Published in: Polymer Degradation & Stability (1998), vol.59, iss.1-3, pp.215-222
Status: Postprint (Author's version)

Block and random copolymers of ϵ-caprolactone

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Abstract: Conditions of the living homopolymerization of ϵ-caprolactone (CL), lactides (LA), and of the homo-oligomerization of γ-butyrolactone (BL) are briefly described. Then block and random copolymerizations of CL with LA are shortly reviewed. The microstructure of the resulting copolyesters in relation to some peculiarities of these processes is discussed in more detail. It is also shown that the otherwise 'non-polymerizable' BL does form high molecular weight copolymers with CL, containing up to 50 mol % repeating units derived from BL. Their molecular weight is controlled by the concentrations of the consumed comonomers and the starting concentration of the initiator. NMR and DSC data indicate the random structure of copolymers. TGA traces of the BL/CL copolymers show that the presence of the γ-oxybutyryl repeating units randomly distributed within the poly(CL) chains improves the thermal stability of the latter.

1. INTRODUCTION

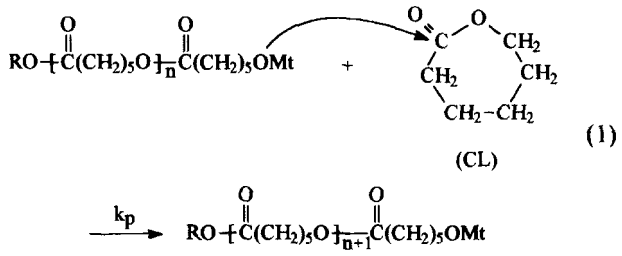
Biodegradability of poly(ϵ-caprolactone) (PCL), as well as biocompatibility of its degradation products, is a well-known phenomenon.[1,2] It was shown, however, that the half-life time of PCL (about 1 year) is too long for some applications. For other aliphatic polyesters such as poly(L-lactide) (PLA), it is of an order of weeks *in vivo.*[12] On the other hand, PCL has some other advantageous features, for example it is permeable for many drugs in contrast to PLA. Also thermal and mechanical parameters of PCL and PLA are substantially different.[3]

Therefore, block or random copolymerization of ϵ-caprolactone (CL) with lactides (LA) may lead to a wide range of polyesters, exhibiting various degradation behaviour, permeability, mechanical properties, etc.

The aim of the present paper is not to give a comprehensive review on CL copolymers but rather to discuss some particular problems, involved during copolymerization of CL with other cyclic esters, taking as examples L-lactide and γ-butyrolactone.

2. HOMOPOLYMERIZATION OF ϵ-CAPROLACTONE

Although the ring-opening polymerization of CL was already described over half a century ago by Carothers,[4] methods of fully controlled polymerization of this monomer have only recently become available.[5-14] These methods are based on covalent (pseudoanionic) polymerization, proceeding on the multivalent metal alkoxides as growing species, e.g.:



(where Mt: -Zn, Al <, Y <, etc.)

The elementary reaction of the polyester chain growth can, formally, be shown as the nucleophilic attack of the alcoholate active species on the monomer ester group, followed by the acyl-oxygen bond scission. Ions, presumably, are not involved in these polymerizations and the monomer addition proceeds via the concerted insertion into the metal-oxygen bond.

