38. Boileau, S.; Kaempf, B.; Raynal, S.; Lacoste, J.; Schué, F. *J.Polym.Sci. Polym.Lett.Ed.*, **1974**, *12*, 211.
39. Jedliński, Z.; Kowalczuk, M. *Macromolecules* **1989**, *22*, 3242.
40. Jedliński, Z.; Kowalczuk, M.; Kurcok, P.; Brzoskowska, L.; Franek, J. *Makromol. Chem.*, **1987**, *188*, 1575.
41. Jedliński, Z.; Kurcok, P.; Adamus, G. *Makromol.Chem.*, **1989**, *190*, 61.
42. Jedliński, Z.; Gaska, B.; Czech, A.; Janeczek, H., *in preparation*
43. Jedliński, Z.; Misiołek, A.; Kurcok, P. *J.Org.Chem.*, **1989**, *54*, 1500.

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POLYMERIZATION OF GLYCOLIDE PROMOTED BY ω-Al-ALKOXIDE POLY(ε-CAPROLACTONE) MACRO-INITIATORS AND FORMATION OF STABLE COLLOIDAL DISPERSIONS

Ibrahim Barakat, Philippe Dubois[a)], Robert Jérôme, Philippe Teyssié* and Mieczyslaw Mazurek[1]

Center for Education and Research on Macromolecules (CERM), University of Liège, Sart-Tilman, B6, 4000 Liège, BELGIUM

[1]*3M Adhesive Technologies Center*
3M Center, St. Paul, MN 55144, USA

ABSTRACT

Block polymerization of glycolide (GA) and ε-caprolactone (ε-CL) has been initiated with aluminum alkoxides, such as $Al(O^iPr)_3$ and Et_2AlOCH_2X (where X = $-CH_2-Br$ and $-CH_2O-C(O)-C(Me)=CH_2$), in THF at 40°C. Structure and composition of block copolyesters have been characterized with respect to the molecular weight by NMR spectroscopy and thermal analysis. Copolymerization is typically living, so that block copolyesters have been synthesized with predictable molecular weight and composition. The inherent insolubility of polyglycolide block is responsible for the heterogeneity of the polymerization medium and formation of stable, non-aqueous colloidal dispersions. This effect is especially pronounced at high GA/ε-CL molar ratios. Colloidal dispersions have been analyzed by transmission electron microscopy (TEM) and photocorrelation spectroscopy (PCS).

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INTRODUCTION

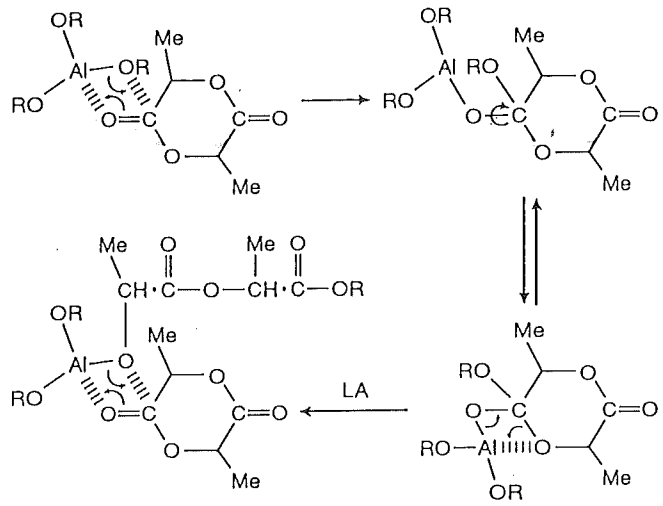
Unique biodegradability of polymers containing aliphatic ester units under well-controlled conditions, and bioinertness of the products of their degradation warrants continued interest in the synthesis and the mechanistic studies of this group of polymers.

Particular interest in polyglycolide (PGA) and copolymers of glycolide (GA) and lactides (LA) are due to their usefulness in medicine, particularly as surgical sutures, and in sustained drug delivery. In addition to satisfactory mechanical properties, these copolymers have a low immunogeneity and an extremely low toxicity. ε-Caprolactone (ε-CL) is another building block of relatively low toxicity and relatively fast biodegradability (Refs. 1-6). With likely growing interest in biodegradable polymers of low toxicity there is a need to explore the use of copolymers of ε-CL, GA and LA with proper structures.

Lactones, lactides and glycolide have been polymerized with various initiators according to different mechanisms (Refs. 7,8). Some of us have been interested for several years in the tailoring of poly (ε-caprolactone) (PCL) and polylactides (PLA) by a "coordination-insertion" mechanism. Polymerization has first been initiated with bimetallic μ-oxo alkoxides (Refs. 9-11), that have later been advantageously replaced by metal alkoxides. Aluminum alkoxides have been investigated as initiators for homopolymerization of unsubstituted lactones and lactides, and for their copolymerization (Refs. 12-15). More recently, a special attention has been paid to the ring-opening polymerization of cyclic anhydrides (Ref. 16) and dioxopan-2-one (Ref. 17) initiated with aluminum isopropoxide. As a rule, polymers of a very narrow molecular weight distribution are formed according to a living mechanism that involves the insertion of the monomer (e.g. LA) into the "Al-O" bond of the initiator through the selective acyl-oxygen cleavage of the monomer (eq. 1).

