4 ^f	B(C ₆ F ₅) ₃	ZnEt ₂	<i>n</i> -BuMA	2.90	2.90	1.0	0	≥90	170	1.33	50	30	3
5 ^f	B(C ₆ F ₅) ₃	ZnEt ₂	<i>n</i> -HexylMA	2.90	2.90	1.0	0	≥90	190	1.33	60	30	3
6 ^f	B(C ₆ F ₅) ₃	Al(octyl) ₃ ^j	<i>t</i> -BuMA	0.9	0.9	0.60	0	20	40	2.0 ^k			

^a Polymerization time = 24 h; [MMA]/[ZnEt₂] = ~4/1; V_{total} = 60–90 mL. ^b Concentration of dimethylzirconocene precursor. ^c Concentration of borane cocatalyst. ^e Solvent: CH₂Cl₂. ^f Solvent: toluene. ^g Determined by GPC, calibrated with PMMA standards; solvent THF. ^h Calculated by monomer to catalyst ([Zr]) ratios. ⁱ N/[Zr] = catalytic efficiency; N = number of polymer chains, determined by M_n and yield of polymerization. ^j Activity of the catalytic system: g of PMMA (mol of Zr[MMA] h)⁻¹. The values presented refer to mean values. ^k Bimodal distribution. ^l [Al(octyl)₃] = 0.205 M; aging = <2 min. ^m Refers to mean values for final polymeric products: 30–40%.

**Figure 1.** Yield of MMA polymerization: (a) as a function of reaction time—experiment series A; (b) as a function of reaction time during the propagation period (150 < *t* < 500 min)—experiment series A.

and [ZnEt₂] = 125–175 mM, where [Zr]₀ ≡ [Cp₂ZrMe₂], while the other involves higher ranges of concentrations (representative values for experiment series B: [Zr]₀ = [B(C₆F₅)₃] = 1.00–1.50 mM, [MMA] = 1300–1500 mM, and [ZnEt₂] = 300–500 mM). Specifically, the polymer yield and M_w were monitored with time (M_w = *f*(*t*), yield (%) = *f*(*t*)) during these kinetics experiments. It was observed that the polymerization process is characterized by a pronounced *induction period* (very slow decrease of the [MMA] for *t* < 100 min—experiment series A) followed by a rapid and constant polymerization rate (150 < *t* < 500 min) (Figure 1, parts a and b—experiment series A). This finding is in contrast to Soga's observations.^{9d} These report that an induction

period was not found for analogous catalytic systems (dimethylzirconocenes/fluoroarylborates/diethyl zinc), perhaps due to the lack of experimental data for the early stages of polymerization (lack of data for *t* < 2 h). Furthermore, the kinetic results that were presented by Soga's group included bimodal molecular weight distributions for the initial period of the polymerization, indicating the presence of two active species during those stages. This phenomenon was not observed in the present study, where only single GPC curves were observed at all the stages of polymerization. This is perhaps due to impurities or atmospheric contaminants that were present in Soga's system. On the other hand, Collins et al.⁸ have reported an analogous induction

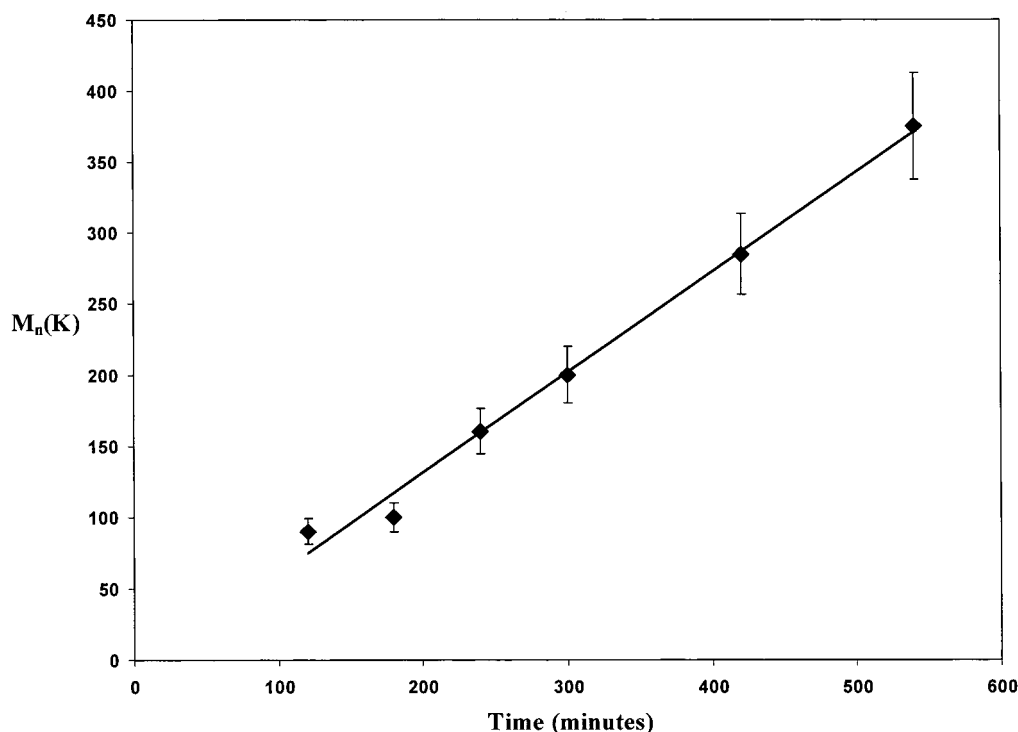


Figure 2. Plot of M_n as a function of reaction time for the MMA polymerization during the propagation period ($150 < t < 500$ min).