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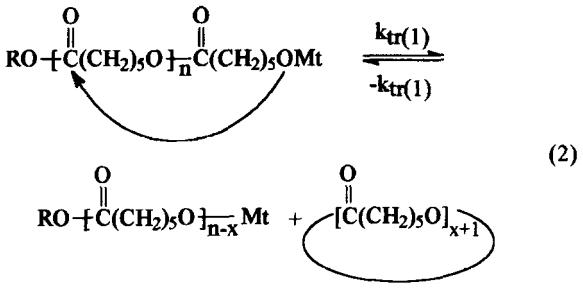
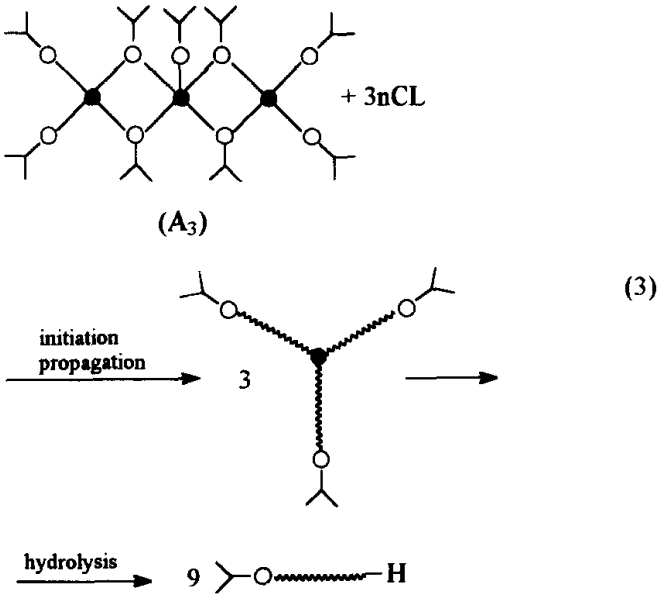
The major side reaction in the CL polymerization, namely the intramolecular (i.e. unimolecular) transesterification (back-biting) leading to the undesired cyclic oligomers:



(2)

is kinetically depressed with these growing species and can be practically eliminated when the correct conditions of polymerization are applied. For example, tris(macroalkoxide)aluminium active species (cf. (3)) are particularly selective and provide k_p = 0.50 mol^{-1} Ls^{-1} and k_p/k_{tr} as high as 10^5 mol^{-1} L (THF, 20°C), as has been measured recently.[15] This means that at 99.99 mol% of the CL monomer conversion, for $[CL]_0$ = 1.0 mol L^{-1}, less than $5x10^{-3}$ mol% cyclic oligomers could be detected. Moreover, when an initiator reacting fast and quantitatively is used, such as aluminium isopropoxide trimer ($\{Al(O^iPr)_3\}_3$,A_3),[11,12] the number average molecular weight ($\bar{M}_n$) of the resulting PCL could be predicted directly from the feed composition, i.e.: $\bar{M}_n$=114.14$[CL]_0/[O^iPr]_0$ and its polydispersity index ($\bar{M}_w/\bar{M}_n$) is equal to 1.03-1.15.[12] Schematically:



(3)

(where ○ and ● denote the oxygen and aluminium atoms, respectively, ⟩— the isopropyl group; ∿∿∿ the PCL chain: —{O(CH$_2$)$_5$C(O)}$_n$—)

3. HOMOPOLYMERIZATION OF LACTIDES

Polylactides are the most readily available and widely used biodegradable thermoplastic materials.[16,17] Systematic studies on their synthesis have also been started by Carothers.[18] The best results are obtained for the pseudoanionic polymerization of the respective cyclic monomer (L,L-LA, D,D-LA, D,L-LA or (D,D + L,L-LA)),[8,19-24] as in the polymerization of CL.

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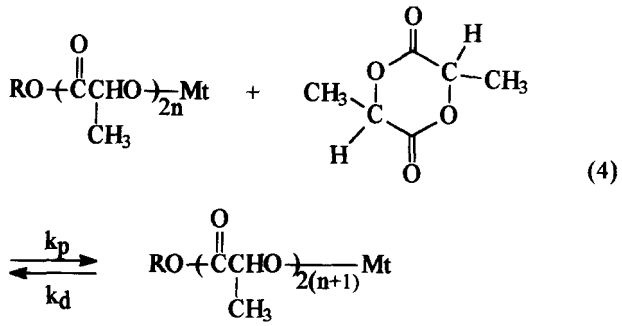
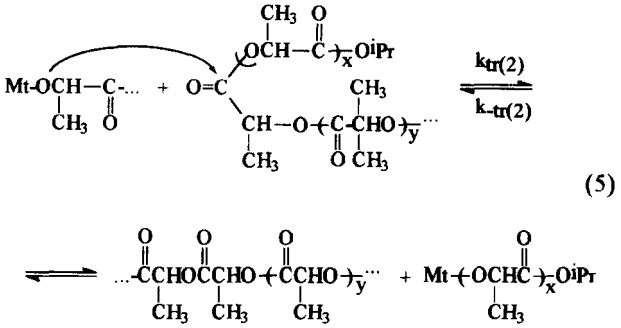


