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1. INTRODUCTION

The ring-opening polymerization of aliphatic cyclic carbonates first was explored with K_2CO_3 as initiator in the melt. The polymers suffered from severe decarboxylation and instead of a polycarbonate a polyoxethane was obtained. In the meantime other initiators have been developed which allow a non-destructive polymerization of aliphatic as well as aromatic cyclic carbonates. The basis of this research is a broad variety of cyclic carbonates available from Bayer AG, Germany.

2. CARBANIONIC INITIATORS

Sec.-BuLi was investigated first as an initiator for the anionic ring-opening polymerization of aliphatic cyclic carbonates. In particular, the polymerization of dimethyltrimethylene carbonate (DTC) was studied which results in a high molecular weight polymer in the regime of kinetic control; this is achieved in apolar solvents and at low temperatures. In the regime of thermodynamic control, a ring-chain equilibrium is obtained which follows the concentration dependence of the cyclic oligomers predicted by Jacobson and Stockmayer (1). Beside DTC, a series of other six membered cyclic carbonates may be used as monomers. Unless severe steric hindrance occurs, a statistical copolymerization of six membered cyclic carbonates is obtained with Bernoullian distribution (2).

Instead of sec.-BuLi, polymeric carbanions such as polystyryl, polybutadienyl and polyisoprenyl anions may be used as an initiator to obtain the respective blockcopolymers (3).

The reaction of the active species with $ClP(O)(OR)_2$ and subsequent ^{31}P -NMR spectroscopy proves the alcoholate being operating (4). Consequently, alcoholates such as BuOK may be used as initiators as well as "living" poly- ϵ -caprolactone obtained with an anionic initiator.

3. ELECTRON TRANSFER REAGENTS

Instead of carbanionic initiators electron transfer reagents such as naphthalene potassium act as initiators for the ring-opening polymerization of cyclic carbonates. Investigation of oligomers obtained in the initial stages of the polymerization by means of gel permeation chromatography and a UV detector revealed the naphthalene being incorporated into the growing chain (5). There are indications, however, that polymers may be obtained which do not contain any naphthalene. In this case, the initiation has to be considered to occur via an electron transfer reaction.

4. INSERTION CATALYSTS

As insertion initiators $Sn(Bu)_2(OCH_3)_2$, $Zn(C_2H_5)_2$, and $Al(OsecBu)_3$ were applied (5). Whereas the tin catalyst results in a ring-chain equilibrium with a relatively broad molecular weight distribution of the polymers, the zinc and aluminium initiators hardly result in any back-biting reaction; only traces of oligomers are observed and the molecular weight distribution of the polymer is rather narrow. The multifunctional initiators only act monofunctionally which is deduced from the molecular weight of the polymers obtained. Time conversion curves show that the aluminium initiator as fast and a 100% conversion is reached after about 1h. The initial rate obtained with the zinc catalyst in THF is comparable with that obtained with the former initiator; the maximum yield reached, however, is ca. 70%. In toluene, the zinc initiator is much slower and with the tin initiator even after 200 h no conversion was observed. This is probably due to the high covalent character of the bonds of the latter initiator.

Whereas the aluminum initiator does not show any transesterification reactions the proportion of these reactions increases under suitable conditions when zinc and even more when tin is used as initiator. Under these conditions (100h, 80°C) sec.-BuLi is also a perfect transesterification catalyst.

5. TETRAPHENYLPORPHYRENE ALUMINUM ORGANIC INITIATORS

The Inoue catalyst of the tetraphenylporphyrine aluminum type with an additional ligand R at the aluminium may act as an efficient initiator for the ring-opening polymerization of cyclic carbonates. If R is a methyl group, no polymerization occurs. If R, however, is chlorine, a high molecular weight polymer is observed in a slow reaction at 50°C.

Particularly suitable initiators are obtained when R is alkoxy. In methylene chloride as a solvent in high yield high molecular weight polymers are obtained exerting a unimodal molecular weight distribution (5).

6. GROUP TRANSFER INITIATORS/CATALYSTS

Group transfer polymerization (GTP) initiators for the polymerization of cyclic carbonates are of particular interest when blockcopolymers with acrylic monomers are to be synthesized. Webster was the first to disclose the living polymerization of methylmethacrylate with a methyl trimethylsilylketene acetate as initiator in conjunction with nucleophilic catalysts. Using silylated alcohols in conjunction with tetrabutylammoniumfluoride the polymerization of cyclic carbonates is achieved; with cyanide as a nucleophile the ring-opening polymerization does not proceed. It is remarkable however, that even with hydrated tetrabutylammoniumfluoride cyclic carbonates may be polymerized resulting in a narrow molecular weight distribution. This initiator, however, must not be used for the preparation of a blockcopolymer with the first block being polymethylmethacrylate. In this case, a water-free system has to be applied and tris(dimethylamino)sulphonium trimethylsilyl difluoride (TASF) is a suitable initiator (6).

