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Anionic Polymerization of (Meth)acrylic Monomers. 7. Macrocyclic Crown Ethers as Promoters of the Living Polymerization of Methyl Methacrylate Using Monofunctional Initiators

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ABSTRACT: It has been previously shown that μ-coordinating inorganic salts, such as LiCl, were effective in preventing the anionic polymerization of methacrylic esters and hindered alkyl acrylates from being disturbed by secondary transfer and termination reactions. That strategy has opened the way to the "living" polymerization of these monomers and their controlled sequential polymerization with monomers lacking a carbonyl-conjugated group. That control is however limited to THF at low temperatures for methyl methacrylate and *tert*-butyl acrylate. It is reported now that the polymerization mechanism remains strictly controlled in apolar solvents, such as toluene, and at temperatures as high as 0 °C, when crown ethers are used in relation to their capability of chelating the alkali-metal counterion and surrounding it with a steric barrier blocking a large enough space area around the metal-containing ion pair.

Introduction

Poly[alkyl (meth)acrylate]-based products are nowadays the basis of an increasingly diversified range of applications.[1] (Meth)acrylic ester monomers are, in principle, good candidates to undergo anionic polymerization. However, when applied to methacrylates, that method suffers severe limitations if carried out under normal conditions. These problems arise from the possible nucleophilic attack of the active species on the carbonyl groups along the chain and possibly the α-hydrogen atom of the acrylates.

Recently, several strategies have been proposed to confer a "living" character to the anionic polymerization of alkyl (meth)acrylates. A first successful series of attempts are based on the appropriate choice of initiator (sterically hindered), solvent (good solvating power), and temperature (−78 °C), together with the careful purification of the monomer by aluminum alkyl derivatives.[2-6] When these experimental conditions do not suppress the secondary reactions (chain termination or transfer) or cannot be satisfied because it is of interest to work in apolar solvents or to increase polymerization temperature, the use of ligands interacting with both the initiator and the propagating species appears to be a general and efficient strategy. Inorganic and organometallic additives such as alkali- and alkaline-earth-metal salts and metal alkyls or alkoxides have been shown to form complexes with the active species that could prevent the course of the anionic polymerization to be disturbed by secondary transfer and termination reactions.[7]

Of course, besides the possible control of the anionic polymerization by external agents (solvent, temperature, ligands), it is conceivable to change the polymerization mechanism itself as demonstrated in the nucleophile-assisted "group transfer polymerization" (GTP) of unsaturated carbonyl-conjugated monomers.[8] Nevertheless, that technique does not allow the direct synthesis of block copolymers containing monomers lacking a carbonyl-conjugated group, e.g. vinyl aromatics and dienes. The same limitation is also met when resonance-stabilized metal-free ammonium methanide initiators are considered, as recommended by Reetz et al.[9] It has been shown, however, that the use of μ-coordinating salts, such as LiCl, was an efficient pathway to avoid secondary reactions that are normally associated to the true anionic polymerization of alkyl methacrylates and *tert*-butyl acrylate (*t*BA) when carried out at low temperature.[10] Using this technique, we were able to control the sequential anionic copolymerization of monomers lacking a carbonyl-conjugated group with the above mentioned (meth)acrylates.[11] Similarly, block copolymers of methyl methacrylate and *tert*-butyl acrylate have been synthesized with a

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predictable molecular weight and a narrow dispersity whichever monomer is first polymerized.[12]

However, in contrast to GTP, these polymerization reactions do not proceed anymore in a living manner at temperatures higher than −40 °C for methyl methacrylate or *tert*-butyl acrylate. The latter, when polymerized at −20 °C does not show any living character, though $\bar{M}_n$ and $\bar{M}_w/\bar{M}_n$ of the prepolymer are rather well controlled. Furthermore, when carried out at 0 °C, the same reaction leads with incomplete conversion to P*t*BA without any control of $\bar{M}_n$ and $\bar{M}_w/\bar{M}_n$.[11e] When toluene is used as a solvent, instead of THF, all the other conditions being constant, kinetics and mechanism become so complex that a multimodal molecular weight distribution is finally observed.[10d]

In order to extend and clarify the possible electronic and steric effects that ligands have on the structure and reactivity of the ion pairs in alkyl (meth)acrylate polymerization, we focused on macrocyclic crown ethers as specific ligands of the alkaline counterion. Crown ethers are indeed well-known for their capability of chelating alkali-metal ions and surrounding them with a steric barrier blocking some space area around the metal-containing ion pair.[13,14] Methyl methacrylate (MMA) has been used as a representative monomer, the anionic polymerization of which has been initiated by a traditional alkylmetal, (diphenylmethyl)sodium, in both THF and toluene. We decided to use Ph_2CHNa rather than our usual lithium-based initiators (αMSLi, Ph_2CHLi, ...) because such systems were previously shown to be unable to promote living character when used in the presence of crown ethers.[11b] Attention will be paid to the polymerization temperature which should be as high as possible while preserving a controlled polymerization mechanism.