Furthermore, functional aluminum alkoxides, such as $(C_2H_5)_{3-p}Al(ORX)_p$ where X is a functional group, have proved to be very successful in the synthesis of end-reactive PCL (Ref. 12) and PLA (Ref. 15). One end-group of the polyester is always alkoxide which becomes an alcohol group upon hydrolysis of the growing species (see eq.1).

The other end of the polymer chain is quantitatively terminated with an ester group, the alkoxy radical of which is derived from the ORX group of the initiator (X : halogen, tertiary amine, unsaturation...).



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With a few exceptions, there is a lack of pertinent data regarding the polymerization mechanism of glycolide in spite of the aforementioned unique biological properties. A need for kinetic and mechanistic studies is evident, particularly in view of the molecular engineering of polymers with unique biological tolerance. One of the factors contributing to a relatively poor representation of the literature data concerning homo- and copolymerization of glycolide is the very limited solubility of both monomeric glycolide and polyglycolide (PGA). Particularly high degree of crystallinity and insolubility of PGA make the mechanistic studies of the polymerization difficult. Most of the available data refer to bulk polymerization, with the exception of two papers by Kricheldorf *et al.* (Refs. 18,19) which deal with copolymerization of GA and ε-CL initiated with cationic, anionic and complexing agents in nitrobenzene and dioxane at high temperatures.

This paper focuses on some mechanistic aspects of the polymerization of glycolide with a special emphasis on the formation of block copolymers with well-defined structures. It is believed that the attachment of the growing PGA chains to polymer blocks characterized by good solubility in the polymerization medium might help to sustain the reaction in the homogeneous state thus facilitating the investigation of the mechanism of GA polymerization. Poly-ε-caprolactone appeared to be an appropriate candidate to perform such a homogenizing function because of its good solubility in the usual organic solvents and the capability of the Al

alkoxide end-group of the living PCL chains to initiate the polymerization of glycolide.

EXPERIMENTAL SECTION

Materials

Glycolide (GA) was purchased from Boehringer and purified by repeated dissolving in THF followed by filtration of the insoluble oligomers. Finally, the monomer was recrystallized from dry ether in order to eliminate glycolic acid. GA was dried for 24 h at 35°C under reduced pressure (10^{-2} mm Hg) before polymerization. ε-CL (Janssen Chimica) was dried over CaH_2 for 48 h at 25°C and distilled under reduced pressure prior to polymerization. Previously distilled aluminum isopropoxide (Aldrich) and triethylaluminum (Fluka) were dissolved in dry toluene. Solution concentration was measured by complexometric titration of Al by a standard solution of ethylene diamine tetraacetic acid (EDTA). 2-Bromoethanol (Aldrich) was repeatedly treated with a saturated aqueous solution of Na_2CO_3, dried over P_2O_5 and freshly distilled under reduced pressure. 2-Hydroxyethylmethacrylate (HEMA) (Janssen Chimica) was dried over molecular sieves (4 Å) at 25°C and distilled under reduced pressure just before use. THF and diethylether were dried by refluxing over a benzophenone-sodium complex and distilled under nitrogen atmosphere. Toluene was dried by refluxing over CaH_2 and distilled under nitrogen atmosphere.

Preparation of the initiators

Diethylaluminum alkoxides were prepared by slow addition of the selected alcohol previously dissolved in toluene, to an equimolar amount of $AlEt_3$ (eq. 2). The glass reactor was equipped with a rubber septum connected to a gas buret through an oil valve. It was previously flamed and purged with nitrogen. The reaction proceeded under vigorous stirring at room temperature. When the emission of ethane stopped, the initiator solution was kept stirred at 25°C for an extra hour.

$$(C_2H_5)_3Al + HO\text{-}CH_2\text{-}X \rightarrow (C_2H_5)_2\text{-}Al\text{-}O\text{-}CH_2X + C_2H_6 \qquad [2]$$

where X = $-CH_2-Br$: 1
$-CH_2-CO(O)-C(CH_3)=CH_2$: 2

Polymerization techniques

Polymerization was carried out in a previously flamed and nitrogen purged glass reactor equipped with a magnetic stirrer. Solvent, monomer and initiator were successively added through a rubber septum with a syringe or a stainless steel capillary.