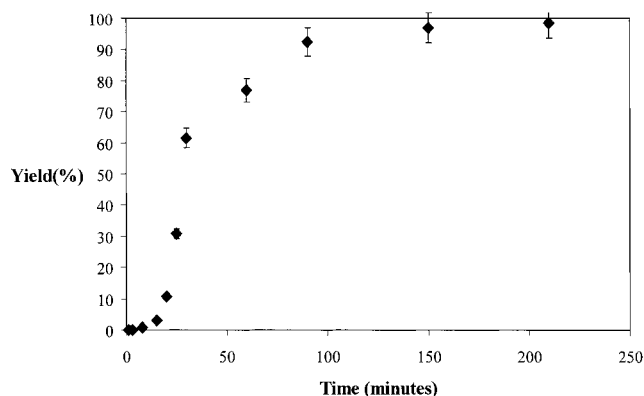


Figure 3. Plot of yield as a function of reaction time for the MMA polymerization—experiment series B.

period for the polymerization of MMA with the catalytic system $\text{Cp}_2\text{ZrMe}_2/\text{Cp}_2\text{ZrMe}(\text{THF})^+\text{BPh}_4^-$, in CH_2Cl_2 . The well-controlled nature of the present catalytic system is indicated by a prolonged period (propagation period: $150 < t < 500$ min, for experiment series A) in which the yield increases with polymerization time (Figure 1b). Moreover, during the same period ($150 < t < 500$ min), the variation of molecular weight seems to increase linearly with time (Figure 2).

The first set of kinetic experiments (experiments A) showed that the polymerization is completed in a period of 7–9 h (Figures 1 and 2), while the corresponding observations using the set of experiments B, showed polymerization completion in 3–4 h (increase of polymerization rate—Figure 3), accompanied by an analogous reduction of the induction period to 30 min. These experimental results point out the possibility of controlling the evolution of the polymerization procedure within a wide range of time intervals. Moreover this offers a possible explanation for the difference in the time needed for the completion of the polymerization

which were presented by several research groups.^{9a,b,10} In particular, Soga et al.^{9b} reported, for the polymerization of MMA with the catalytic system **1**, that the polymerization is completed in 24 h, whereas Cameron et al.,¹⁰ utilizing the catalytic system $\text{Cp}_2\text{ZrMe}_2/\text{B}(\text{C}_6\text{F}_5)_3$ (the third component, a Lewis acid, is absent in this system), reports polymerization of MMA in 1 h. The typical concentration values for the catalytic system, according to Soga protocol, are: $[\text{Zr}]_0 = [\text{B}(\text{C}_6\text{F}_5)_3] = 0.200$ mM, $[\text{MMA}] = 800\text{--}900$ mM, and $[\text{ZnEt}_2] = 214$ mM, whereas Cameron et al. used highly concentrated solutions: $[\text{Zr}]_0 = [\text{B}(\text{C}_6\text{F}_5)_3] = 17.0$ mM, and $[\text{MMA}] = 3500$ mM. Taking in consideration the above experimental data, it becomes obvious that the differences obtained by our results and those reported in the literature can be attributed to significant difference between the concentrations of the catalytic system.

The catalytic efficiency ($N/[\text{Zr}]$ (%), where N = number of polymer chains and $[\text{Zr}]$ = concentration of the zirconocene precursor) remains unaffected with time (in the frame of the experimental error) for the discrete catalytic system. The values of the catalytic efficiency, for the first 2–4 h of the polymerization procedure, are calculated in the range of 40–45%, and are reduced, after 8–15 h, to values in the range of 30–35%. This implies that the great majority of active centers remain active during the polymerization; i.e., in the studied catalytic system (**1**), deactivation and termination reactions of the active centers are practically absent.