Experimental Section

MMA obtained from Norsolor Co. was first vacuum-distilled from CaH_2 after reflux and then stored under a nitrogen atmosphere at −20 °C. Before polymerization, it was added to a 10 wt % triethylaluminum solution in toluene until a persistent yellowish green color was observed.[6b] It was then redistilled under reduced pressure just prior to polymerization. The initiator used in this study was (diphenylmethyl)sodium Ph_2CHNa. It was prepared at room temperature by reacting diphenylmethane with sodium naphthalene prepared from sodium and naphthalene in THF at room temperature.[15]

Macrocyclic crown ethers used were 1,4,7,10-tetraoxacyclododecane (12-CE-4) (mp 16 °C), 1,4,7,10,13-pentaoxacyclopentadecane (15-CE-5) (bp 130 °C/0.2 mmHg), 1,4,7,10,13,16-hexaoxacyclooctadecane (18-CE-6) (mp 42 °C), 2,3:11,12-dibenzo-1,4,7,10,13,16-hexaoxacyclooctadeca-2,11-diene (DB-18-CE-6) (mp 164 °C), 2,3-benzo-1,4,7,10-13-pentaoxacyclopentadec-2-ene (B-15-CE-5) (mp 78 °C), 2,3:14,15-dicyclohexano-1,4,7,10,13,16,19,-22-octaoxacyclotetracosane (DCH-24-CE-8) (mp 110 °C). 12-CE-4, 15-CE-5 and DCH-24-CE-8 were dried over finely ground CaH_2 under a high-purity nitrogen atmosphere for 2 days and distilled under vacuum. B-15-CE-5, 18-CE-6, and DB-18-CE-6 were recrystallized from petroleum ether.

THF was purified by refluxing over fresh sodium–benzophenone complex (a deep purple color indicating an oxygen- and moisture-free solvent). Toluene was distilled under dry nitrogen over poly(styryllithium) after being refluxed over CaH_2 for several days.

MMA polymerization was carried out in a previously flamed glass reactor under inert atmosphere, the monomer, solvent, and initiator being transferred by a syringe and capillary technique. Purified MMA was then added to the initiator solution, previously cooled to the desired temperature. A typical example involved introducing 1.20×10^{-3} mol of crown ether (dried as previously explained) into the flask. Toluene (200 mL) and the initiator (0.6×10^{-3} mol) were transferred into the reactor by means of a stainless steel capillary or a glass syringe. After the catalyst solution was cooled to a desired temperature, 0.047 mol of MMA was added. Polymerization was performed for 5 min and then stopped by adding acidified methanol. The polymer was recovered by precipitation into heptane and dried under vacuum at 80 °C for 48 h.

The dependence of the experimental molecular weight ($\bar{M}_{n,exp}$) on the monomer/initiator molar ratio (i.e., $\bar{M}_{n,calcd}$) was investigated by determining polymer molecular weights with a Hewlett-Packard 1090 liquid chromatograph equipped with four columns (10^5, 10^3, 500, and 100 Å) and a Hewlett-Packard 1037A refractive index detector. Polystyrene standards were used for calibration and the number ($\bar{M}_n$) and weight ($\bar{M}_w$) average molecular weights as well as polydispersity of the polymer were accordingly calculated.

The glass transition temperature (T_g) of the polymeric samples was determined by differential scanning calorimetry (DSC) on a Du Pont 9000 instrument, calibrated with indium and mercury. Samples were heated at 170 °C, cooled to 20 °C, and scanned repeatedly at 20 °C/min. Polymer chain tacticity was determined by ^1H NMR spectroscopy using a Bruker AN-400 spectrometer.

Results

Effect of Macrocyclic Crown Ethers on the MMA Polymerization by (Diphenylmethyl)sodium in Toluene at −20 °C. As recalled in the Introduction, the addition of a common cation μ-type ligand, such as LiCl is an interesting strategy for a better control of growth centers in the anionic polymerization of (meth)acrylic esters. That strategy can lead to the perfect control of molecular weight and ensures a very low polydispersity, provided that the polymerization proceeds in a polar solvent (THF) and at a low temperature (−78 °C). It also has some beneficial effects on the living character of the polymerization in lower polarity media.[10] Any further progress in the field should preserve these results while working under more severe conditions, i.e. in an apolar solvent and/or at a higher temperature. A series of macrocyclic crown ethers have been considered as specific ligands of the Na^+ counterion in the anionic polymerization of MMA initiated by (diphenylmethyl)sodium in a typically apolar solvent (toluene) at a substantially higher temperature than usual (−20 °C). The crown ether has been used in an equimolar amount and a 2-fold molar excess compared to the initiator, respectively. Table I reports characteristic data of monomer conversion, experimental molecular weight, polydispersity ($\bar{M}_w/\bar{M}_n$), and initiator efficiency which is calculated as ($\bar{M}_{n,calcd}/\bar{M}_{n,exp}$) × (% conversion).