Block copolymerization was carried out as follows. ε-CL polymerization was initiated with $Al(O^iPr)_3$ or with one of the two Al monoalkoxides (1 and 2) in THF at 25°C. A sample of PCL was withdrawn from the reaction flask and precipitated into cold heptane for characterization by size exclusion chromatography (SEC) and ^1H NMR analysis. A known amount of the living PCL solution was transferred to a 5 wt % solution of glycolide in THF at 40°C through a stainless steel capillary. Possible changes in the homogeneity of the polymerization medium was carefully observed. Polymerization was stopped by adding an excess (with respect to the initiator) of acetic acid (in THF) and the polymer was precipitated in cold n-heptane. After filtration and drying, the polymer was dispersed in toluene, and the insoluble unreacted monomer was removed by filtration. The polymer was coagulated by dropwise addition of heptane to a toluene solution. After filtration, it was dried under vacuum to a constant weight.

Analytical techniques

Molecular weight and molecular weight distribution of PCL were measured by size exclusion chromatography in THF (SEC : Hewlett-Packard 1090). The universal calibration curve was set up from the viscosimetric relationships, for PCL and polystyrene standards (PS) in THF at 30°C (Refs. 20,21) :

$$[\eta] = 2.49\ 10^{-4}\ M^{0.730} \qquad [PCL]$$
$$[\eta] = 1.25\ 10^{-2}\ M^{0.717} \qquad [PS]$$

Molecular weight of PCL was also calculated from ^1H NMR spectra on the basis of the relative intensity of the α-hydroxymethylene end-group and the ester methylene protons in the polyester chain. Good agreement was observed in all the cases for Mn values measured by SEC and NMR, respectively.

The primary structure of GA/ε-CL copolyesters was investigated by NMR spectroscopy. In addition to molecular composition, molecular weight and

nature of the end-groups of low molecular weight chains were analyzed. ^1H NMR spectra were recorded in $CDCl_3$ and in a $CDCl_3/CF_3COOH$ (V/V 2/3) mixture at 25°C, with a Bruker AM 400 apparatus operating at 400.13 MHz.

Size of copolyester micelles was measured by quasi-elastic light scattering (linear Brookhaven correlator BI2030) in toluene at a 0.1 % and 0.5 wt % concentration. These micelles containing systems were previously treated with ultrasonics for 30 min.

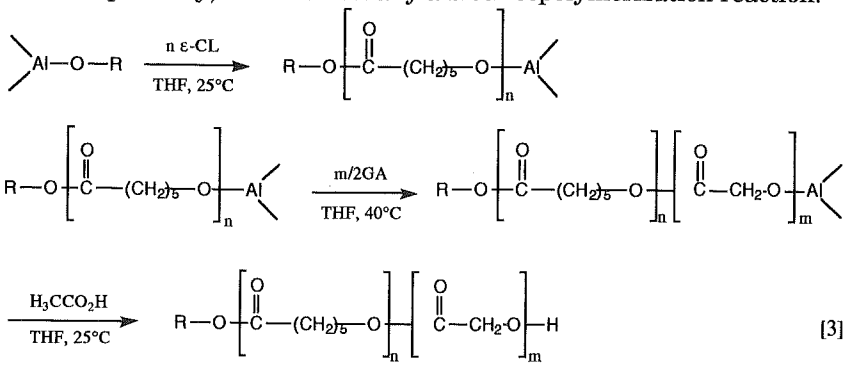
The auto correlation function was measured with an argon ion laser (20 mW) operating at 448 nm. Time dependent scattering light fluctuations were usually measured at 90°C.

DSC measurements were carried out with a DuPont 9000 apparatus. Samples of 10 mg were heated at a 20°C min^{-1} rate.

RESULTS AND DISCUSSION

Phenomenological description of the system

It is currently known that Al alkoxides are efficient initiators for the ε-CL and LA polymerization in toluene at 0°C and 70°C, respectively. The living polymerization mechanism has successfully been extended to both the random and block copolymerization of ε-CL and lactides (Refs. 13,22). This paper is concerned with the glycolide polymerization with Al alkoxides. Since no common solvent is known for PGA polymer it is proposed to keep the growing PGA chains in the polymerization medium by the use of a highly soluble macroinitiator. Equation 3 schematizes the reaction pathway, which is actually a block copolymerization reaction.