A series of experiments has been performed to clarify the polymerization characteristics of this system, such as the dependence of the molecular weight on the monomer-to-initiator ratios $[\text{MMA}]_0/[\text{Zr}]_0$ —Figure 4a). The molecular weight of PMMA increases proportionally to the ratio $[\text{MMA}]_0/[\text{Zr}]_0$, while the molecular polydispersity (I ; M_w/M_n) remains constant and narrow across the molecular weight range, indicating that the control of the molecular weights of the final products within a

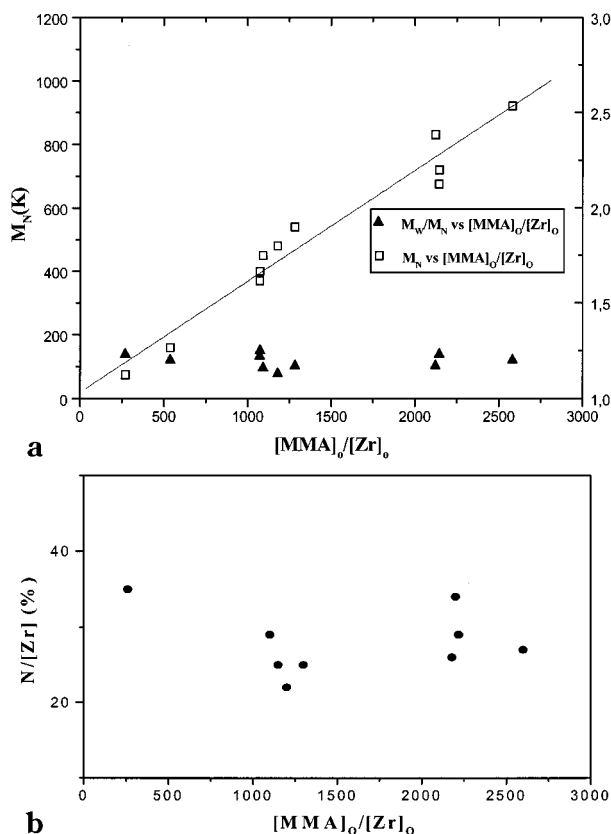


Figure 4. (a) Plots of M_n and M_w/M_n as a function of $[MMA]_0/[Zr]_0$ for the polymerization of MMA with the catalytic system 1. (b) Plot of number of polymer chain as a function of $[MMA]_0/[Zr]_0$ for the polymerization of MMA with the catalytic system 1.

wide range of values is possible. Moreover, the well-controlled fashion in which the polymerization proceeds is further confirmed by the fact that the catalytic efficiency remains practically unchanged and unaffected by the monomer-to-initiator ratios (Figure 4b). It is important to notice here that the initiator efficiency remains under 40% (refers to final products) in all cases. These very low values can be interpreted as providing

evidence for a bimolecular mechanism; similar to the one proposed by Collins.⁷

The PMMA which was synthesized during the present study showed significantly improved molecular characteristics (regarding to the molecular weight distribution, the wider range of molecular weights and the polymerization yield) than those reported in previous studies.^{9a,b,10} The key factor for this achievement seems to be the thorough purification of the reagents used and the careful exclusion of air and moisture during polymerization. The purification protocol followed at the present study was similar to the one used in anionic polymerization techniques,¹⁵ and more extensive than that of Soga's group (purification consisted of distillation from CaH_2 for monomer and solvent). The molecular weight distribution ranges from 1.12 to 1.22 even for polymeric products with M_w over 1000K (for a dilute solution where $[Zr]_0 = [B(C_6F_5)_3] = 0.100\text{--}1.00\text{ mM}$, $[MMA] = 300\text{--}900\text{ mM}$, and $[ZnEt_2] = 100\text{--}250\text{ mM}$), while the molecular weights of the final products vary in a wide range of values: 60K to over 1000K. A representative size exclusion chromatogram is displayed in Figure 5. It is important to mention the improved behavior of the present catalytic system (1), with respect to the molecular characteristics of the final products, in comparison with the two component catalytic system proposed by Cameron et al.¹⁰ ($Cp_2ZrMe_2/B(C_6F_5)_3$). Cameron reports not only a quite narrow range for molecular weights of the final products ($M_n = 20\text{--}110K$) but also wider molecular weight distributions that increase with the molecular weight and range from 1.20 to 1.30.

The effect of the concentration variation of the third component (activator— $ZnEt_2$) as well as the temperature of polymerization on the molecular characteristics of the final polymeric product was also studied. The results of polymerization in the presence of various concentrations of the activator (the other experimental parameters remain constant during these series of experiments, i.e., $[MMA]_0/[Zr]_0$) are presented in Table 2. The use of $ZnEt_2$ in concentrations that fulfill the ratio $[MMA]/[ZnEt_2] \approx 4$ (a ratio in the range 3.5–4.5 did not cause significant differentiation in the polymerization procedure) led to the best possible results, regarding the