Let us note that the initiator solution in toluene becomes heterogeneous upon the addition of a 2-fold excess of macrocyclic crown ether, whatever its nature. The heterogeneity disappears, however, instantaneously when a few drops of MMA are added, indicating a very fast reaction leading to the formation of soluble oligomers of MMA at the early stages of the reaction. When the MMA polymerization is carried out under the experimental conditions reported in Table I (toluene, −20 °C) and in the absence of any additive (crown ether), an 85% conversion is observed after a 5-min polymerization time, the molecular weight distribution is rather broad ($\bar{M}_w/\bar{M}_n = 1.8$) and the initiator efficiency is low (0.63). These data indicate nothing but the result of secondary transfer and termination reactions perturbing both the initiation and the propagation steps. The addition of a macrocyclic crown ether, whatever its structure and relative amount compared to the initiator (1 or 2), enhances the polymerization efficiency (and rate), since the monomer conversion is now complete under the same experimental conditions. The 15-CE-5 additive has an obvious beneficial effect on the course of the polymerization since, besides the complete-

Table I
Effect of Macrocyclic Crown Ethers on the Anionic Polymerization of MMA in Toluene at -20 °C Using Ph_2CHNa as an Initiator[a]

crown ether (CE)	CE/I	conv (%)	$10^{-3}\bar{M}_{n,exp}$	$\bar{M}_w/\bar{M}_n$	initiation efficiency	T_g (°C)[b]		microstructure (%)		
						i	m	i	h	s
		84.5	10.6	1.80	0.63	72	78	60.5	31.0	8.5
15-CE-5	1	97.0	10.0	1.60	0.78	113	123	7.5	33.5	59.0
15-CE-5	2	100.0	9.5	1.50	0.82	114	123	8.0	32.0	60.0
B-15-CE-5	1	100.0	10.5	1.70	0.73	113	125	7.5	33.5	59.0
B-15-CE-5	2	100.0	10.0	1.70	0.74	112	122	7.5	33.5	59.0
18-CE-6	1	96.0	8.6	1.40	0.90	114	122	10.3	36.5	53.2
18-CE-6	2	100.0	8.3	1.40	0.93	115	124	10.7	30.0	59.3
DB-18-CE-6	1	100.0	8.3	1.20	0.93	113	123	9.0	37.0	54.0
DB-18-CE-6	2	100.0	8.3	1.05	0.93	113	123	9.5	33.5	57.0
DCH-24-CE-8	1	100.0	8.5	1.50	0.90	114	123	11.7	34.0	57.3

[a] Conditions: polymerization time = 5 min; MMA = 0.047 mol; toluene = 200 mL; initiator = 0.60×10^{-3} mol. [b] T_g's were recorded from the second scan; i and m designate the beginning and the middle of the observed transition.

ness of the reaction, the molecular weight distribution is narrower (ca. 1.55 against 1.80) and the initiator efficiency has increased by more than 25%. A 2-fold excess of 15-CE-5 rather than the stoichiometric amount relative to the initiator has no additional effect and this is a general rule whatever the additive reported in Table I. Modification of 15-CE-5 by an aromatic ring seems to have a deleterious effect on its regulating influence on the course of the anionic polymerization. In contrast, increasing the size of the crown ether from 15-CE-5 to 18-CE-6 is very favorable, as supported by a polydispersity of 1.40 and an initiator efficiency which is now at least equal to 0.90. The best results however are observed when 18-CE-6 comprises two aromatic rings: the initiation is still highly efficient and the chain length distribution very narrow with a $\bar{M}_w/\bar{M}_n$ ratio as low as 1.05 when a 2-fold molar excess of the crown ether is used. A further increase of the crown ether size from 18-CE-6 to 24-CE-8 does not change the situation anymore. Thus, among the macrocyclic crown ethers considered in this study, DB-18-CE-6 proves to provide a very fine control of the initiating and growth centers in the anionic polymerization of MMA. This outcome actually represents a substantial progress compared to the control provided by the μ-type inorganic ligands. The two approaches offer a straightforward high-yield synthesis of PMMA with a predictable molecular weight and a low polydispersity, but the superiority of the crown ether-based technique has to be found in the experimental conditions under which these results are obtained. In addition to a possible electronic effect (charge separation), DB-18-CE-6 would be the best sterically balanced sodium complexing agent. Actually, it allows a fast and complete polymerization of MMA to occur in toluene at -20 °C, while the attack of the carbonyl groups by both the initiator and the growing species is avoided. Figure 1 illustrates the beneficial effect of aliphatic and partly aromatic 18-CE-6 on the molecular weight distribution of PMMA.