We were able to prove by NMR spectroscopy that the initiating species of the living poly-MMA chain upon addition of DTC is the carbanion which is transformed to the alcoholate anion with a metal-free counter ion (5).

In the same way as cyclic aliphatic carbonates cyclic aromatic carbonates may be polymerized (7). There are para- as well as ortho-derivatives available. The active species is a phenolate. It is notable, however, that some derivatives show a high tendency for the formation of cyclic dimers and some are not eligible for polymerization at all. Molecular modelling computations indicate in these cases that severe steric hindrance might be the reason.

7. LITERATURE

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INTRODUCTION

The important development of polyalkyl(meth)acrylate-based products during the last decade¹ has been due both to the growth of well-established general purpose polymers (i.e. polymethylmethacrylate PMMA, and rubbery or adhesive polyalkylacrylates such as ethyl, butyl and ethylhexyl derivatives), and the surge of new materials for highly specialized technologies (f.i. optical fibers, microlithography, biomedical hydrogels). All of these products are currently obtained by free radical polymerization, with all the drawbacks inherently involved in that type of process: i.e. lack of kinetic and structural control of the reaction mechanism, and of the polymer architecture and molecular parameters. Several strategies have thus been envisioned to meet that macromolecular engineering challenge, and up to now, the more efficient one has been the application of the nucleophile-assisted "living" group transfer polymerization (GTP) of unsaturated carbonyl-conjugated monomers.² Although that technique offers obvious advantages, in particular a polymerization temperature above room temperature, it does not allow the combination with monomers lacking a carbonyl conjugated group, such as styrenes and dienes. Since in principle, the presence of a stabilizing electron-withdrawing substituent on these (meth)acrylic esters make them fit for an anionic polymerization mechanism, that possibility has been actively revisited during the last decade, despite the already recognized difficulties arising from secondary reaction of the carbanions with the carbonyl groups and acidic α -hydrogen present. Up to now, the best general answer to that problem has been the use of different ligands able to control the electronic and (mainly) steric environment of the growing ion-pair^{3,4,5}: μ -complexes with metal derivatives have proved to be quite efficient, lithium chloride (LiCl) appearing as a specially interesting candidate on practical grounds.⁶ The efficiency of that ligand has already been convincingly demonstrated,^{7,8,9} in terms of controlling not only a perfectly living homopolymerization of different methacrylates and tertiary or secondary acrylates in solvents of variable polarity, but also the precisely tailored synthesis of different block copolymers^{10,11} including poly(meth)acrylate and polyhydrocarbon blocks (styrenes, dienes). The present paper describes the extension of the performances of the LiCl-modified initiators to the controlled synthesis of new molecular architectures, including star-block copolymers and α - or ω -end functionalized building blocks such as macromonomers for polyaddition and polysubstitution reactions.

EXPERIMENTAL

Solvents and monomers were purified and dried using current techniques in anionic polymerization, in particular treatment of the esters with aluminum alkyls.¹² LiCl was a previously dried analytical grade salt. All reactions were carried out under nitrogen, in flamed glass reactors, using stainless steel capillary and rubber septums for injections and transfers. Transalcoholysis and hydrolysis of tBA blocks was performed in the presence of p.toluene sulfonic acid as described elsewhere.¹⁰ Products were characterized by usual procedures, using SEC (size exclusion chromatography: Hewlett-Packard 1090 equipped with ultraviolet detector, NMR spectroscopy (Bruker 400), an automated dynamic viscoelastometer (DMA), tensile testers, and transmission electron microscopy (TEM).

