

Macromolecular engineering of poly lactones and poly lactides:

13. Synthesis of telechelic polyesters by coupling reactions*

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Aromatic diisocyanates, such as phenylene-1,4-diisocyanate have proved to be very effective coupling agents of α -X functional ω -hydroxy poly- ϵ -caprolactone (PCL). Very high yields (>98%) have been observed in the presence of triethylamine, in tetrahydrofuran. Accordingly α,ω -X functional PCL of a two-fold molecular weight have been obtained and characterized by size exclusion chromatography and nuclear magnetic resonance spectroscopy. More interestingly, the same coupling reactions have been successfully carried out when applied to the precursor living polyester (X-CH₂-O-PCL-O-AlEt₂) rather than to the chains recovered after hydrolysis of the living propagating sites. Terephthalic acid chloride has been the most efficient coupling agent and, in the presence of pyridine, has yielded quantitatively the expected α,ω -functional polyesters.

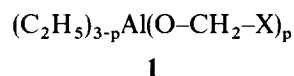
(Keywords: poly lactones; synthesis; telechelic polyesters)

INTRODUCTION

The intentional synthesis of end-reactive polymers with well-controlled molecular characteristics, i.e. molecular weight, chain length distribution, tacticity and nature of the end-groups, is a valuable target, which effectively contributes to the tailoring of polymeric materials. There are two main synthetic pathways to end-functional polymers. Both of them require the availability of a reactive compound bearing the required functional group. In one approach, the reactive compound participates in an addition reaction with the propagating chains (deactivation process). In the alternative process, the reactive compound serves as the initiator of a polyaddition reaction (initiation process). The end-functionalization yield depends on the selectivity of the deactivation and initiation reaction, respectively. Best results are reported when the polymerization reaction is living and the reactivity of the functional reactive compound is high enough towards either the propagating species or the monomer, depending on the functionalization method.

Functional aluminium alkoxides have proved to be very successful in the synthesis of end-reactive polyesters such as poly- ϵ -caprolactone (PCL) and poly(D,L or L,L)lactides (PLA)¹⁻⁶. These functional initiators (**1**) can actually be comprised of 1-3 (p) functional alkoxide

groups, associated to 2-0 (3-p) inactive alkyl groups, respectively:



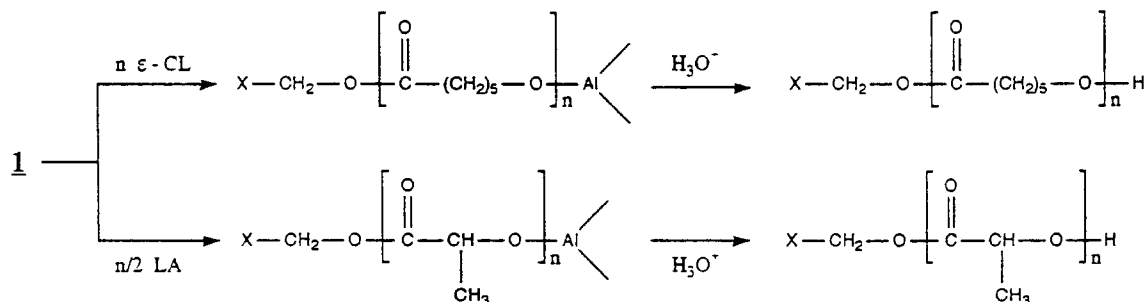
where X is a functional group, e.g. CH₂Br, (CH₂)₂-CH=CH₂, (CH₂)₂NEt₂, CH₂OC(O)C(CH₃)=CH₂. The coordination-insertion type of polymerization is perfectly living and yields linear chains of a predictable molecular weight and a narrow molecular weight distribution. The organic function associated with the active alkoxy group is selectively attached to one chain-end, the second of which is systematically capped with a hydroxyl group resulting from the hydrolysis of the living growing site (*Scheme 1*, where X is as defined above).