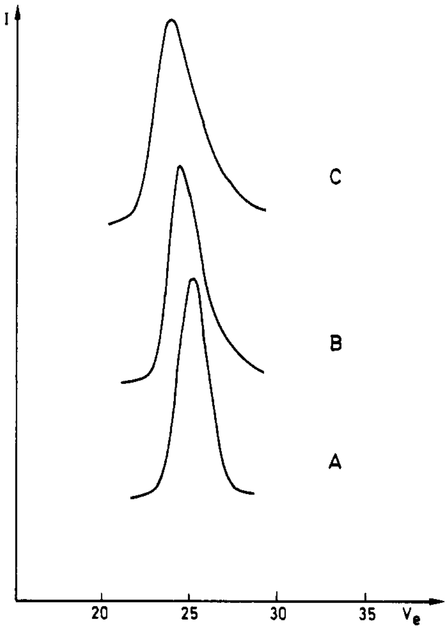

Figure 1. Size exclusion chromatograms of PMMA synthesized in toluene at -20 °C: The initiator was (diphenylmethyl)sodium as modified by some crown ethers used in a 1/1 molar ratio: (**A**) DB-18-CE-6 ($\bar{M}_w/\bar{M}_n$ = 1.20); (**B**) 18-CE-6 ($\bar{M}_w/\bar{M}_n$ = 1.40); (**C**) no crown ether ($\bar{M}_w/\bar{M}_n$ = 1.80).

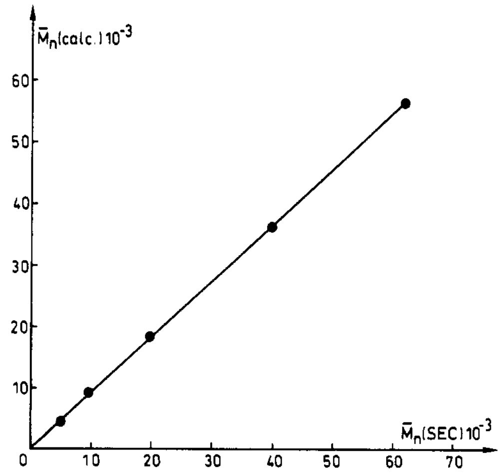

Figure 2. Dependence of experimental $\bar{M}_n$ as determined by SEC on $\bar{M}_n$ values calculated from the monomer/initiator ratio and the monomer conversion. Experimental conditions: toluene; -20 °C; initiator, (diphenylmethyl)sodium as modified by a 2-fold molar excess of DB-18-CE-6.

In order to demonstrate the living character of the PMMA macroanions in toluene at -20 °C in the presence of DB-18-CE-6, a series of MMA polymerizations has been carried out using various monomer/initiator molar ratios (or theoretical molecular weights, $\bar{M}_{n,calcd}$) and a constant additive/initiator molar ratio of 2. Figure 2 compares the experimental molecular weight ($\bar{M}_{n,exp}$) and the theoretical value corresponding to the actual monomer conversion (100[MMA]/[I] × % conv). A linear plot is observed in a molecular weight range extending up to 7×10^4. The slope of the straight line is 0.90 in good agreement with the initiator efficiency reported in Table I for DB-18-CE-6. The initiation efficiency value (slightly less than 1) might indicate that a small part of this initiator is either killed in the reaction medium or inactive. Further evidence for the living polymerization of MMA initiated by (diphenylmethyl)sodium complexed with DB-18-CE-6 is pro-

Table II
Effect of Macrocyclic Crown Ethers on the Anionic Polymerization of MMA in THF at -20 °C Using Ph_2CHNa as an Initiator[a]

crown ether (CE)	CE/I	conv (%)	$10^{-3}\bar{M}_{n,exp}$	$\bar{M}_w/\bar{M}_n$	initiation efficiency	T_g (°C)[b]		microstructure (%)		
						i	m	i	h	s
		30.0	bimodal	4.50		108	113	12.5	48.0	39.5
12-CE-4	1	38.0	bimodal	4.40		110	115	12.0	42.0	46.0
12-CE-4	2	88.0	15.0	2.20	0.46	110	115	12.0	43.0	45.0
15-CE-5	1	79.0	13.9	4.00	0.45	110	118	6.0	37.0	57.0
15-CE-5	2	95.0	13.0	3.00	0.60	110	116	6.5	37.0	56.5
B-15-CE-5	1	79.0	13.0	2.90	0.48	111	116	10.0	34.0	56.0
B-15-CE-5	2	96.0	11.8	2.70	0.56	111	116	11.5	34.5	54.0
18-CE-6	1	100.0	13.0	3.00	0.60	116	124	6.0	36.5	57.5
18-CE-6	2	100.0	12.0	1.50	0.66	112	124	7.0	36.5	56.5
DB-18-CE-6	1	100.0	8.0	1.05	0.97	112	121	9.8	39.9	50.2
DB-18-CE-6	2	100.0	8.0	1.04	0.97	112	120	7.5	38.8	53.7

[a] Conditions: polymerization time = 5 min; MMA = 0.047 mol; THF = 200 mL; initiator = 0.60×10^{-3} mol. [b] T_g's were recorded from the second scan; i and m designate the beginning and the middle of the observed transition.

vided by monomer resumption experiments. A first dose of MMA (0.047 mol) is first polymerized (Ph_2CHNa, 0.60×10^{-3} mol; CE/initiator = 2.0) in toluene at -20 °C, and 10 min later the same amount of freshly distilled MMA (0.047 mol) is added. $\bar{M}_n$ of the first PMMA sample was 8300 ($\bar{M}_w/\bar{M}_n = 1.05$) and, quite consistently, $\bar{M}_n$ of the final PMMA was 16 000 ($\bar{M}_w/\bar{M}_n = 1.10$).