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For this strategy to be successful, a first monomer has to be polymerized in a living manner, so that the active species are able to initiate the GA ring-opening polymerization. In a preliminary experiment, a mixture of ε-CL and GA was attempted to be copolymerized with Al monoalkoxide 1 in THF at 40°C. GA was polymerized, as indicated by the rapid precipitation of the PGA polymer, while ε-CL remained essentially unreacted. From this experiment, it appears that glycolide polymerization can be initiated with $Et_2AlO(CH_2)_2Br$ 1 and that the Al alkoxide derived from this monomer is not active enough to initiate the ε-CL polymerization under the reaction conditions. This obviously does not preclude that polymerization of GA cannot be initiated by the Al alkoxide at the end of the living PCL chains. It is the reason why living PCL have been considered as potential macroinitiators for the GA ring-opening polymerization. An attractive feature of such an approach is that living PCL of narrow molecular weight distribution (Mw/Mn = 1.05-1.20) is easily prepared in both toluene and THF. As previously mentioned it is assumed that a macroinitiator with a high enough molecular weight is able to maintain PGA segments in solution, thus allowing the polymerization mechanism of glycolide to be investigated under suitable experimental conditions. However, a series of preliminary experiments has shown that an initially clear polymerization medium turns hazy as soon as the polymerization of GA takes place in THF. Increasing the molecular weight of the PCL macroinitiator does not prevent an apparent heterogeneity of the reaction medium to occur at the early stage of the copolymerization process. Surprisingly enough, once the polymerization medium has turned hazy, it does not change further even for relatively long periods of time, in most cases long enough for the glycolide conversion to be complete. This apparent stability of what appears to be a colloidal dispersion has prompted us to analyze in a systematic way a series of polymers, or copolymers formed under such conditions.

Table I shows that various Al alkoxides have been used to prepare living PCL macroinitiators of different molecular weights in THF at 25°C. Their use in the polymerization of GA at 40°C leads to the formation of stable colloidal particles whatever the degree of GA conversion. Consequently, the polymerization medium becomes translucent, and at a high GA/ ε-CL molar ratio the medium becomes hazy. When the copolymer formed upon reaction of the macroinitiator with GA is precipitated in heptane, a very fine precipitate is observed, which after drying is easily redispersed in toluene or chloroform by shaking.

Table I - Copolymerization of glycolide with living polycaprolactone in THF at 40°C

INITIATOR	MnPCL (1)	GA polymerization (2)		
		Conversion (%) (3)	Mn_{theor} (4)	Mn_{exp} (5)
$Al(O^iPr)_3$	10500	45	1350	1750
	32000	100	4000	3900
	2400	100	4000	4150
	4500	81	3240	2250
	16500	96	2880	2900
	28500	89	13350	13600
$Br(CH_2)_2OAlEt_2$	5500	12	480	420
	4000	73	2920	2700
	18500	58	1740	1500
	18500	68	4080	2800
$CH_2=CH(Me)CO_2(CH_2)_2OAlEt_2$	6000	30	1200	900
	9000	27	1080	800
	39000	96	62400	61000
	-	100	65000 + 10000 (6)	74500

(1) ε-CL polymerization in THF at 25°C, $[CL]_o$ = 0.8 mol.l^{-1}, quantitative conversion, Mn_{exp} measured by SEC, Mw/Mn ≃ 1.05-1.2

(2) GA polymerization in THF at 40°C, $[GA]_o$ = 0.5 mol.l^{-1}

(3) Conversion measured by gravimetry and confirmed by ^{1}H NMR spectroscopy

(4) Mn(theor) calculated as follows

$$Mn_{theor} = \frac{[GA]_o.116.X}{[Al]\,.\,100}$$ where X = monomer conversion

(5) Calculated from ^{1}H NMR spectra and Mn PCL

(6) GA resumption experiment

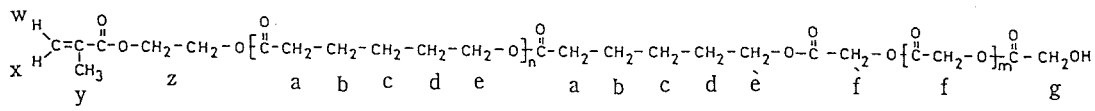
When the precipitate is redispersed in toluene and precipitated again by dropwise addition of heptane, an interesting phenomenon of "clearing" out occurs just before the precipitation starts. This might be attributed to a decrease in the particle size of the colloïd as the solvent becomes poor enough towards PCL.

Copolyester composition

Composition of crude copolyesters has been analyzed by ^{1}H NMR. When the copolymer is "dissolved" in $CDCl_3$, the signal characteristic of PGA can barely be detected although the signals of PCL and glycolide monomer are clearly observed (fig. 1). Upon addition of trifluoroacetic acid to the dispersion, the characteristic polyglycolide signals are well-defined (fig. 2), although when the GA/ε-CL molar ratio is high, signal intensity may be smaller than expected based on the PGA concentration. This could be a sign of the residual crystallinity in the PGA component of the copolymer. Indeed, the observations strongly suggest that the PGA segment of the copolymer cannot be detected by NMR in solvent which does not solubilize it completely. Crystallinity of the PGA hopomopolymers is well known (Ref. 23). The strong effect of the medium on the NMR of the PGA/ ε-CL copolymer provides a striking example of the phenomena known from the other phase-separated block copolymers : depending on the composition of the medium one or the other component of block copolymer gives stronger, or better resolved NMR spectra. That block copolymer is formed upon polymerization of GA on the PCL macroinitiator is evidenced by the presence of the methylene ester protons of both PCL (e') at δ = 4.17 ppm and PGA (f') at δ = 4.69 ppm (Table II).