This strategy has been successfully extended to the synthesis of asymmetric telechelic diblock copolyesters (*Scheme 2*)⁷. ϵ -Caprolactone (ϵ -CL) and lactides can indeed be polymerized in a sequential way with formation of the related telechelic diblock copolymer (*Table 1*). The quantitative functionalization of each polyester end-group (X-PCL-OH) has been attested by ¹H nuclear magnetic resonance (n.m.r.) spectroscopy. It is worth noting that the use of an aluminium alkoxide bearing a methacrylic double bond is a straightforward route to P[CL-*b*-LA] macromonomers, which are precursors of graft copolymers containing well-defined diblock copolyester branches (*Table 1*, entry b).

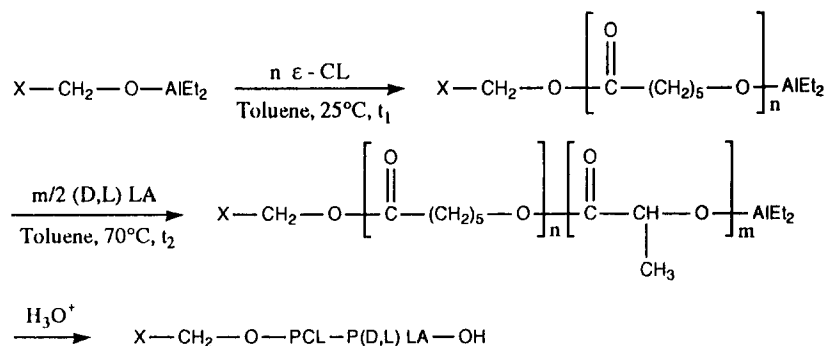
All these results provide very exciting prospects for the macromolecular engineering of asymmetric telechelic homo- and copolyesters, including controlled synthesis of macromonomers.

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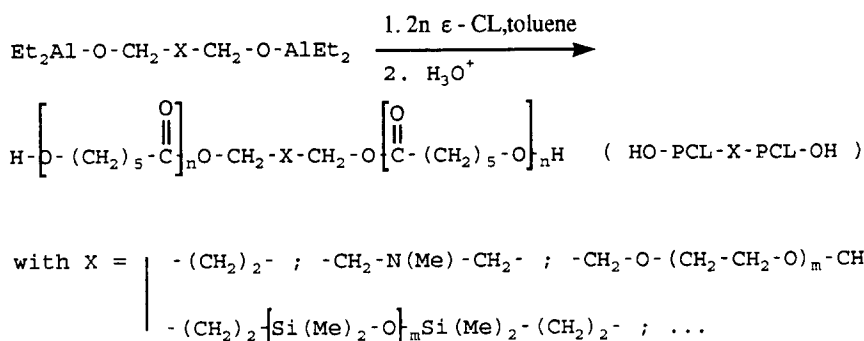
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Scheme 1



Scheme 2



Scheme 3

Table 1 Sequential polymerization of ϵ -CL and (D,L)LA as initiated by functional Al alkoxides ($X-CH_2-O-AlEt_2$) in toluene (see Scheme 2)

Entry	(Initiator) X-	$M_{n,Theor}$		(D,L)LA conversion ^c (%)	t_1 (PCL) (h)	t_2 (PLA) (h)	$M_{n,PCL}$ (s.e.c.)	$M_{n,PLA}$ (¹ H n.m.r.) ^d	M_w/M_n
		PCL ^a	PLA ^b						
a	Br-CH ₂ -	3000	5250	98	6	42.5	2950	4850	1.2
b	CH ₂ =C(CH ₃)CO ₂ -CH ₂ -	3000	3250	97	19	46	3100	3100	1.3

^a $M_{n,PCL,Theor} = [CL]_0/[Al] \times 114$ (at complete conversion)

^b $M_{n,PLA,Theor} = [LA]_0/[Al] \times 144$ (at complete conversion)

^c ϵ -CL conversion is quantitative in each experiment

^d Determined by comparison of relative intensities of ¹H n.m.r. signals corresponding to lactide and lactone repeat units; $M_{n,PCL}$ calculated by s.e.c.

A strategy has been proposed for preparing symmetric telechelic polyesters, and particularly α,ω -hydroxy polyesters. Actually, diols have been reacted with a two-fold molar excess of $AlEt_3$, making an Al dialkoxide ($Et_2Al-O-CH_2-X-CH_2-O-AlEt_2$) available for the controlled synthesis of the required telechelic PCL (Scheme 3)^{8,9}. In this regard, 2,2'-methyliminodiethanol is a functional diol that offers the opportunity to incorporate a tertiary amine in the central position of hydroxy telechelic PCL.