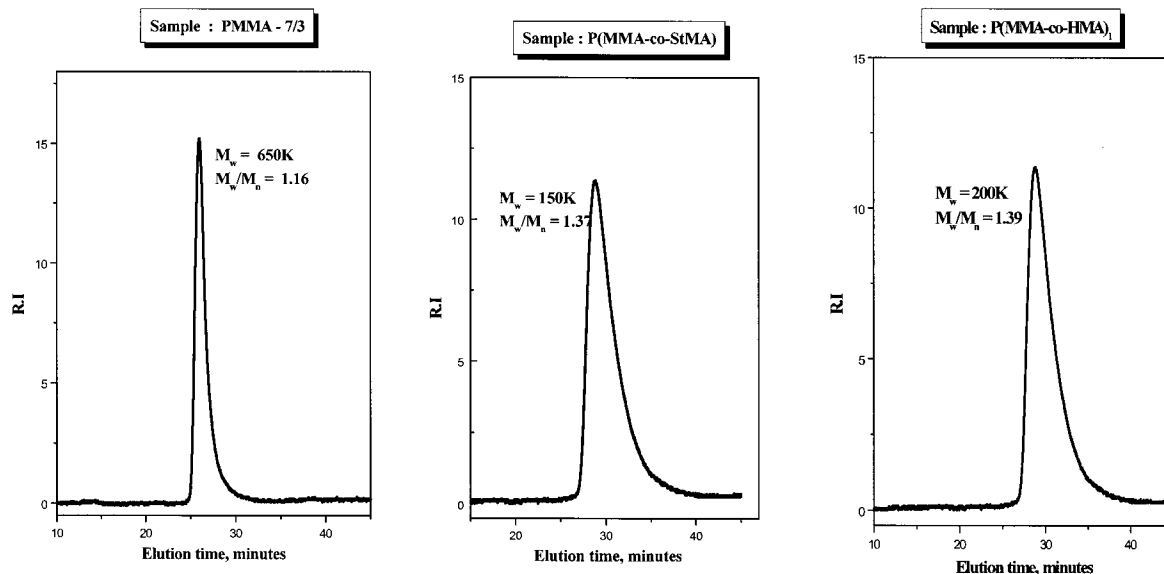


Figure 5. Representative SEC chromatograms of poly(methyl methacrylate), poly(MMA-co-SMA), and poly(MMA-co-HMA)₁ synthesized with the catalytic system 1.

Table 2. Effect of [ZnEt₂] on the Molecular Characteristics of PMMA

sample	[ZnEt ₂] (mM)	M_w^a	M_w/M_n^a
2/2-A	260	500	1.22
2/2-B	60	730	1.80
7/3-19h	150	590	1.13

^a Determined by SEC in THF, calibrated with PMMA standards.**Table 3. Temperature Effect on the Molecular Characteristics of PMMA**

sample	T_p (°C)	M_w^a	M_w/M_n^a
PMMA 40 °C	40	60	1.80
PMMA 20 °C	20	100	1.52
PMMA 0 °C	0	200	1.35
PMMA -10 °C	-10	220	1.22

^a Determined by SEC in THF, calibrated with PMMA standards.

molecular characteristics of the final products (M_w/M_n , M_w), for the studied catalytic system (**1**). Specifically, the use of lower concentrations of the activator led to polymeric products with significantly increased molecular weights and broadened molecular weight distributions (Table 2—entry 2/2-B), while no effect was recorded in the polymerization yield (quantitative polymerization). The latest finding contrasts the observations of Soga, who observed a significant decrease in the polymerization yield with decreasing concentration of the activator.^{9d} A possible explanation for this differentiation comes once more from the extensive purification protocol, used in the present work, resulting in the crucial limitation of the function of ZnEt₂ as an internal scavenger for the catalytic system. The experimental data showed that increase in the concentration of the activator led to a small decrease in the molecular weight of the final product which was accompanied by an increase in the molecular polydispersity (Table 2—entry 2/2-A). It is worth notice that the above-mentioned observations are, generally, in agreement with the proposed role of ZnEt₂, which is limited to the activation of the monomer at the initiation process.

The role of temperature in polymerization procedure is shown in Table 3. The increase of polymerization temperature from -10 to +40 °C led to a dramatic decrease in the molecular weight of the final product, while molecular polydispersity increased significantly. Polymerization yield was higher than 90% in all cases.

Further studies on the discrete catalytic system (**1**) involved polymerization efforts with other alkyl methacrylate monomers. The polymerization of *n*-alkyl methacrylates, with side group of four (*n*-BuMA) and six (*n*-HMA) carbon atoms (Table 1—entries 3 and 4 respectively), led to syndiotactic polymeric products with high molecular weights and rather narrow molecular weight distributions ($M_w/M_n = 1.30$ – 1.33), in almost quantitative yields. In all cases syndiotactic triads (rr) in the final polymeric product were found to range from

70% to 79% (Table 1, run 5, sample PHMA: rr = 79%, mr = 20.5%, mm = 0.5%). Unfortunately, efforts for the polymerization, under the same conditions, of SMA and *t*-BuMA were unsuccessful, although upon the catalyst–cocatalyst addition to monomer a color change from colorless to bright yellow was observed (this color remained even after 15–20 h). It is postulated that this color change represents the first product of conjugate monomer addition, subsequent attack being blocked by the bulky side group of the monomer. Nevertheless, the homopolymerization of *t*-BuMA under modified experimental conditions (Table 1—entry 6), led to polymeric products with poor molecular characteristics (bimodal molecular weights distribution and low M_w) in low yields.