This is the most convincing evidence for the efficiency of the block copolymerization reaction. Indeed, in case of GA homopolymerization, PGA spontaneously separates from the reaction medium in which PCL is soluble.

If GA is not polymerized by the PCL macroinitiators, the insolubility of the unreacted monomer in toluene allows it to be separated from PCL. Thus, the NMR data are only consistent with block copolymerization, all the more since they are in good agreement with the comonomer feed composition and comonomer conversion. When the copolymerization of GA on living PCL is carried out in THF, the reaction medium becomes hazy upon conversion of GA, as mentioned, while the reaction medium becomes translucent, with blueish tint, when the copolymer is dispersed



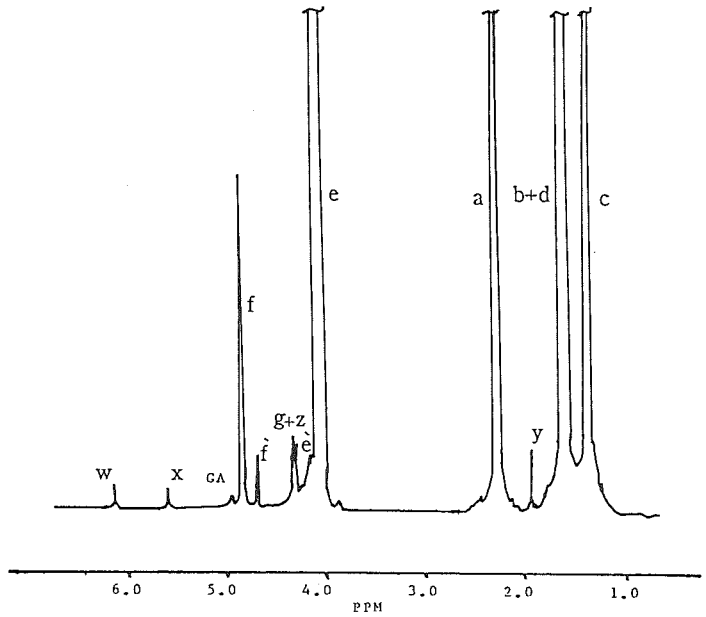
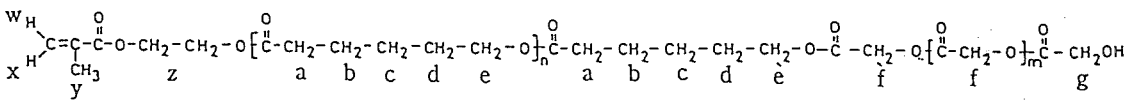


Figure 1 ^1H NMR spectrum of P[CL-b-GA] macromonomer (Mn_{PCL} = 6000, Mn_{PGA} = 900) as recovered after hydrolysis (solvent : $CDCl_3$).



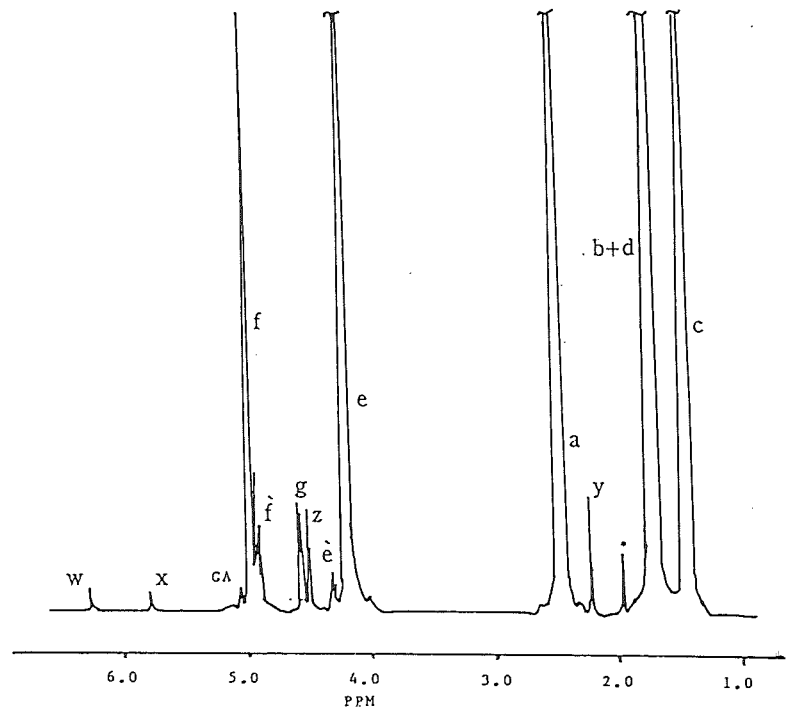


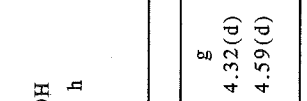
Figure 2 ^1H NMR spectrum of P[CL-b-GA] macromonomer (Mn_{PCL} = 6000, Mn_{PGA} = 900) as recovered after hydrolysis (solvent : $CDCl_3/CF_3COOH$).

in toluene. This characteristic feature agrees with a very fine dispersion of stable diblock particles in toluene.