A more general approach to symmetric telechelic polyesters relies upon the proper control of both the

initiation and termination steps. This paper aims at reporting results on the synthesis of well-defined symmetric telechelic PCL other than α,ω -hydroxy PCL. Combination of a functional initiator and an effective coupling agent is the proposed strategy. Actually, asymmetric α -X functional, ω -OH PCL have been reacted with a difunctional agent with the purpose of preparing α,ω -X functional PCL of a two-fold molecular weight. The interest of this approach would of course be increased if the living α -X functional polyester could be coupled rather than the parent α -X functional, ω -hydroxy polymer.

EXPERIMENTAL

Materials

ϵ -CL (Janssen Chimica) was dried over calcium hydride for 48 h at room temperature and distilled under reduced pressure just before use. 2-Bromoethanol (Aldrich) was repeatedly treated with a saturated solution of K_2CO_3 , dried over phosphorus pentoxide and freshly distilled under reduced pressure. Triethylamine (Janssen Chimica) and pyridine (Aldrich) were dried over BaO and KOH, respectively, for a week and freshly distilled under reduced pressure. Diazobicyclo[2,2,2]octane (DABCO), α,α' -dibromo-*p*-xylene and terephthalic acid chloride (Janssen Chimica) were dried by repeated (three times) azeotropic distillation of toluene before use. 1,4-Phenylene diisocyanate (Aldrich) was dissolved in dry tetrahydrofuran (THF), the hydrolysed by-products (urea) were filtered under N_2 , THF was then distilled off and the aromatic diisocyanate was dried overnight at 25°C under reduced pressure. Triethylaluminium (Fluka) and 1,6-diisocyanatohexane (Janssen Chimica) were used without further purification.

Measurements

1H n.m.r. spectra of PCL were recorded in $CDCl_3$ by using a Bruker AM400 spectrometer. Size exclusion chromatography (s.e.c.) was performed in THF by using a Hewlett-Packard 1090 liquid chromatograph equipped with a Hewlett-Packard 1037 A Refractometer index detector and a set of columns with pore sizes of 10^5 , 10^3 , 500 and 100 Å. Molecular weight and molecular weight distribution were calculated by using a calibration curve set up with polystyrene standards.

Synthesis and coupling of α -X, ω -OH PCL

The ϵ -CL polymerization was initiated by functional diethylaluminium alkoxide ($X-(CH_2)_2-O-AlEt_2$), as previously reported^{1,2}. α -X, ω -OH PCL chains were coupled with a diisocyanate reactive towards the hydroxyl end-groups. As an example, 3.74 g of α -bromo, ω -hydroxy PCL ($M_n = 1450$; $M_w/M_n = 1.25$) were dissolved in 40 ml of dry THF at 50°C. A solution of triethylamine (0.40 ml) and 1,4-phenylene diisocyanate (0.25 g) in 10 ml of dry THF was added dropwise. After reaction for 6 h at 50°C, PCL was precipitated in cold methanol (500 ml) under vigorous stirring. The α,ω -bromo polyester was recovered by filtration and characterized as reported in Table 2 (first entry).

Coupling of living α -X, ω -Al alkoxide PCL

Living PCL chains were coupled with formation of a symmetric telechelic polyester in a 'one-pot' process. Terephthalic acid chloride was a very successful coupling agent, in the presence of pyridine. As an example, polymerization of ϵ -CL (9.0×10^{-2} mol) was initiated by polymerization of $Br-(CH_2)_2-O-AlEt_2$ in toluene (100 ml). When the monomer conversion was complete, toluene was distilled off and the 'living' PCL chains were dissolved in carefully dried THF (100 ml). A sample (20 ml) of this solution was removed, hydrolysed and the polymer analysed by s.e.c. ($M_n = 2900$; $M_w/M_n = 1.2$). Dry pyridine (2.8 mmol) and terephthalic acid chloride (1.4 mmol) were added dropwise to the THF solution of living $Br-(CH_2)_2-O-PCL-O-AlEt_2$. After reaction for 22 h at 25°C, the reaction medium was hydrolysed with a small amount of HCl, washed with H_2O , filtered, concentrated and precipitated in heptane (500 ml) under vigorous stirring. After filtration and purification, the α,ω -bromo PCL was recovered and the molecular weight was measured by s.e.c. ($M_n = 6100$; $M_w/M_n = 1.3$).