The copolymerization of the alkyl methacrylates with catalytic system **1** was also studied. For the copolymerization of MMA with HMA two experiments were conducted with different monomer feed ratios (Table 4), which led to polymeric products in high yields [Table 4—copolymers P(MMA-*co*-HMA)₁ and P(MMA-*co*-HMA)₂] with reasonably narrow molecular weight distribution, slightly increased in comparison to homopolymers ($M_w/M_n = 1.39$), and high molecular weights. ¹³C NMR experiments revealed that the final copolymers possess syndiotactic microstructure (e.g., Table 4, sample P(MMA-*co*-HMA)₁: rr = 76%, mr = 23.5%, mm = 0.5%). Representative SEC chromatograms are given in Figure 5. To further study the copolymerization of MMA and HMA a set of five experiments was conducted. Different feed ratios were employed each time (MMA/HMA (w/w): 80/20, 60/40, 50/50, 40/60, and 20/80), and the copolymerization reaction was quenched at low yield (~10%). The copolymerization procedure was monitored by ¹H NMR experiments and the experimental results were processed in the basis of Finemann–Ross and inverted-Finemann–Ross equations.¹⁶ The results showed that the copolymerization procedure gives copolymers with a structure consisting of alternating blocks ($r_{\text{MMA}} = 1.25$ and $r_{\text{HMA}} = 1.09$, for the Finemann–Ross equation; $r_{\text{MMA}} = 1.38$ and $r_{\text{HMA}} = 1.29$, for the inverted-Finemann–Ross equation). This reveals that copolymerization of *n*-alkyl methacrylates (where the difference in alkyl groups does not exceed the 6-C) with the present catalytic system leads to polymeric chains with randomly distributed blocks (consisting of a few monomeric units) of the different comonomers. Copolymerization of MMA with SMA was also achieved, with the studied catalytic system (**1**), leading to high molecular weight polymeric products with reasonably narrow molecular weight distributions in good yields (slightly higher than 70%—Table 4—copolymer P(MMA-*co*-SMA)). The ¹H NMR and ¹³C NMR of the latter copolymer show that 40% of the total monomeric units in the polymeric chains consist of SMA units (Figure 6). DSC experiments revealed the existence of T_m (T_m

Table 4. Copolymerization of MMA with Other Alkyl Methacrylates by the Catalytic System 1: Molecular Characteristics of Polymeric Products

copolymers	catalyst concn (mM)	feed ratio (mol/mol)	molar ratio in the polymer ^a	M_n^b ($\times 10^3$)	M_w/M_n^b	yield (%)	T_g/T_m^c (°C)
P(MMA- <i>co</i> -HMA) ₁ ^e	1.11	HMA:MMA 1:0.92	HMA:MMA 1:1.09	115	1.39	≥90	50.12/...
P(MMA- <i>co</i> -HMA) ₂ ^e	1.11	HMA:MMA 1:0.45	HMA:MMA 1:0.51	120	1.39	≥90	28.30/...
P(MMA- <i>co</i> -SMA) ^e	1.30	SMA:MMA 1:1.55	SMA:MMA 1:2.50	110	1.37	≈70	.../21.55
P(MMA- <i>co</i> - <i>t</i> -BuMA) ^e	1.17	<i>t</i> -BuMA:MMA 1:1.91	<i>t</i> -BuMA:MMA 1:8.06	40	2.0 ^d	≈25	

^a Determined by the ¹H NMR spectra of the final product in CDCl₃. ^b Determined by GPC, calibrated with PMMA standards; solvent THF. ^c Determined by DSC. ^d Bimodal distribution. ^e T_g and T_m values for the respective homopolymers are as follows: T_g (PHMA) = -5 to 1 °C, T_g (syn-PMMA) = 100–105 °C, T_g (PSMA) = -100 °C, T_m (syn-PSMA) = 39 °C.¹⁹