It is worth recalling that the "ligand" lithium salts that have been used up to now to form μ-type complexes with the ion pairs have no significant influence on the polymerization stereoselectivity, the chain microstructure being essentially controlled by solvent polarity and temperature.[10d,16] The situation changes dramatically when macrocyclic crown ethers are used as complexing agents rather than Li salts, at least in toluene. Actually, ^1H NMR analysis shows that PMMA chains formed in toluene at -20 °C without any additive are rich in isotactic triads (i = 60.5%, s = 8.5%, and h = 31.0%). The addition of a small amount of any crown ether considered in Table I has a dramatic effect, since less than 10% isotactic triads are left, essentially in favor of the syndiotactic ones. Undoubtedly, binding of crown ethers with sodium is tighter than complexation of lithium salts with the active center. In sharp contrast to μ-type complexation, the binding of these crown ethers strongly influences the stereoselectivity of the propagation reaction. This might be due to a cooperation of two effects: the first (steric in nature) is the increase of the size of the cation by chelation with the macrocyclic ligand, and the second (electronic in nature) could be explained by the preferential formation (at low temperature) of a crown ether contact ion pair rather than a contact (crown ether free) ion pair. It has been shown by Höcker et al.[22] that unassociated growing species follow a syndiotactic mode of addition governed by Bernoullian statistics. On the other hand, the polymers obtained in a noncoordinating solvent by the growth of intramolecularly associated chains seems to be governed by first order Markovian statistics, resulting in an isotactic placement.

The syndiotacticity observed for PMMA synthesized in toluene in the presence of crown ethers clearly demonstrates that the lithium is coordinatively saturated, preventing its coordination with the penultimate ester group of the chain. Therefore, the monomers approach in a sterically more favorable syndiotactic-like mode.[23]

The glass transition temperature of PMMA is mainly dictated by the chain microstructure, and accordingly, the T_g of PMMA formed in the presence of crown ethers is higher by ca. 40 °C than that of the polymer synthesized without any additive. Although macrocyclic crown ethers have an effect on the initiation and propagation steps, size and composition of these additives do not influence significantly the overall microstructure of the final polymer (Table I).

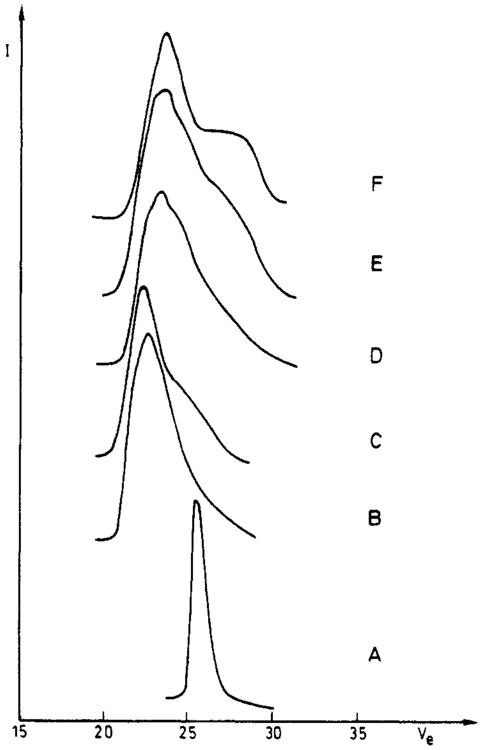

Figure 3. Size exclusion chromatograms of PMMA synthesized in THF at -20 °C. The initiator was (diphenylmethyl)sodium as modified by a series of crown ethers used in a 1/1 molar ratio: (A) DB-18-CE-6 ($\bar{M}_w/\bar{M}_n = 1.05$); (B) 18-CE-6 ($\bar{M}_w/\bar{M}_n = 3.0$); (C) B-15-CE-5 ($\bar{M}_w/\bar{M}_n = 2.9$); (D) 15-CE-5 ($\bar{M}_w/\bar{M}_n = 4.0$); (E) 12-CE-4 ($\bar{M}_w/\bar{M}_n = 4.4$); (F) no crown ether ($\bar{M}_w/\bar{M}_n = 4.5$).