Star-block copolymers

The possibility of closely controlling the essential molecular parameters (i.e. number mean molecular weight \bar{M}_n , and a low dispersity $\bar{M}_w/\bar{M}_n = MWD$) of homopolymers and block copolymers of alkyl(meth)acrylates by using a molar excess of LiCl (ca. 10) versus the initiator (usually sec.butyl lithium reacted with α -methylstyrene or diphenylethylene), has already been demonstrated.⁹ In particular, well-defined diblock copolymers of tBA with both styrene or MMA have been prepared in THF, and it must be stressed that the so obtained PMMA blocks exhibit an essentially (70-80 %) syndiotactic structure providing for an appealing Tg value close to 130°C. The block polymerization of tBA and MMA can be carried out in both directions, although slightly more delicate in the one $MMA \rightarrow tBA$, due to a selective back-biting reaction which also prevents random copolymerization.^{13,14} Since these reactions generally have to be performed in the sequence of decreasing monomer reactivities (i.e. styrene first), and since potentially feasible coupling reactions involve temperature conditions where the anions might be killed, it appeared that the easiest access to multiblock structures might be through addition of a difunctional monomer, promoting the formation of "arm-first" core-star architectures. That technique, developed by Rempp et al. for styrenes¹⁵ and applied by Sogah in GTP of (meth)acrylates,¹⁶ is indeed simple and efficient, using for instance ethylene(glycol) bismethacrylate (EBMA). Table I lists the structural characteristics of a series of star-block copolymers of different types obtained by that approach.

Table I: Characteristics of star block copolymers
(α MSLi/10 LiCl in THF at -78°C, 99-100 % yield)

EBMA I	$\bar{M}_n \times 10^{-3}$ for Arm (MWD)	% coupling	$\bar{M}_n \times 10^{-3}$ for Star (MWD)	
				"n"
PS-b-PtBA				
1	0.97-0.70 (1.12)	77	ca. 6	ca. 3
5	0.97-0.80 (1.12)	98	35.5 (b)	20
10	0.97-0.80 (1.10)	99	59 (b)	31
1	5.7-6.8 (1.06)	92	35 (1.15)	2.8
5	5.2-6.4 (1.10)	98	59 (1.15)	5.0
10	6.2-6.8 (1.07)	98	73 (1.16)	5.6
4	19 - 47 (1.15)	80	225 (1.25)	3.4
20	25 - 40 (1.18)	81	404 (1.20)	6.2
PMMA-b-PtBA				
10	24 - 97 (1.08)	73	630 (1.25)	5.2

These first results call for a number of remarks:

- for sufficient arm lengths (i.e. above a few thousands), the products remain soluble even upon centrifugation at 1500 rpm;
- the polydispersity of the star-copolymers remain nearly as narrow as the one of the starting arm;
- expectedly, the coupling efficiency is inversely dependent upon \bar{M}_n of the arm; however, it remains acceptable and can probably be optimized;
- the apparent mean number of arms "n", simply calculated from the ratio of arm and star \bar{M}_n 's as determined from SEC traces has of course no absolute meaning, since there is no corresponding increase of the hydrodynamic volume when increasing that number of arms. Other in-depth investigations will be necessary to solve that problem;
- it is worth mentioning that by GTP, stars with up to 200

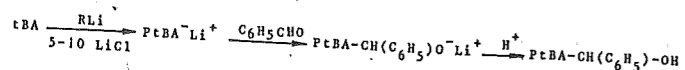
arms per core could be produced (using a 4-fold excess of EBMA), while in this case, the reaction seems approximately limited to an asymptotic value of about 6 arms, possibly indicating a more pronounced intramolecular propagation within the core.

Remembering now that PtBA blocks can quantitatively and selectively be converted into other polyacrylates by transesterification, the corresponding star-thermoplastic elastomers (TPE) including n-butyl or 2-ethylhexylpolyacrylate sequences are in an easy reach, and their main physico-mechanical properties have been investigated. DMA experiments confirm very well the biphasic character of these s-TPE (maxima of $\tan \delta$ and sharp decrease in $\log E'$ at -19.5 and +103°C respectively (at 1 Hz) for the P(S-b-nBA) star), which has also been observed directly by TEM as ca. 20 nm domains. The tensile properties evidence the TPE characteristic behaviour, with σ_B values ca. 1.0 to 1.5 Kg/mm² and ϵ_B 's comprised between 300 and 500 % confirming values obtained on triblock copolymers of polyhexamethylene-dimethacrylate with n-butylmethacrylate by GTP technique.¹⁶ Finally, amphiphilic polyacrylic acid (PAA)-based stars can as easily be obtained by simple hydrolysis of the above structures, providing for new materials prone to a number of specific applications.