(4)

(Mt = Al<, Y<, -Sn<, -Ti<, etc.)

Stannous octoate ($SnOct_2$, tin(II)2-ethylhex-anoate), used commonly as an initiator (catalyst?) is not providing a controlled polymerization of LA (see e.g. Ref. 25) and aluminium trialkoxides appear to be the most versatile and useful initiators for this purpose.

The intramolecular transesterification seems to be of lower importance in LA polymerization.[19,26] However, the intermolecular transesterification, not changing the number of the growing macro-molecules but broadening the molecular weight distribution with monomer conversion (α), takes place:[19,22,23]



(5)

This side reaction has recently been studied quantitatively. The_$k_p/k_{tr(2)}$ ratios were determined directly from the $M_w/M_n = f(\alpha)$ plots for a series of multivalent metal-based initiators.[22,23] For example, $Al(O^iPr)_3$ trimer belongs to the most selective ones and is characterized by: $k_p = 8.5x10^{-3}$ mol^{-1} Ls^{-1} and $k_p/k_{tr}=100$ (THF, 80°C).

Another important feature of the LA polymerization is its reversibility, resulting in a relatively high concentration of the unreacted monomer at equilibrium ($[LA]_{eq}$), particularly at the elevated temperatures, at which LA is usually polymerized. It increases from $5.5x10^{-2}$ to $1.5x10^{-1}$ mol L^{-1} in the temperature range from 80 to 130°C (L,L-LA in 1,4-dioxane as a solvent).[27]

4. HOMO-OLIGOMERIZATION OF γ-BUTYROLACTONE

γ-Butyrolactone, the five-membered cyclic ester, is usually classified as a compound not applicable for ring-opening polymerization,[28] which is sometimes incorrectly identified with an inability of BL to undergo the ring-opening reaction at all.

On the other hand, a few reports in the literature can be found,[29-33] including our recent work,[33] showing that BL does form high molecular weight copolymers ($\bar{M}_n = 10^4$-10^5) with other lactones, with up to 50 mol% of the γ-oxybutyryl repeating units.

Thermodynamic data for the selected, medium size lactones[27,34,35] show that the entropy change during polymerization ((ΔS_p^0)) is typically negative (see Table 1). Thus, the driving force of polymerization is the negative change of enthalpy ((ΔH_p^0)), practically equivalent to the ring-strain (for more details, cf. Ref. 17). However, for BL, ΔH_p^0 is even positive. This means that a *high molecular weight hompolymer of BL* cannot be prepared at normal conditions, because the Gibbs energy of the equilibrium:

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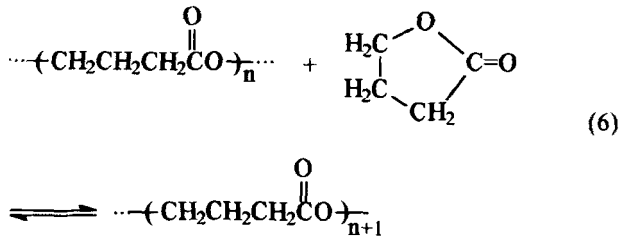
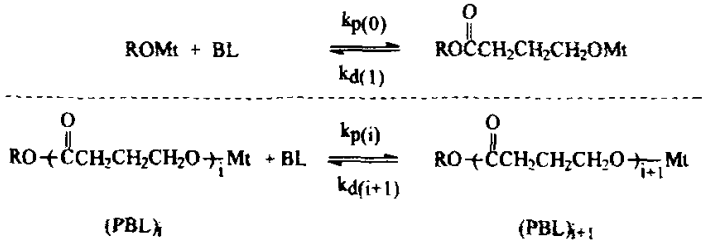