Effect of Macrocyclic Crown Ethers on the MMA Polymerization Initiated by (Diphenylmethyl)sodium, in THF at -20 °C. Polarity of the solvent is of the utmost importance for the anionic polymerization of MMA. It is known that in apolar solvents dormant species are in equilibrium with active ones,[10d] and as recalled in this paper, complexation of the anionic species by μ-type ligands is effective in preventing secondary reactions from occurring in THF at -78 °C but not in pure toluene.

Table II and Figure 3 show that the MMA polymerization, in THF at -20 °C, is a very complex process, the conversion being limited and the chain length distribution being very broad and multimodal. The addition of the smallest macrocyclic crown ether available in this study (12-CE-4) has no beneficial effect, except if used in a 2-

Table III
Anionic Polymerization of MMA in Toluene Initiated by Ph_2CHNa in the Presence of DB-18-CE-6 at Different Temperatures

CE/I (molar ratio)	temperature (°C)	conv (%)	$10^{-3}\bar{M}_{n,exp}$	$\bar{M}_w/\bar{M}_n$	initiation efficiency	T_g (°C)		microstructure (%)		
						i	m	i	h	s
1.0	0	98.0	8.5	1.20	0.91	98	109	17.3	34.0	48.7
2.0	0	100.0	8.5	1.05	0.91	98	110	17.5	34.0	48.5
1.0	+25	99.0	10.5	1.40	0.74	113	123	12.5	36.0	51.5
2.0	+25	100.0	10.5	1.30	0.74	112	124	10.5	36.5	53.0
4.0	+25	100.0	10.0	1.15	0.78	112	125	11.5	34.0	54.5

fold molar excess toward the initiator (Table II). This crown ether, though specific toward Li^+, could form "sandwich" 2/1 complexes with bigger cations. The initiator efficiency is, however, low (0.46), which is also the case when the next 15-CE-5 crown ether (in an increasing size scale) is used in stoichiometric amount. Increased by a factor of 2, the amount of 15-CE-5 improves significantly the monomer conversion from 79 to 95%, the initiator efficiency from 0.45 to 0.60, and the width of the molecular weight distribution ($\bar{M}_w/\bar{M}_n$ decreases from 4.0 to 3.0). In contrast to toluene, when THF is the solvent, using an excess of the Na binding crown ether has an extra beneficial effect compared to the stoichiometric amount. When the size of the macrocyclic ligand is further increased (18-CE-6), the polymerization is now complete (100%) for the same polymerization time. The polydispersity can be as low as 1.5, but the initiator efficiency remains too low, i.e. 0.66 at best compared to 0.93 in toluene (Tables I and II). By reference to Table I, the control of the anionic polymerization might still be enhanced by incorporating aromatic moieties in the structure of the crown ether. Although substituting 15-CE-5 by B-15-CE-5 has no noticeable effect, the MMA polymerization is under complete control when DB-18-CE-6 is used instead of its aliphatic counterpart. All the experimental criteria tend to ideal values: 100% conversion, $\bar{M}_w/\bar{M}_n = 1.05$ (Figure 3), and initiator efficiency of at least 95%, i.e. the highest value observed in this work. Very interestingly, the PMMA microstructure is practically independent of the solvent when a macrocyclic crown ether is added to the initiator (compare Tables I and II).

Effect of Temperature on the MMA Polymerization Initiated by (Diphenylmethyl)sodium, in the Presence of Macrocyclic Crown Ethers in Toluene and THF. Promoting a living mechanism in toluene at −20 °C is already a remarkable improvement in the control of the anionic polymerization of MMA. That beneficial effect due to the complexation of the metal counterion by an appropriate crown ether is far more spectacular than that exhibited by a μ-type ligand.[10c] Nevertheless, maintaining a living polymerization at 0 °C and still better at 25 °C is of a paramount importance for the convenience and the economy of a production process. It is the reason why the anionic polymerization of MMA has been performed at 0 and 25 °C, respectively, in the presence of DB-18-CE-6, which has shown the highest efficiency at −20 °C.

Table III indicates that when the polymerization is promoted by (diphenylmethyl)sodium in toluene at 0 °C, the results are exactly the same as those reported at −20 °C, all the other conditions being the same (Table I), i.e. an initiator efficiency of at least 90% and a molecular weight distribution in the range from 1.2 to 1.05. Polymerization has proved to be living at −20 °C and from the comparison of Tables I and III, it should still be so at 0 °C. When the polymerization temperature is raised up to 25 °C, the initiator efficiency drops dramatically down to ca. 75%, which is good evidence for the occurrence of secondary reactions. Using an excess of crown ether compared to a 1/1 complex does not improve the initiator efficiency although it leads to a significantly narrower molecular weight distribution.