End-functionalized macromolecules

Obviously, the "living" poly(meth)acrylates mentioned above, instead of being used in block copolymers, can also be end-functionalized by reacting their terminal carbanion(s) with appropriate compounds. A very broad array of α -monofunctional and α, ω -difunctional macromolecules, which can be useful in polyaddition and polysubstitution reactions, so become accessible in a rather straight-forward manner, which will be illustrated here by three specific examples.

Starting from a difunctional initiator (i.e. naphthalene-Li/10 LiCl) of tBA polymerization, and deactivating the resulting "living" polymer with a large excess of CO₂, one efficiently obtains (98 % yield, 90 % efficiency) a dicarboxylic telechelic PtBA displaying a functionality of 1.95 and a MWD of 1.3 for a 16000 M_n. Exactly neutralized with a Ba⁺⁺ salt, it generates an halatotelechelic polymer which is one of the first ion-containing polymers to exhibit a small and large scale regular organization¹⁷ as seen from its SAXS diagrams (8 Bragg's spacings going from 14 to 67 nm, probably indicating an overall hexagonal lattice). Another example is their end-functionalization by benzaldehyde, yielding mono- or difunctional hydroxyl terminated polymers or oligomers, depending on the type and amount of the initiator used:



The corresponding hydroxyl telechelic structures, whatever the nature of the monomer used, can obviously be used in many subsequent reactions, such f.i. in polyurethane chemistry.

Last but not least, well-tailored macromonomers can be readily obtained along the same lines, as already demonstrated by Rempp et al., who synthesized ω -styryl- and ω -methacryloyloxy-PtBA, using p.vinylbenzylchloride and chlorodimethylsilylpropyl methacrylate, respectively.¹⁸ These procedures have now been extended by the use of other electrophiles, i.e. acid chlorides such as methacryloyl or 4-vinylbenzoyl chlorides (preferably in conjunction with benzaldehyde as mentioned above), 4(chlorodimethylsilyl)styrene, p.vinylbenzylbromide, etc... Such macromonomers, based on methacrylates as well as on tBA, represent of course a source of comb copolymers readily available from radical initiation. In that case again, the post-hydrolysis of the PtBA branches may lead to very interesting amphiphilic materials, and the same remarks may apply to the networks formed from α, ω difunctional (bis)macromonomers. In all of the cases implied in these two last classes of products, narrow MWD (below 1.2, often below 1.1, from SEC), and high efficiency (functionalization between 90 and

100 %, from NMR spectroscopy) were currently achieved in a range of M_n between 2.000 and 20.000.

IN CONCLUSION, one can safely say that "living" anionic polymerization techniques are becoming a key tool in the macromolecular engineering of polyalkyl(meth)acrylate-based materials. These advances have been made possible by the coordination chemistry of ligands influencing the electronic distribution and the steric environment of the growing ion-pair; more research is now needed to better understand and further develop these coordinative effects.

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EFFECT OF LITHIUM CHLORIDE ON THE KINETICS AND MWD IN THE ANIONIC POLYMERIZATION OF (METH)ACRYLATES

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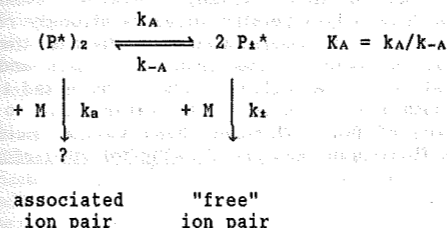
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INTRODUCTION:

The anionic polymerization of methacrylates proceeds in an ideal way when larger counterions (e.g. Cs⁺) are used in polar solvents (e.g. THF) at temperatures below -60 °C. This was demonstrated by first-order kinetics of monomer conversion, a linear dependence of the number-average degree of polymerization on conversion and narrow molecular weight distributions (MWD).^{1,2} It was shown that the active species are externally solvated contact ion pairs.

The existence of associated chain ends was demonstrated kinetically by a decrease of the propagation rate constants, k_p , with increasing concentration of active centres, [P*], even in the presence of common-ion salt.³⁻⁵ This is true for Li⁺ and Na⁺ counterions and is confirmed by viscosity measurements on living and terminated PMMA-Li⁺.⁶ The kinetic data indicate that the reactivity of the associates is much lower than that of the "free" ion pairs.