The particle size has been analyzed by photon correlation spectrometry (PCS), that shows a bimodal distribution. The smallest particles usually dominate the size distribution curve. Their average size is in the range of ca. 10 to 40 nm when the diblocks with compositions given in Table III are dispersed in toluene at concentration of 0.1 wt %.
The average size increases as the concentration of the dispersion increases, which might be due to the aggregation of the smallest particles in favor of the much larger particles. Hypothetical behavior of the growing copolymer chains might consist of the following events : initiation of the GA polymerization by soluble living PCL chains. Initiation is followed by the PGA chain propagation, which leads to the formation of the insoluble segment. Thus a competition might be taking place between the tendency of the copolymer to precipitate out from solution or to form a stable dispersion by hiding-away the insoluble, crystallizable PGA segment (core) within particles stabilized by the well-soluble PCL segments of the copolymer (shell).

The hypothesis that the PGA core might prevent further growing of the "living" PGA blocks may be disregarded, since a GA conversion close to completion is reported when the PGA block is very long (molecular weight of 60-70K) and even longer than the original PCL block (last examples in Table I). It is not clear why there is no apparent relationship between the particle size and molecular weight and composition of the diblocks. The complete history of the samples (from synthesis, through precipitation and redispersion) is expected to be of importance with respect to the size of the final particles. One can however speculate that when low molecular weight PGA segments are formed, they would require more partners to form a crystallite, when compared with longer chain PGA segments. What also requires further studies is the correlation between the molecular weight of the macroinitiator and the degree of conversion of GA. One could assume that when molecular weight of the polycaprolactone macroinitiator and the assumed molecular weight of PGA are not matched (too high concentration of GA), copolymerization might be terminated by formation of the colloidal particles before complete conversion of the glycolide monomer is reached. This aspect requires further studies before any reliable conclusion can be drawn.
Formation of a crystalline PGA core is confirmed by DSC analysis which shows a crystalline melting transition at 195°C (fig. 3).

Table II - ^1H NMR chemical shift δ(ppm, relative to internal TMS) of P[CL-b-GA] copolymers initiated by ω-Al alkoxide polycaprolactone in $CDCl_3$ and F_3CCO_2H(1)



Solvent	Chemical shifts δ ppm (multiplicity)									
	a	b	c	d	e	e'	f'	f	g	h
$CDCl_3$	2.30(t)	1.64(m)	1.37(m)	1.64(m)	4.06(t)	4.17(t)	4.69(s)	4.83(s)	4.32(d)	variable
F_3CCO_2H(1)	2.47(t)	1.73(m)	1.44(m)	1.73(m)	4.19(t)	4.26(t)	4.87(s)	4.97(s)	4.59(d)	"

X-R-O	Solvent	chemical shifs δ ppm (intensity)						
		w	x	y	z	e'	f'	g
$(H_3C)_2CH$-O-	F_3CCO_2H(1)	1.28(1.68)	5.15(-)			4.26(0.58)	4.87(-)	4.54(0.56)
w x	$CDCl_3$	1.22(-)	5.02(0.56)			4.17(-)		4.32(0.59)
Br-CH_2-CH_2-O-	F_3CCO_2H(1)	3.58(0.27)	4.55(0.24)			4.26(-)	4.87(0.21)	4.59(0.30)
w x	$CDCl_3$	3.54(1.10)	4.39(1.34)			4.17(1.52)	4.69(1.29)	4.32(1.52)
H_2C=C(CH_3)-C(O)O-CH_2-CH_2-	F_3CCO_2H(1)	6.24(0)	5.78(0)	2.21(0.028)	4.49(0.048)	4.27(-)	4.87(-)	4.59(0.080)
w,x y z	$CDCl_3$	6.12(0.57)	5.60(0.37)	1.98(1.35)	4.37(-)	4.17(-)	4.68(0.98)	4.32(-)

(1) F_3CCO_2H in the presence of $CDCl_3$ (40 vol. %).

Table III - Particles size of the P[CL-b-GA], obtained by photon correlation spectrometry (PCS) in toluene.