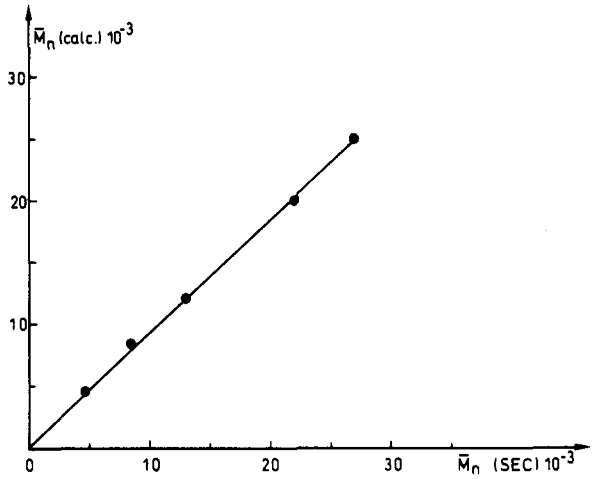

Figure 4. Dependence of experimental $\bar{M}_n$ as determined by SEC on $\bar{M}_n$ values calculated from the monomer/initiator ratio and the monomer conversion. Experimental conditions: THF; 0 °C; initiator, (diphenylmethyl)sodium as modified by a 2-fold molar excess of DB-18-CE-6.

Moreover, when toluene is substituted by THF, conclusions regarding the effect of temperature are still valid. Indeed, at 0 °C, the main characteristics of the MMA polymerization are not different from those reported at −20 °C. Since the living character has not been proved in THF at −20 °C, a series of polymerizations has been carried out in that solvent at 0 °C. Figure 4 shows a very good agreement between the experimental molecular weight (at 100% monomer conversion), as determined by size exclusion chromatography, and the values calculated from the monomer/initiator molar ratio. The slope of that plot allows an average initiator efficiency of 0.90 to be calculated. Thus at least in a molecular weight range up to 30 000, the polyaddition obeys a living mechanism. For the sake of comparison, it is worth noting that when MMA is polymerized in THF at 0 °C in the absence of a crown ether, the monomer conversion is limited to ca. 10% and only oligomers are recovered. The control of the living character of anionic polymerization of MMA is however lost again when the temperature is further increased from 0 to 25 °C. This probably indicates that either the Na^+/crown ether complex is no longer stable enough or the ligated sodium counterion does not block anymore enough space area around the active ion pairs.

Discussion

Complexation of a metal cation by a ligand is an enthalpy-driven process since the entropy contribution has systematically a destabilizing effect ($\Delta S < 0$). Therefore, the enthalpy change has to be negative as well. In a solvent of low solvating power, such as toluene, the enthalpic stabilization is expectedly high since the expenditure of energy in the cation desolvation step is very small. From

Table IV
Anionic Polymerization of MMA in THF Initiated by Ph_2CHNa in the Presence of DB-18-CE-6 at Different Temperatures

CE/I (molar ratio)	temperature (°C)	conv (%)	$10^{-3}\bar{M}_{n,exp}$	$\bar{M}_w/\bar{M}_n$	initiation efficiency	T_g (°C)		microstructure (%)		
						i	m	i	h	s
1.0	0	100.0	8.5	1.15	0.91	106	115	10.0	38.0	52.0
2.0	0	100.0	8.1	1.05	0.96	106	115	9.0	38.0	53.0
2.0	+25	100.0	10.5	1.40	0.74	103	107	16.0	32.0	52.0
4.0	+25	100.0	10.2	1.10	0.75	103	108	16.5	32.0	51.5

Table I, it is obvious that the Na counterion in toluene is complexed by all the crown ethers that have been tested. Actually, the microstructure of PMMA changes dramatically when one crown ether is added per Na cation. Whatever the crown ether used, the isotactic content drops from 60.5% down to ca. 9.5% whereas the syndiotactic triads increase from 8.5% up to 56%. The coordination of the Na$^+$ counterion with the penultimate ester group is very weak, and the latter could be displaced by any stronger ligand (crown ether or THF), thus restoring the syndiotactic microstructure (Table II). The so-formed complexes are not necessarily able to prevent the side reactions from occurring. Only well-choosen binding agents can give a living character to the polymerization reaction.

The stability constants of Na$^+$/18-CE-6 or Na$^+$/DB-18-CE-6 complexes in THF are reported in the literature.[17,18] The values of log K_s are 5.59 and 4.60, respectively. We can easily see that the formation of these crown ether complexes is highly favored, despite the large amount of THF present, which competes with the macrocyclic ligand to form a highly solvated crown ether free cation. Nevertheless, solvation of Na$^+$ by THF or complexation by a crown ether has a quite comparable effect on the incorporation mode of the monomer into the growing chain.

Solvation of the counterion usually increases the reactivity of the ion pairs which might thus participate more actively in secondary reactions at the expense of the propagation step. When solvation is promoted by a cation-binding macrocyclic crown ether, polymerization of MMA is actually better controlled as supported by an increasing initiator efficiency and a decreasing molecular weight distribution. It should accordingly be concluded that the beneficial effect of the crown ether on the course of the MMA polymerization is of a steric origin rather than due to a change in the electronic distribution around the ion pair.