(6)

is positive, for any real concentration of BL, i.e.:

$$\Delta G_p = \Delta H_p^0 - T\Delta S^0 - RT \ln[BL] > 0 \quad (7)$$

Drastic changes to the polymerization conditions may sometimes shift the equilibrium (6) more to the right-hand side. For example, under a pressure of $2x10^4$atm at 160°C, PBL with $\bar{M}_n$ up to $3.5x10^3$ was prepared[35,36] (and thus obtained PBL was used in the thermochemical measurements[37]). More detailed analysis of the reversibility of the polymerization indicates that particularly the first addition differs from the next one, since the product of depropagation is now a starting metal alcoholate (ROMt):



(8)

Indeed, a given equilibrium constant may differ substantially from these for the high molecular weight species, due to an influence of the head- and tail-end groups. Moreover the concentration term contribution to the Gibbs energy:

$$\Delta G_i = \Delta H_i^0 - T\Delta S_i^0 + RT \ln[(PBL)_{i+1}]/[BL][(PBL)_i] \quad (9)$$

in the very beginning of the BL ring-opening, when $[(PBL)]_i > > [PBL]_{i+1}$ may outweigh a sum of the enthalpic and entropic contributions and give eventually the negative value of ΔG. Therefore, even when $\Delta H^0 \approx 0$ as for the reaction (8), the formation of short BL oligomers is not forbidden thermodynamically.

Table 1: *Comparison of the thermodynamic parameters of polymerization of γ-butyrolactone, L,L-lactide and ϵ-caprolactone*

Monomer	**Monomer and polymer states**[a]	ΔH_p^0 **(kJ mol^{-1})**	ΔS_p^0 **(J mol^{-1} K^{-1})**	$[Monomer]_{eq}$ **at 25°C(mol L^{-1})**	**Ref.**
γ-butyrolactone	lc	5	-65	$2x10^4$	35
L,L-lactide	ss[b]	-22.9	-41.1	$1.35x10^{-2}$	27
ϵ-caprolactone	lc	-28.8	-53.9	$1.12x10^{-2}$	36

[a]1 = liquid, c = condensed, s = solution.[b]1,4-dioxane as a solvent, $[LA]_0$= 1 mol L^{-1}.

This conclusion is in agreement with results from our recent studies[37] on BL oligomerization initiated with $Al(O^iPr)_3$ trimer. ^1H and ^{27}Al NMR, HPLC and MS measurements allowed for the proposition of the reaction scheme shown below in (10). Using MS with chemical ionization we observed the formation of BPL oligomers with *m* up to at least 10.

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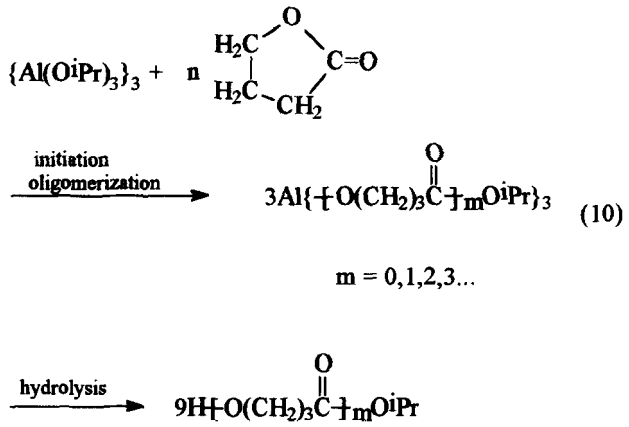
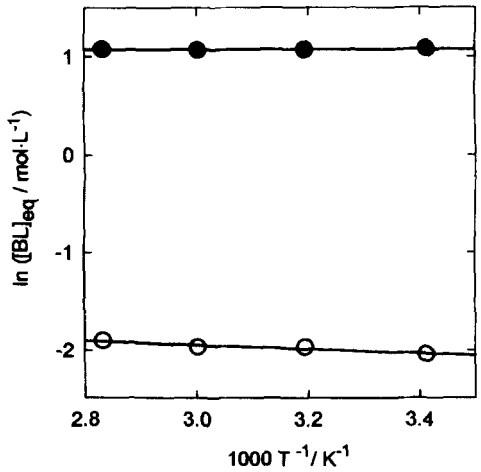