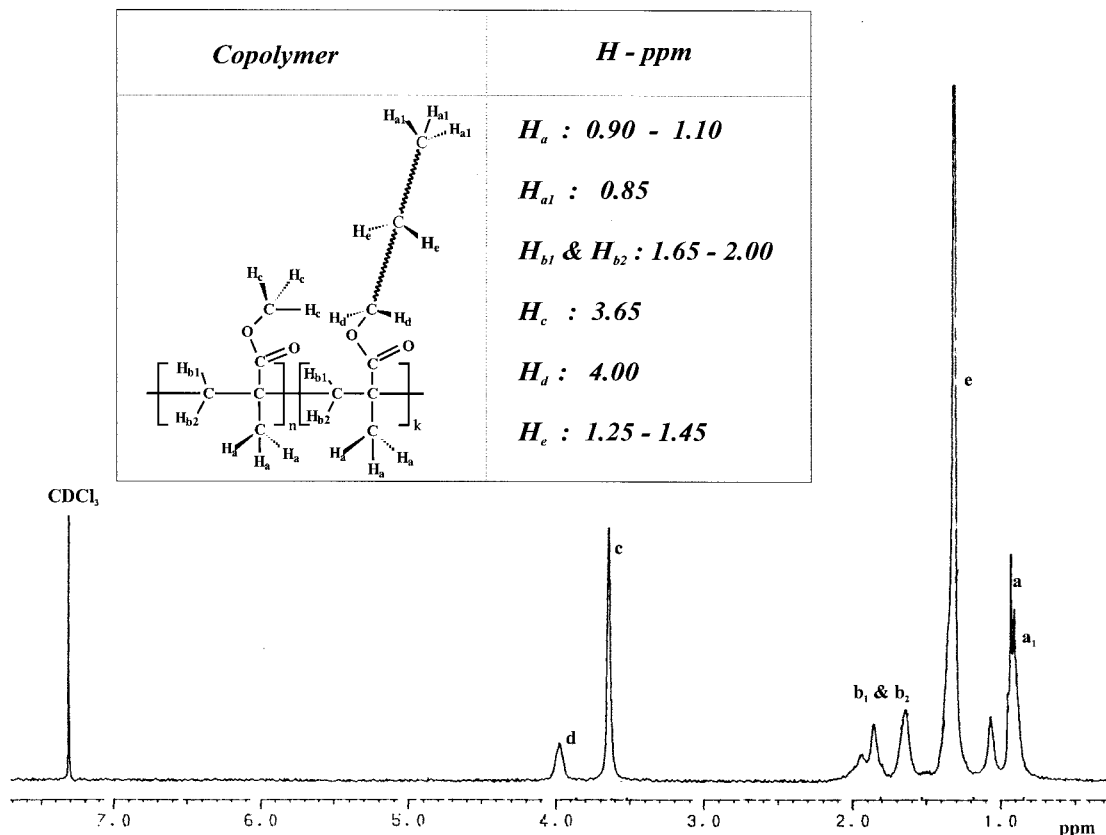


Figure 6. ^1H NMR spectra of P(MMA-*co*-SMA) copolymer.

= 21.6 °C and $\Delta H_m = 14.7$ J/g) for P(MMA-*co*-SMA), while T_g was not detectable. Unfortunately, copolymerization efforts for *t*-BuMA with MMA did not have the same success [Table 4—copolymer P(MMA-*co*-*t*-BuMA)]. The polymeric products possess poor molecular characteristics (wide molecular weight distribution and low molecular weights) and low yield (less than 30%). ^1H NMR experiments have shown that only 12% of the macromolecule's monomeric units consist of *t*-BuMA units (Figure 7).

Association Behavior. To measure the absolute molecular weights of the copolymers, LALLS experiments were conducted in THF, which is a good solvent for polymethacrylates. However the $Kc/\Delta R_\theta$ vs c plots (where K = optical constant, ΔR_θ = excess of Rayleigh ratio, and c = concentration) were not linear, showing an initial decrease of the $Kc/\Delta R_\theta$ values followed by an increase at higher concentrations. A typical LALLS plot is given in Figure 8. This behavior is typical of an aggregating system.¹⁷ The molecular weights calculated by extrapolating from the higher concentration regime were found to be much higher than those obtained by SEC. The results are given in Table 5. This behavior can be attributed to the existence either of traces of the catalyst, which are probably chemically connected to the polymer chains or of traces of the oxidation products of ZnEt_2 which interact with the carbonyl groups of the MMA units leading to partial cross-linking. A similar result was also obtained using a PMMA homopolymer. The SEC data seem to be reliable, since during the flow of the polymer solutions through the columns the applied shear forces are able to disrupt the aggregates. Reproducible results concerning the shape of the SEC curves and the molecular characteristics of the samples

were obtained using carrier solvents with different polarity (THF and CHCl_3).

All the samples were extensively purified to remove inorganic impurities. Specifically dilute solutions of the polymers in THF (~1 g of the polymeric material was diluted in 10 mL of solvent) were filtered, ultracentrifuged at 2000–3000 rpm, condensed in vacuo to a final volume of 5 mL, and passed through silica columns (silica gel 60, 0.040–0.060 mm). The samples were eluted for several times with MeOH and hexanes and finally with THF. THF fractions were collected and condensed in vacuo to a final volume of 5 mL, and the polymeric material was precipitated in MeOH. This procedure was repeated twice in all cases. The existence of aggregation in the system means that the metal moieties are either chemically connected or very strongly interacted with the polymer chains. Recently zirconium traces in polyolefins prepared by zirconocene catalysts were quantitatively measured by inductive coupled plasma isotope dilution mass spectroscopy.¹⁸

To overcome this problem DMF was used for the characterization of the polymers, since this solvent is more polar than THF, being able to prevent association through solvation of the metal moieties. The result obtained by LALLS measurements in DMF for the sample PMMA 24h is in very close agreement with that given by the SEC measurements (Table 6). Unfortunately PHMA and PSMA are not soluble in DMF. Only the sample P(MMA-*co*-HMA)₁ with the lowest HMA content was soluble, giving in DMF a much lower molecular weight than that measured in THF.