It has been suggested elsewhere that 2/1 complexes might have a sandwich structure in contrast to the "coin-in-the-hole" model accepted for a 1/1 complex.[19,20] A sandwich structure, in which the metal ion is located between two ligand molecules should deeply affect the reactivity of the ion pairs and accordingly the polymerization process. The absence of any effect upon addition of 2 equiv of macrocyclic ligand instead of 1 suggests a high stability of the 1/1 complex and the relative inability of a second crown ether to compete with the first one for the cation complexation.

Although increasing the size of 15-CE-5 by addition of a benzene group does not significantly affect the MMA polymerization in toluene, substitution of 18-CE-6 for 15-CE-5 allows a further remarkable improvement in the molecular weight distribution (1.7 to 1.4) and the initiator efficiency which increases from ca. 0.75–0.80 up to at least 0.90. Using dibenzo-substituted 18-CE-6 does not change the initiator efficiency anymore but still decreases the molecular weight distribution (1.4 to ca. 1.1). The change due to the aromatic substituents should be attributed to ligand bulkiness rather than to an electronic effect. Indeed the electron-withdrawing effect of the benzo groups reduces the electron-donor ability of the oxygen atoms, resulting in a relatively weaker metal–ligand interaction (see log K_s values previously mentioned). That deleterious electronic modification has no effect on the MMA polymerization, indicating that the binding ability of the DB-18-CE-6 is not involved but rather its bulkiness. An additional increase in the crown ether size (DCH-24-CE-8) does not change the situation significantly since results are quite similar to those reported for unsubstituted 18-CE-6.

In THF, the beneficial effect of crown ethers is still effective. Compared to toluene, formation of the Na$^+$/crown ether complexes should be affected by the necessity for the crown ether to displace THF molecules solvating the sodium counterion. As far as smaller cyclic polyether ligands are concerned (12-CE-4 and 15-CE-5), the Na$^+$/crown ether molar ratio now has an effect since the control on the MMA polymerization is improved when a 2/1 ratio is used rather than the 1/1 ratio. As expected, the "coin-in-the-hole" model does not fit a possible 1/1 Na$^+$/12-CE-4 complex, because the hole diameter of the crown ether (≤1.8 Å) cannot easily accommodate the Na$^+$ counterion (1.9 Å).[21] 15-CE-5 exhibits a larger cavity (2.1 Å), but the stability might not be optimum, possibly as a result of the ligand being unable to reduce the two-dimensional cavity size by twisting to adjust to the size of the smaller cation. It is only when the crown ether is as large as DB-18-CE-6 (hole of 4 Å) that the control is optimum with an ideal initiation efficiency (0.97), a very narrow molecular weight distribution ($\bar{M}_w/\bar{M}_n = 1.05$), and a quantitive yield. When unsubstituted 18-CE-6 is used, the results are less favorable, although the stability of the complex is expectedly higher in the absence of electron-withdrawing benzo groups. This supports again the critical effect of the steric hindrance promoted by the ligand in the immediate vicinity of the active species. When 18-CE-6 or DB-18-CE-6 is considered, the use of the ratio Na$^+$/CE = 2 or more has no effect, again suggesting a higher stability of the 1/1 complex compared to smaller cyclic polyethers. The large cyclic polyethers are supposed to be wrapped around the cation to form a three-dimensional cavity with all oxygen atoms coordinated to the cation. Since crown ether is expected to compete with THF for solvating the Na counterions, it is not surprising that the microstructure of PMMA is unaffected by the addition of the macrocyclic ligand when THF is the polymerization solvent.

The deleterious effect of increasing temperature (from 0 to 25 °C) observed in THF, as well as in toluene as a solvent, could be explained by the formation of a crown ether free propagation species (contact ion pair), which is probably not very stable and readily leads to a dead chain. This is also easily consistent with a higher activation energy of the noxious side reactions compared to that of polymerization.

$$\underset{\text{crown ether contact ion pair}}{\mathrm{PMMA^{-}\cdot(Na/CE)^{+}}} \rightleftharpoons \mathrm{CE} + \underset{\text{contact ion pair}}{\mathrm{PMMA^{-}\cdot Na^{+}}} \rightarrow \text{dead chain}$$

This could be an explanation of the higher polydispersity ratio and lower efficiency factor observed when reactions were carried out at room temperature in the presence of 2 equiv of ligand (Tables III and IV). Increasing the amount of ligand to 4 equiv drives this equilibrium in the other direction and favors again the formation of a crown ether contact ion pair.

Conclusion

Experimental data reported in this paper strongly support that ligated anionic initiators are highly efficient tools for controlling the living polymerization of methacrylic esters, such as MMA. Clearly, specific crown ethers can bring about better benefits than those already promoted by inorganic-type ligands. When structure and size of the organic ligand are properly balanced, the metal cation is incorporated into a stable complex and is surrounded by a steric barrier blocking enough space area around the active ion pairs to minimize undesirable side reactions even at temperature as high as 0 °C, independent of solvent polarity.

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