The dynamics of the association equilibrium has a significant influence on the MWD of the polymers formed. Although termination is virtually absent, the MWD for polymers formed with Li⁺ counterion in THF at -65 °C show polydispersity indices which decrease with monomer conversion and finally reach values of $M_w/M_n \geq 1.3$. We assume that this is due to a rate of interconversion of associated and non-associated ion pairs which is comparable to the rate of monomer addition. It was shown earlier that this can lead to a considerable broadening of the MWD's.^{7,8} For tBMA association is much less pronounced; consequently the MWD's are very narrow ($M_w/M_n \leq 1.05$).⁹

For acrylates the polymerization mechanism has not been understood well. It was not possible to reproducibly prepare polymers with narrow MWD for a long time. Only recently, Teyssié and coworkers¹⁰ reported on the drastic effect of alkali halogenides (especially LiCl) on the polymerization of tert-butyl acrylate, leading to polydispersity indices of ca. 1.2. The authors suggested the formation of adducts, thus preventing termination or transfer reactions.

We wish to report on kinetic experiments in the anionic polymerization of methyl methacrylate (MMA), tert-butyl methacrylate (tBMA), and tert-butyl acrylate (tBuA), in the absence and presence of LiCl. We shall demonstrate how kinetics of propagation and termination as well as the MWD are controlled by multiple equilibria between associated and non-associated ion pairs and ion pair-ligand adducts.

RESULTS AND DISCUSSION:

Firstly, kinetic experiments of the anionic polymerization of MMA and tBMA were performed in THF at -65°C in the presence of LiCl. Methyl- α -lithioisobutyrate (MIB-Li), which is a model of the active centre, served as the initiator. The ratio of the concentrations of lithium chloride to active centres, $R = [LiCl]/[P^*]$, was varied from 0 to 12.

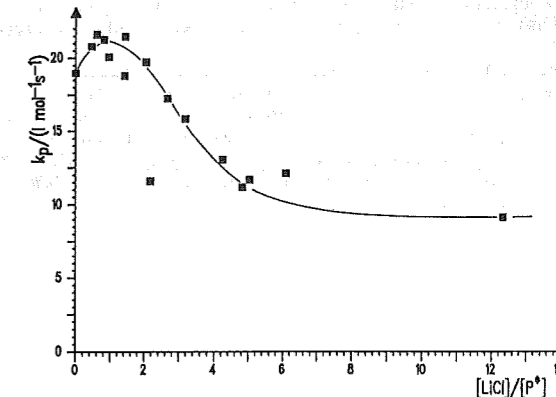
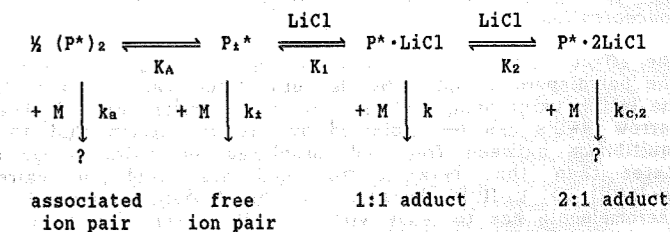


Fig. 1: Dependence of the rate constant of polymerization on the concentration of LiCl in the anionic polymerization of MMA with Li⁺ in THF at -65°C.

Fig. 1 shows that LiCl exerts a significant effect on the kinetics. In the polymerization of MMA the rate constants slightly increase for $R < 1$ and then gradually decrease to a value of ca. 50% for $R = 12$. This result is consistent with the formation of adducts of the active centres with LiCl, the formation of which competes with association:



It is necessary to assume two different complexes in order to explain the maximum of k_p for $R=1$. The 2:1 adduct is assumed to have only a low reactivity. The same kinetic behaviour was observed upon addition of THF in the polymerization of styrene in benzene,¹¹ the monoetherate having a higher reactivity than the dietherate.

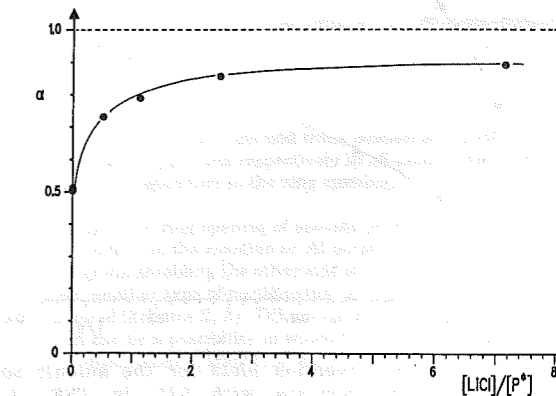


Fig. 2: Fraction of non-associated species as determined by viscometry of living and terminated polymer solution of PMMA-Li⁺ as a function of LiCl concentration.