RESULTS AND DISCUSSION

Synthesis of α,ω -X PCL by coupling reaction of α -X functional, ω -hydroxy PCL

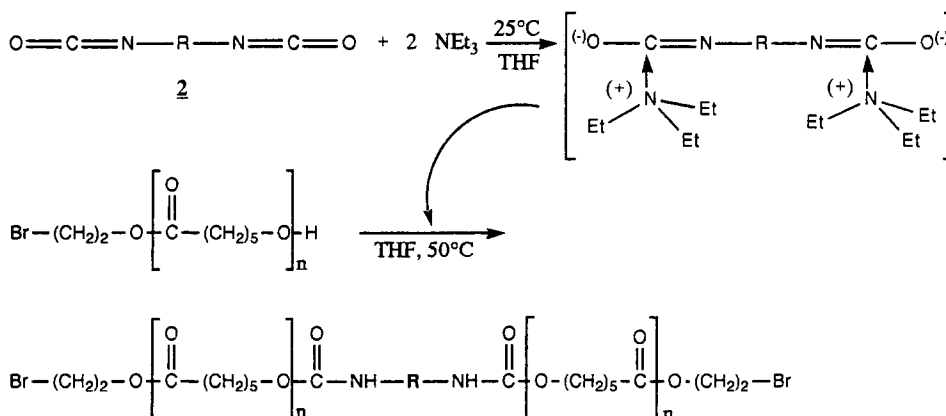
It has recently been reported³ that the hydroxyl end-group of PCL can be esterified by methacrylic acid to give PCL macromonomers, with very high yields (>99%)³. In this regard, methacrylic acid has been activated by dicyclohexylcarbodiimide, and the formed O-acylisourea has been added to the THF solution of ω -hydroxy PCL in the presence of triethylamine and

Table 2 Coupling reactions of α -bromo, ω -hydroxy PCL by the **2a** and **2b** diisocyanates in THF at 50°C

Coupling agent	-R-	Time (h)	Coupling efficiency as determined by		
			G.p.c.	1H n.m.r.	M_w/M_n
2a	$-C_6H_4-$	6	100 ^a	>98	1.3
2b	$-(CH_2)_6-$	19	52	56	_b