To further study the aggregation behavior of the system, dynamic light scattering (DLS) experiments were conducted in two solvents of different polarity, toluene and THF. Linear PMMA samples having dif-

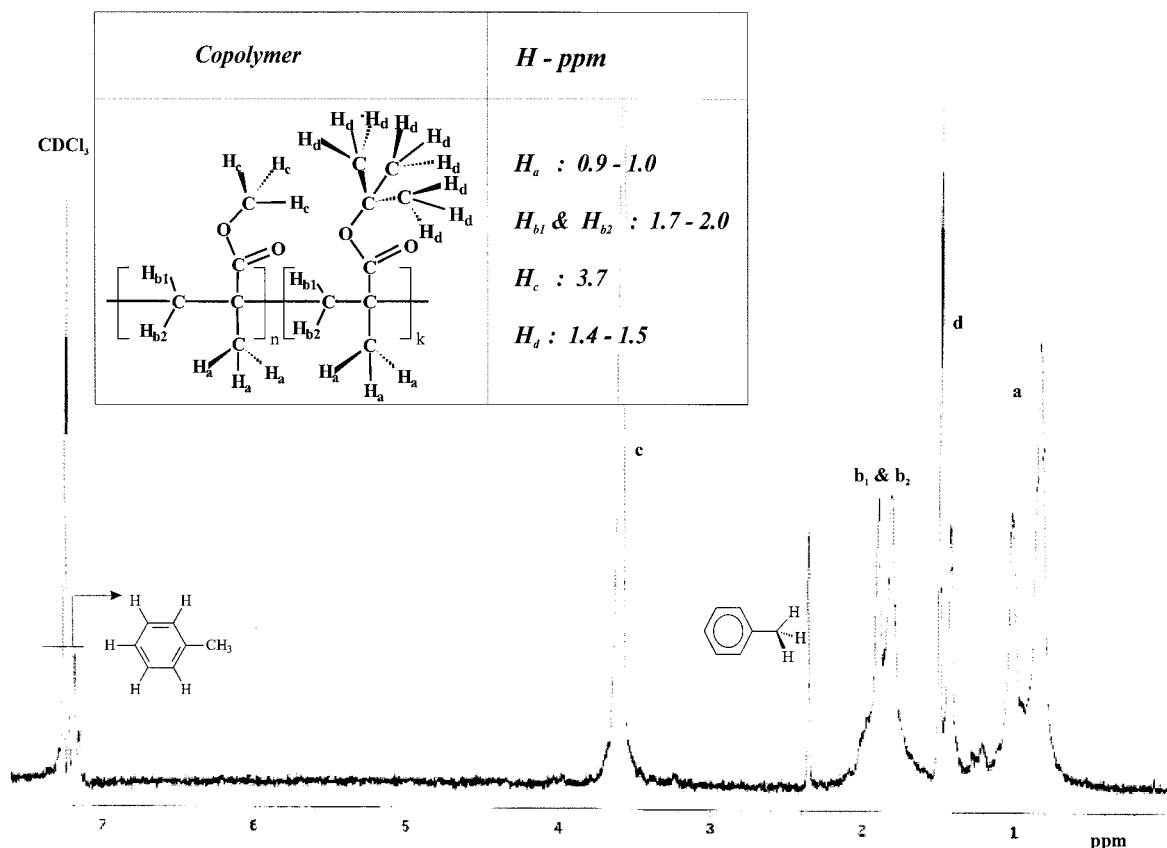


Figure 7. ^1H NMR spectra of P(MMA-co-*t*-BuMA) copolymer.

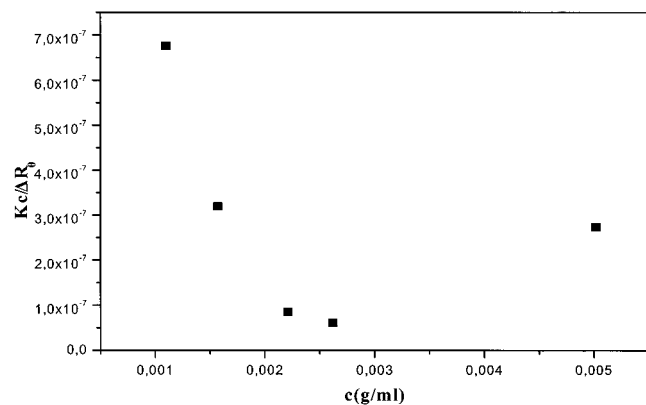


Figure 8. Plot of $Kc/\Delta R_\theta$ as a function of concentration for LALLS experiments in THF.

Table 5. Aggregation Numbers of Several Polymers in THF and DMF

sample	M_w			N_w^a	
	SEC ^b ($\times 10^3$)	LALLS in THF ($\times 10^6$)	LALLS in DMF ($\times 10^3$)	THF	DMF
PMMA-24 h	870	16	950	18.4	1.1
P(MMA-co-HMA) ₁	160	2	350	12.5	2.2
P(MMA-co-SMA)	150	10		66.7	

^a $N_w = (M_w)_{\text{SEC}} / (M_w)_{\text{THF or DMF}}$. ^b In THF.