Copolyester	Mn		PCS particle size					
			0.1 % in toluene			0.5 % in toluene		
			nm (%)			nm (%)		
	PCL	PGA	Particles	Aggregates		Particles	Aggregates	
iPrO[PCL-b-PGA]-OH	32000	3900	21 (85)	204 (15)		84 (91)	520 (9)	
	4500	2250	21 (86)	493 (14)		73 (90)	202 (10)	
	16500	2900	12 (100)	-		36 (92)	317 (8)	
Br(CH$_2$)$_2$O[PCL-b-PGA]-OH	4000	2700	13 (88)	60 (12)		234 (100)	-	
	18500	1500	38 (47)	150 (53)		184 (91)	1604 (9)	
	18500	2800	42 (57)	2050 (43)		149 (81)	1951 (19)	
CH$_2$=CH(Me)CO$_2$(CH$_2$)$_2$O[PCL-b-PGA]-OH	6000	900	24 (100)	-		141 (79)	951 (21)	

Melting of PCL blocks at 47°C and glass transition for each block are also observed in agreement with a two-phase character of the material.

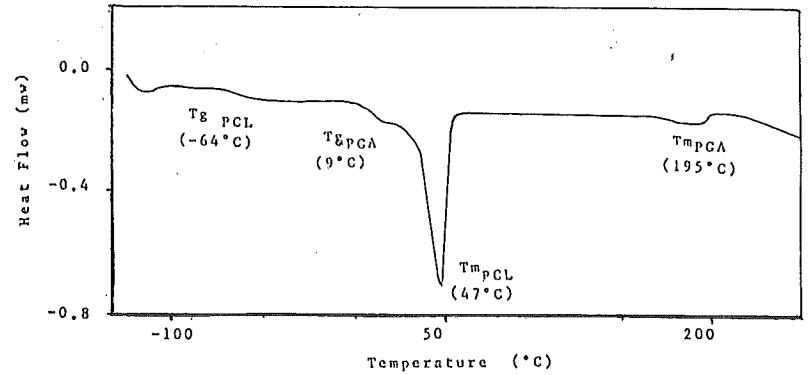


Figure 3 Differential scanning calorimetry of a P[CL-b-GA] macromonomer (Mn_{PCL} = 39000, Mn_{PGA} = 61000) recorded at a heating rate of 20°C.

Living character of the polymerization

In addition to the formation of a diblock structure which is ascertained by protons e' and f' (Table II) characteristic of the ε-CL and GA monomer units directly connected to each other, polymerization of GA appears to be living.

Indeed, the experimental molecular weight of the PGA segments has been estimated by ^{1}H NMR spectroscopy from Mn of the PCL block and the relative intensity of the (CH$_2$-OC(O)) methylene ester protons of PCL ($\delta = 4.19$ ppm) and PGA blocks ($\delta = 4.97$ ppm), respectively. There is a good agreement with the theoretical molecular weight calculated from eq. 5 (Table I).

$$Mn_{th} = \frac{[GA]_o \,.\, 116.\, X}{[Al]_o \,.\, 100} \qquad [5]$$

The living propagation of GA is also proved by the accurate agreement between the mean degree of polymerization of GA at complete conversion and the monomer to initiator molar ratio (Fig. 4).

Moreover, the sequential addition of two glycolide feeds to living PCL yields the expected molecular weight for the PGA block. This GA resumption experiment is reported in Table I.

It is worth noting that no homo PGA is formed in THF, although only an average of 0.9 active site per Al is known to participate to the ε-CL polymerization (Ref. 13). This indicates that the addition of GA does not allow new Al alkoxide bonds to contribute to the second polymerization step, as it occurs when β-propiolactone and lactide are the second comonomer.

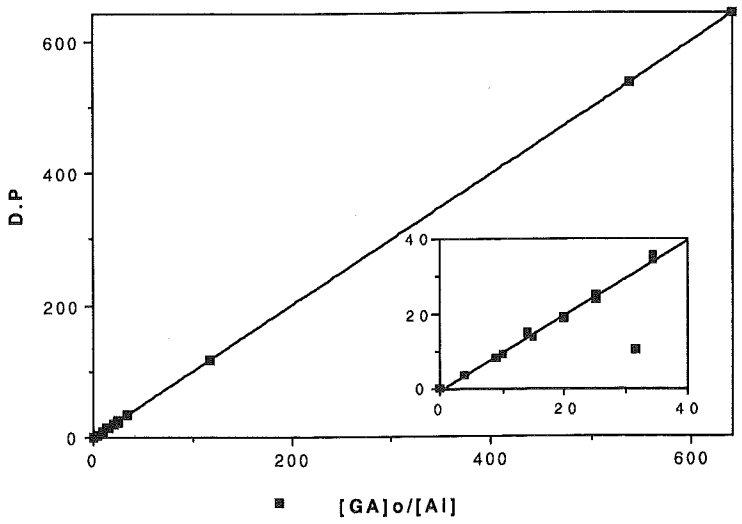


Figure 4 Dependence of DP at quantitative monomer conversion on the monomer to initiator molar ratio for the copolymerization of GA with ω-Al alkoxide polycaprolactone in THF at 40°C ($[GA]_0$ = 0.5 mol.l^{-1}).