^a M_n (g.p.c.) = 2700

^b Bimodal distribution



Scheme 4

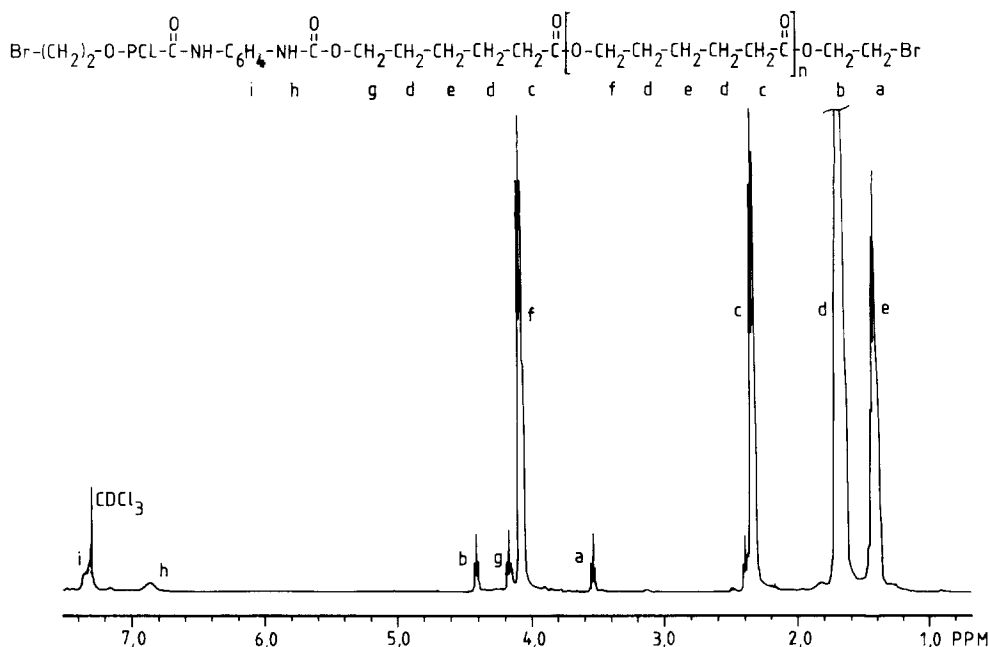


Figure 1 ^1H n.m.r. spectrum of α,ω -bromo PCL resulting from the coupling reaction of α -OH, ω -Br PCL. The aromatic diisocyanate **2a** is the coupling agent (solvent = CDCl_3)

Proton	Mult.	δ (ppm)	Intensity
a	t	3.52	3.545
b	t	4.40	3.632
c	t	2.32	52.120
d	m	1.64	97.779
e	m	1.39	46.583
f	t	4.06	50.836
g	t	4.15	—
h	m	6.86	1.781
i	m	7.31	—

4-(dimethylamino) pyridine. On the basis of this strategy, the synthesis of α,ω -X functional PCL ($\text{X}-\text{CH}_2-\text{O}-\text{PCL}-\text{O}-\text{CH}_2-\text{X}$) seems to be feasible by coupling the parent asymmetric α -X, ω -OH polyester. Potential coupling agents are difunctional reagents, such as diisocyanates ($\text{OCN}-\text{R}-\text{NCO}$), diacid chlorides and dicarboxylic acids ($\text{X}-\text{C}(\text{O})-\text{R}-\text{C}(\text{O})-\text{X}$, with $\text{X}=\text{Cl}$ or OH).

α -Bromo, ω -hydroxy PCL ($M_n=1450$; $M_w/M_n=1.25$) was reacted with an aromatic diisocyanate (1,4-phenylene diisocyanate **2a**) and an aliphatic diisocyanate (1,6-diisocyanatohexane **2b**), respectively. Coupling agents were added dropwise to the previously dried α -X, ω -OH PCL in THF at 50°C . Triethylamine was used as a catalyst of the addition reaction^{10,11}. The OH/isocyanate stoichiometry was carefully set to 1/1 and solvent and reagents were thoroughly dried (Scheme 4; Table 2).

The reaction mechanism is usually described as a nucleophilic addition of the hydroxyl group onto the carbon atom of the isocyanate^{12,13}. Triethylamine is believed to activate the isocyanate function as shown by Scheme 4^{14,15}.

Under the reported experimental conditions, 1,4-phenylene diisocyanate **2a** quantitatively yields α,ω -dibromo PCL in contrast to the **2b** aliphatic diisocyanate, which is obviously not reactive enough (Table 2). The observed lower reactivity of the **2b** diisocyanate corroborates the nucleophilic addition of the alcohol onto the carbon atom of the isocyanate.

Completeness of the coupling reaction of α -Br, α -OH PCL by the **2a** aromatic diisocyanate is confirmed by ^1H n.m.r. spectroscopy (Figure 1). Indeed, the signal of the α -hydroxymethylene end-groups ($-\text{CH}_2\text{OH}$) at 3.64 ppm^2 has completely disappeared in favour of a new signal at 4.15 ppm , which can be assigned to the urethane methylene group ($-\text{NH}-\text{C}(\text{O})\text{O}-\text{CH}_2-$). Furthermore, the aromatic protons of the coupling agent are observed (signal i) at a chemical shift close to that of the solvent (CDCl_3). Molecular weight of the symmetric telechelic PCL has been measured by s.e.c. ($M_n=2700$) and is close to the expected value for the coupled product (i.e. 2×1450). The polydispersity of the hydroxy-terminated oligomer is essentially unaffected by the coupling reaction ($M_w/M_n=1.3$ compared to 1.25).