ferent molecular weights were used. The results are given in Table 6. The translational diffusion coefficient at infinite dilution, D_0 was obtained from the D vs c plots with extrapolation to zero concentration using the equation

$$D = D_0(1 + k_D c) \quad (1)$$

where k_D is a coefficient given by the equation

$$k_D = 2A_2M - k_f - u \quad (2)$$

A_2 is the second virial coefficient, M the molecular weight, k_f the coefficient in the concentration dependence of the friction coefficient and u the partial specific volume of the polymer in the solution. The D_0 values were used to calculate the hydrodynamic radius by the Stokes-Einstein equation

$$R_h = KT/6\pi\eta_s D_0 \quad (3)$$

where K is the Boltzmann constant, T the absolute temperature and η_s the solvent viscosity. The viscometric radii were obtained using the equation

$$R_v = (3/10\pi N_A)^{1/3}([\eta]M_w)^{1/3} \quad (4)$$

N_A is the Avogadro number and $[\eta]$ the intrinsic viscosity. The intrinsic viscosities were calculated using literature results concerning the molecular weight dependence of the intrinsic viscosity in THF and toluene at 25 °C.¹⁹

$$[\eta] = 8.12 \times 10^{-3} M_w^{0.71} \text{ mL/g (THF)} \quad (5)$$

$$[\eta] = 7.5 \times 10^{-3} M_w^{0.72} \text{ mL/g (toluene)} \quad (6)$$

For nonaggregating polymers the ratio R_v/R_h is approximately equal to unity.²⁰ In the nonpolar solvent toluene, the R_h values were much higher than the corresponding R_v values, indicating that very large aggregates are formed in this solvent. Furthermore, huge k_D values were obtained, due to the contribution

Table 6. Experimental Results by Dynamic Light Scattering in THF and Toluene

sample	M_n^a ($\times 10^3$)	M_w/M_n^a	THF				toluene			
			$R_h(\text{exptl})^b$ (nm)	$K_d(\text{exptl})^b$	$R_{vo}(\text{theor})^c$	R_{vo}/R_h	$R_h(\text{exptl})^b$ (nm)	$K_d(\text{exptl})^b$	$R_{vo}(\text{theor})^d$	R_{vo}/R_h
PMMA 9/3–2h	90	1.50	59.8	4017	9.33	0.16	88.0	4183	9.4	0.11
PMMA 15/3–5h	125	1.45	16.6	–760	10.8	0.65	n.d			
PMMA 23/3–7h	225	1.33	19.2	–1624	14.4	0.75	104	8858	14.6	0.14
PMMA 7/3–19h	530	1.22	29.5	–3263	22.4	0.76	136	20 674	22.8	0.17
PMMA 3/2–24h	725	1.20	31.5	–3195	27.8	0.88	193	57 550	28.3	0.15

^a Determined by GPC, calibrated with PMMA standards. ^b Values determined by experimental data (DLS). ^c Calculated values using eqs 4 and 5. ^d Calculated values using eqs 4 and 6.

of the very high molecular weight of the aggregates. In the more polar solvent THF, much higher R_v/R_h values were obtained. This result is in agreement with the observation that by increasing the polarity of the solvent the degree of association is reduced. By LALLS it was shown that the weight-average degree of association, N_w , defined as the ratio of the M_w by LALLS in THF over the M_w by SEC, is 2.2 for PMMA in THF. This result is in agreement with the DLS observations, where the highest R_v/R_h value was obtained for this specific sample. Nevertheless the ratio is still lower than unity meaning that a weak aggregation still exists in this system. Negative k_D values were observed for the samples having the lower degrees of association (higher R_v/R_h values) due to the low A_2 values, which are expected to exist in aggregating systems.²¹

However, the fact that the number, nature, and position of the polar groups in the polymer chains are unknown makes the analysis of the results and the connection with specific association models very difficult.

Conclusions

In summary, it was demonstrated that the three component catalytic system **1** ($\text{Cp}_2\text{ZrMe}_2/\text{B}(\text{C}_6\text{F}_5)_3/\text{ZnEt}_2$), promotes the polymerization of MMA in a well-controlled fashion, leading to polymeric products with high molecular weights and low polydispersity in almost quantitative yields. Previous studies have utilized a poor purification protocol, resulting to rather low yields and poorer molecular characteristics for the final polymeric products. This leads to the conclusion that the zirconocene catalyst system has not been evaluated under the best possible conditions. The polymerization process is characterized by a pronounced induction period followed by a rapid and constant rate of polymerization. The kinetics of the polymerization was also recorded. The control of the molecular weight of PMMA within a wide range of values is possible. The effect of $[\text{ZnEt}_2]$ and temperature on the molecular characteristics of the final products seems to be of great importance for the specific catalytic system. The catalytic system was found to promote the polymerization of other alkyl methacrylates to syndiotactic polymeric products with high molecular weight and narrow polydispersities, in high yields. Copolymerization of MMA with HMA as well as with SMA was also achieved. Efforts for further molecular characterization of the final products have been made. In THF all polymers gave huge molecular weights and the LALLS plots were not linear. A decrease in the $K_d/\Delta R_\theta$ values was initially observed followed by an increase at higher concentrations, which is typical of an aggregating system. The aggregation of the polymeric chains was further confirmed with dynamic light scattering measurements.

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