CONCLUSIONS

This paper has emphasized that the ring-opening polymerization of glycolide is living when initiated with living Al alkoxide-ended PCL chains in THF at 40°C. The diblock copolymer chains which are accordingly synthesized form stable colloidal particles in toluene, the size of which has been measured by photon correlation spectrometry.
These colloidal particles of diblocks consisting of two biocompatible polyesters with drastically different physical properties, such as melting temperatures and biodegradability, make them very attractive for biomedical applications.

^{1}H NMR analysis of these colloidal copolymeric particles has proved to be very sensitive to the solvent. Only the solvated component is detected by NMR, which allows dynamics of this "tethered" polymer to be studied as a function of the solvating medium. In the particular case of poly (ε-CL-b-GA) copolymers, the PCL blocks are indeed "tethered polymers", since each of them has one chain-end attached to the crystalline PGA core of the particles.

The poly (ε-CL-b-GA) particles are a new class of stable non-aqueous dispersions in which a PGA core is stabilized by a PCL shell. The crystalline structure of PGA block would deserve a special attention in the future.

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REFERENCES

(1) D.J. Lyman, S.M. Rowland, *"Biomaterials", Encyclopedia of Polymer Science and Engineering*, 2nd Ed., **2,** 267 (1985).
(2) M. Vert, *Die Angew. Makromol. Chem.*, **166/167,** 155 (1989).
(3) M. Vert, *Makromol. Chem., Macromol. Symp.*, **6,** 109 (1986).
(4) J.P. Singhal, H. Singh, A.R. Ray, *J. Macromol. Sci., Rev. Macromol. Chem. Phys.*, **C28,** 475 (1988).
(5) J.W. Leenslag, M.T. Kroes, A.J. Pennings, B. Van der Lei, *New Polym. Mater,* **1**(2), 111 (1988).
(6) S. Gogolewski, A.J. Pennings, *Makromol. Chem., Rapid Commun.,* **3,** 839 (1982).
(7) C.L. Brode, J.V. Koleske, *J. Macromol. Sci. Chem.*, **A6,** 1109 (1972).
(8) R.H. Young, M. Matzner, L.A. Pilato, *"Ring Opening Polymerization" ACS Symp. Series,* Ed. by Saegusa T. and Goethals E., **59,** 152 (1977).
(9) J. Heuschen, R. Jérôme, Ph. Teyssié, *Macromolecules*, **14,** 142 (1981).

(10) A. Hamitou, R. Jérôme, Ph. Teyssié, *J. Polym. Sci., Polym. Chem.* Ed., **15,** 1035 (1977).
(11) T. Ouhadi, A. Hamitou, R. Jérôme, Ph. Teyssié, *Macromolecules,* **9,** 927 (1976).
(12) Ph. Dubois, R. Jérôme, Ph. Teyssié, *Polym. Bull.,* **22,** 475 (1989).
(13) Ch. Jacobs, Ph. Dubois, R. Jérôme, Ph. Teyssié, *Macromolecules,* **24,** 3027 (1991).
(14) Ph. Dubois, R. Jérôme, Ph. Teyssié, *Makromol. Chem., Macromol. Symp.,* **42/43**, 103 (1991).
(15) I. Barakat, Ph. Dubois, R. Jérôme, Ph. Teyssié, *J. Polym. Sci., Polym. Chem. Ed.,* **31,** 505 (1993).
(16) N. Ropson, Ph. Dubois, R. Jérôme, Ph. Teyssié, *Macromolecules,* **25,** 2820 (1992).
(17) A. Löfgren, A.C. Albertsson, Ph. Dubois, I. Barakat, R. Jérôme, Ph. Teyssié, Communication to "*Frontiers in Polymerization*", October 6, 1993, University of Liège (Belgium).
(18) H.R. Kricheldorf, M. Thomas, J.M. Jonte, *Macromolecules,* **17,** 2173 (1984).
(19) H.R. Kricheldorf, M. Thomas, J.M. Jonte, M. Perl, *Makromol. Chem. Suppl.,* **12,** 26 (1985).
(20) G. Kraus, C.J. Stacy, *J. Polym. Sci.,* A2, **10,** 657 (1972).
(21) J. Heuschen, Ph.D. Thesis, University of Liège, Liège, Belgium (1981).
(22) P. Vanhoorne, Ph. Dubois, R. Jérôme, Ph. Teyssié, *Macromolecules,* **25,** 37 (1992).
(23) R. Hariharan, A.G. Pinkus, *Polym. Bulletin,* **30,** 91 (1993).