Synthesis of α,ω -X PCL by coupling reaction of 'living' α -X functional PCL chains

Although successful, synthesis of α,ω -X PCL by coupling α -X, ω -OH PCL with an aromatic diisocyanate is not a straightforward process. Indeed, it requires hydrolysis of living PCL chains with formation of hydroxy end-groups, purification of the hydroxyl-terminated PCL (extraction of Al residues by ethylenediaminetetraacetic acid) and drying of this polymer before the coupling reaction is carried out. This multistep process might, however, be advantageously replaced by a 'one-pot'

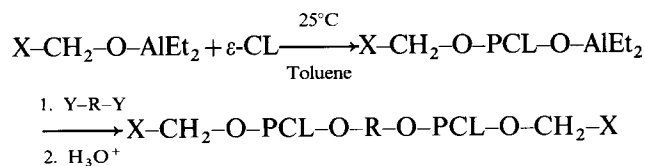
Table 3 Coupling of Br-(CH₂)₂-O-PCL-O-AlEt₂ by various difunctional agents (Y-R-Y) in the presence of a catalyst at temperature *T* for time *t* in toluene or THF

Entry	Y-R-Y	<i>M_n</i> (s.e.c.) ^a	<i>M_w</i> / <i>M_n</i> ^a	Catalyst	Solvent	<i>T</i> (°C)	<i>t</i> (h)	Coupling efficiency (%)		<i>M_n</i> (g.p.c.) ^b	<i>M_w</i> / <i>M_n</i> ^b
								¹ H n.m.r.	G.p.c.		
a	Br-CH ₂ - <i>p</i> C ₆ H ₄ -CH ₂ -Br	1800	1.1	–	Toluene	25	24	0	0	1750	1.2
b		1800	1.1	–	Toluene	70	43	0	0	1200	1.6 ^c
c		1700	1.2	Pyridine	THF	50	3	–	0	2300	1.3
d		1700	1.2	Pyridine	THF	50	26	–	0	2050	1.9 ^c
e	OCN-(CH ₂) ₆ -NCO	2750	1.1	NEt ₃	Toluene	50	22	<5	<5	2800	1.3
f		2000	1.2	Pyridine	THF	50	5	56	54	2750	1.3
g		2000	1.2	Pyridine	THF	50	24	–	50	1800	1.8 ^c
h		2000	1.2	Pyridine	THF	75	5	–	30	1700	1.6 ^c
i		2000	1.2	Pyridine	THF	75	24	–	– ^c	1600	2.0 ^c
j	OCN- <i>p</i> C ₆ H ₄ -NCO	1700	1.3	Pyridine	THF	50	27	76	70	3200	1.5
k		1700	1.3	Pyridine	THF	50	50	–	– ^c	2000	1.8 ^c
l		2350	1.2	Pyridine	THF	50	19	60	58	4450	1.9 ^c
m		2300	1.2	DABCO	THF	25	18	77	74	3250	1.3
n		2300	1.2	DABCO	THF	25	46	–	– ^c	1950	1.7 ^c
o		2300	1.2	DABCO	THF	50	18	–	– ^c	2000	1.7 ^c
p	Cl-C(O)- <i>p</i> C ₆ H ₄ -C(O)-Cl	1700	1.3	Pyridine	Toluene	25	3	–	5	1950	1.4
q		1700	1.3	Pyridine	Toluene	25	23	>90	>90	3750	1.4
r		2900	1.2	Pyridine	THF	25	3.5	64	59	5600	1.4
s		2900	1.2	Pyridine	THF	25	22.5	100	100	6100	1.3
t		2900	1.2	Pyridine	THF	50	5	100	95	6100	1.3
u		2900	1.2	Pyridine	THF	50	23	76	– ^c	4900	1.6 ^c
v		2900	1.2	Pyridine	THF	75	3.5	100	100	5850	1.4
w		2900	1.2	Pyridine	THF	75	22.5	78	– ^c	4450	1.9 ^c

^a Molecular weight (*M_n*) and polydispersity of 'living' PCL chains^b Molecular weight (*M_n*) and polydispersity of the PCL chains after coupling and hydrolysis^c Evidence of degradation

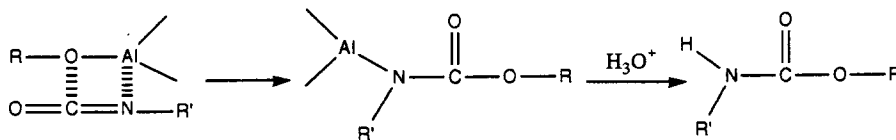
technique, if the propagating aluminium alkoxide group of living PCL chains can react quantitatively with a difunctional reagent. In this regard, it is worth recalling that growing PCL chains, which have been initiated by an Al alkoxide, have been reacted with methacryloyl chloride and the quantitative formation of PCL macromonomers has been reported³.