Thermodynamic analysis in terms of the simplified temperature dependence of $[BL]_{eq}$, i.e.:

$$\ln[BL]_{eq} = \Delta H/RT - \Delta S/R \qquad (11)$$

applied to the equilibrium (8) gives values of *AH* close to 0, for two different starting concentrations of BL(Fig. 1), namely ΔH = 0.1 and -1.8 kJ mol^{-1} for $[BL]_0$ = 3.8 and 0.6 mol L^{-1}, respectively ($[BL]_{eq}$ at a given temperature was measured directly by the ^1H NMR of the reacting mixtures). The resulting values of ΔH indicate the low BL ring-strain, in agreement with the thermochemical measurements reported previously.[35]

Fig. 1: *Reaction of $Al(O^iPr)_3$ trimer with γ-butyrolactone. Dependence of the equilibrium γ-butyrolactone concentration ($[BL]_{eq}$) on the reciprocal of the absolute temperature. Conditions: $[Al(O^iPr)_3]_0$ = 0.2 mol L^{-1}, $[BL]_0$ = 3.8 (●), 0.6 (○) mol L^{-1}; benzene-d_6 as a solvent.*[37]



5. COPOLYMERIZATION OF ϵ-CAPROLACTONE WITH LACTIDES INITIATED WITH $Al(O^iPr)_3$ TRIMER

5.1 Block copolymerization

Both CL and LA can be homopolymerized in a living manner with $Al(O^iPr)_3$ as an initiator, providing that the reactive, trimeric form of $Al(O^iPr)_3$ is used.[11-13,20] The involved active species have, exclusively, the structure of the aluminium tris-(macroalkoxide)s. Therefore the sequential polymerization of CL and LA initiated with A_3 should lead to the respective block copolymers.

Indeed, this is the case when CL is polymerized first (see (12)). The initial problems with the non-quantitative initiation by $Al(O^iPr)_3$ during formation of the PCL homoblock[38] have been resolved more recently[39] by using pure, isolated A_3 instead of the mixture containing the unreactive (in the conditions of CL polymerization)

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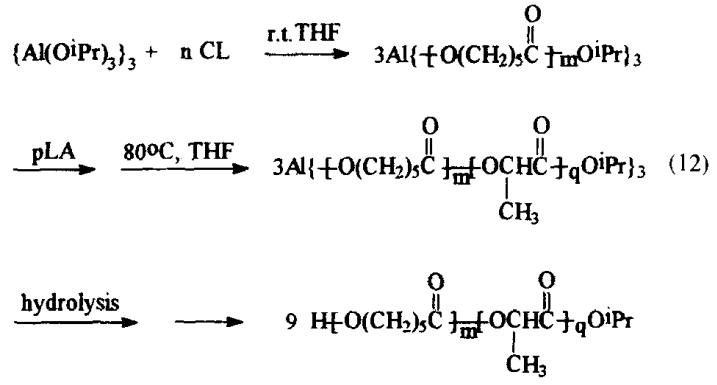
tetrameric aggregate (A_4). ^{13}C NMR spectra of thus prepared poly(CL-*b*-LA) exhibit only two signals of the >C = O group, corresponding to the PCL and PLA homoblocks (173.5 and 169.5 ppm, respectively; $CHCl_3$ at 22°C). GPC traces show mono-modal molecular weight distribution curves, giving $\bar{M}_n$ (with laser light scattering detection) close to that calculated on the basis of the feed composition: $\bar{M}_n = (114[CL]_0 + 144([LA]_0) - [LA]_{eq}))/[O^iPr]_0$. Moreover, during the time required for the second comonomer conversion no transesterification was observed. Thus, the pure block CL/LA copolymers were formed.[39] Only later on, when the living copolymer was kept for a longer time, do the new ^{13}C NMR peaks appear.