On that basis, the coupling of living PCL chains (X-CH₂-O-PCL-O-AlEt₂) might be considered as a straightforward way to α,ω-X functional PCL. Various difunctional compounds are potential coupling agents. By analogy with methacryloyl chloride, diacid chlorides should be tested; aromatic dibromomethylenes, and aromatic or aliphatic diisocyanates in the presence of a Lewis base (triethylamine, pyridine, etc.), are also valuable candidates. A systematic study of the coupling reaction has been undertaken in order to identify an effective coupling agent (Y-R-Y) and to define the most suitable conditions of temperature (*T*), reaction time (*t*), catalyst and solvent⁵ (Scheme 5 and Table 3).



Scheme 5

Entries a–d of Table 3 show that α,α'-dibromo-*p*-xylene does not react with the Al alkoxide end-groups of living PCL chains. Although reaction of alcohols with isocyanates is well documented in the scientific literature^{10,15} and has been discussed in the previous section as a coupling reaction of hydroxyl-terminated PCL, very little is known on the reaction of the parent metal alkoxides. Of course, metal alkoxides, such as stannous and lead alkoxides, are commonly used as catalysts in alcohol-isocyanate reactions^{10,16}. Moreover, polymerization of aliphatic isocyanates has been successfully initiated by Al, Zn μ-oxoalkoxides¹⁷. There is addition



Scheme 6

of the metal alkoxide to the N=C double bond of isocyanate. Hydrolysis of the addition product yields a carbamate group as shown by *Scheme 6*.

These experimental observations, which show evidence of metal alkoxide-isocyanate interactions, have prompted us to test diisocyanates as coupling agents of Al alkoxide-terminated chains. A partial coupling is clearly observed whatever the diisocyanate, aliphatic or aromatic, at least when the reaction occurs in THF, in the presence of catalyst (pyridine or DABCO). Combination of high temperature, long reaction time and DABCO as a catalyst is, however, responsible for degradation of

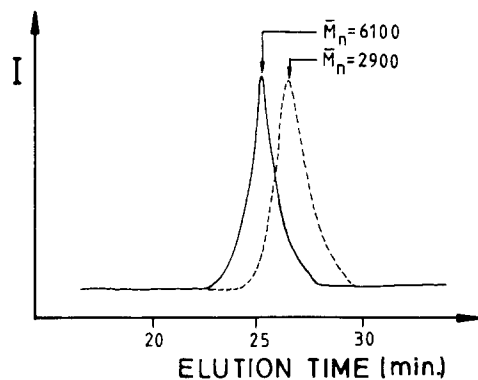


Figure 2 Size exclusion chromatograms of PCL chains before (---) and after (—) coupling with terephthalic acid chloride, in the presence of pyridine in THF at 25°C (22.5 h) (entry s; *Table 3*)

PCL, as shown by an abnormal decrease in M_n (e.g. entries i, n, o, *Table 3*) and increase in polydispersity. Similarly to coupling of α -X, ω -OH PCL with a diisocyanate, 1,6-diisocyanatohexane is less reactive than the aromatic derivative (1,4-phenylene-diisocyanate) towards Al alkoxides. Indeed, a coupling efficiency of 70% is promoted by the aromatic diisocyanate (entry j, *Table 3*) compared to 50% for the aliphatic reagent (entry g, *Table 3*) under the same reaction conditions (50°C, ~25 h, THF, pyridine); 75% coupling is the best reported result.

Terephthalic acid chloride has proved to be a very efficient coupling agent under appropriate experimental conditions. Within limits of experimental errors, a coupling efficiency of 100% has been reported (entries s, t and v, *Table 3*) with a moderate increase in polydispersity (1.2 to 1.3–1.4) and the expected increase in M_n . As an example, *Figure 2* compares the s.e.c. trace of a living PCL chain (M_n 2900, M_w/M_n 1.2) and the chromatogram of the coupling reaction product (M_n 6100, M_w/M_n 1.3). ^1H n.m.r. of PCL recovered by precipitation into cold methanol after coupling under mild conditions (22.5 h at 25°C; entry s, *Table 3*) confirms the completeness of the coupling. Indeed, *Figure 3* shows that the signal characteristic of the α -hydroxymethylene protons [$\delta(-\text{CH}_2\text{OH}) = 3.64$ ppm] has disappeared, with concomitant formation of a new triplet at $\delta = 4.34$ ppm. This new signal has to be assigned to protons of the aromatic ester methylene group ($-\text{CH}_2\text{CO}-\text{C}_6\text{H}_4-$). It is, however, essential to carry out the coupling reaction under mild conditions, otherwise degradation reactions occur

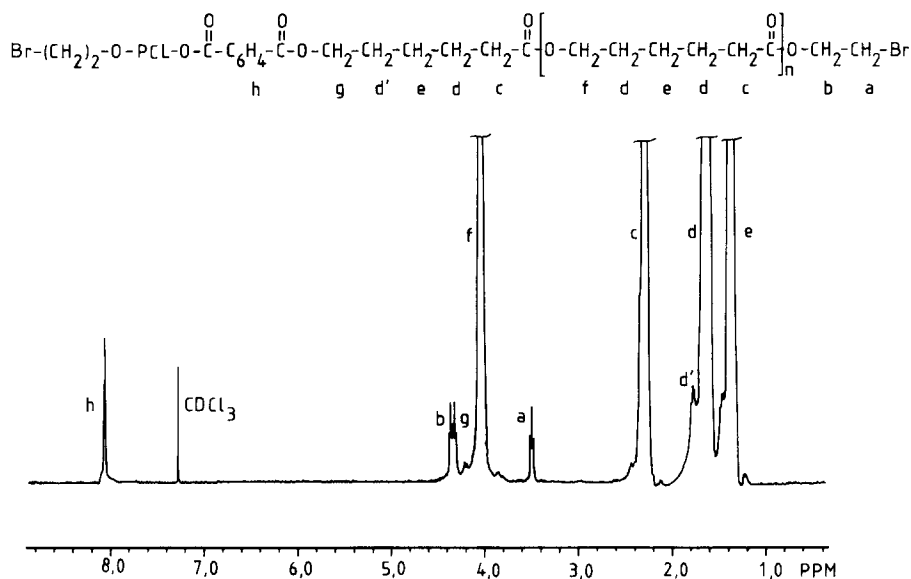


Figure 3 ^1H n.m.r. spectrum of α,ω -bromo PCL resulting from coupling of 'living' α -bromo, ω -OAlEt₂ chains. Terephthalic acid chloride is the coupling agent (solvent = CDCl_3)

Protons	Mult.	δ (ppm)	Intensity
a	t	3.52	2.20
b	t	4.40	5.14
g	t	4.34	
c	t	2.32	58.29
d	m	1.64	169.72
e	m	1.39	
f	t	4.06	57.65
h	s	8.05	2.54

(entries u and w, Table 3), as previously reported for coupling with a diisocyanate.

In conclusion, symmetric telechelic PCL can be prepared by coupling living α -X functional, ω -Al alkoxide PCL. Terephthalic acid chloride is the most efficient coupling agent and, in the presence of a Lewis base such as pyridine, it yields quantitatively the expected α,ω -functional polyester of a two-fold molecular weight and a slightly increased dispersity. Symmetric telechelic polyesters ($X-CH_2-O-PCL-O-CH_2-X$) are actually difunctional polymeric reagents which can be incorporated into specialized materials. If X is a polymerizable methacrylic function, model tridimensional networks could be formed in the presence of a radical promoter. Similarly, telechelic polyesters could be converted into 'ionomers' by quaternization of amino end-groups ($X=NEt_2$) or by reaction of halide extremities ($X=Br$) with a tertiary amine. If the quaternization agent is difunctional, one can expect a chain extension process to occur with formation of 'ionene' subunits. Clearly, telechelic PCLs are valuable intermediates for the macromolecular engineering of biocompatible and biodegradable polyesters.

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