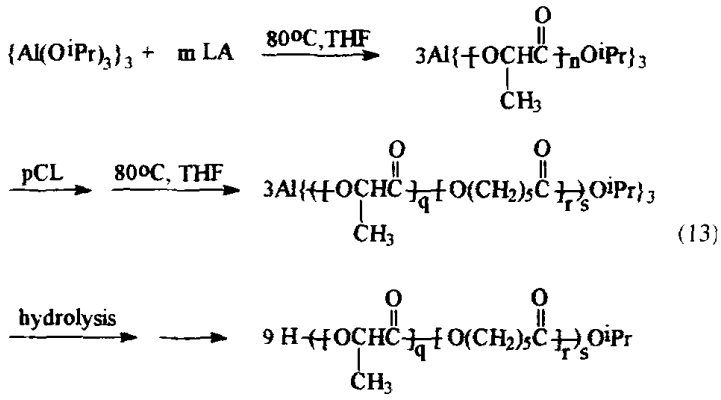
(12)

poly(CL-*b*-LA)

Apart from A_3, only the recently applied yttrium alkoxides[40] seem to allow for the similar control of the microstructure and molecular weights of the CL/LA copolymers. Another possibility of preparation of the CL block copolymers provides polymerization started from the hydroxytelechelic PCL homopolymers (PCL-OH) as the chain-transfer agents.[41,42]

Attempts for the application of the reversed sequence of the comonomers addition, i.e. to polymerize LA first, in order to prepare poly(LA-*b*-CL), create some problems. First reports (e.g. Ref. 43), have even claimed that CL does not polymerize at all, at the covalent alcoholate chain-end of PLA. More recent results[39] have revealed, however, that the living PLA does initiate CL polymerization. The latter polymerization is much slower than CL homopolymerization. The rate constant of the CL consumption in block copolymerization measured at 80°C[39] is equal to 2.5×10^{-4} mol^{-1} Ls^{-1}, whereas for homopropagation $k_p = 6.2 \times 10^{-1}$ mol^{-1} Ls^{-1} at 25°C (THF solvent).[12] Reasons for this difference in CL consumption rates will be discussed below, in the section describing a random copolymerization.

Moreover, analysis of the ^{13}C NMR spectra of the resulting poly(LA-*co*-CL)s, recorded at various degrees of CL consumption, exhibits the PLA block length decreasing and randomnization of the copolymer microstructure. Eventually, after complete CL incorporation, we observed the ^{13}C NMR pattern characteristic for the random copolymers, i.e.:



(13)

poly(LA-*co*-CL)

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At least two phenomena may give such a result, namely the presence of the unreacted LA comonomer at equilibrium (pronounced depropagation) and transesterification (bi- and/or unimolecular).

5.2 Random copolymerization

When a mixture of two comonomers, differing very much in the homopropagation rates, is polymerized we usually expect the formation of a copolymer containing two homoblocks, separated by the short tappered copolymer sequence, with the 'faster' comonomer polymerized first.

This is the case in CL/LA copolymerization. Reactivies of the comonomers differ considerably, according to the determined rate constants.[5,12,19,39] For example, in THF as a solvent at 25°C k_p(CL) = 0.62 $mol^{-1}Ls^{-1}$, k_p(LA) = $7.5x10^{-5}$ mol^{-1} Ls^{-1}.

Contrary to expectations, polymerization of a mixture of CL and LA starts from the lactidyl blocks formation. Only when the LA monomer is being exhausted does CL apparently start to polymerize but still with the rate well below that of the CL homopropagation.[3,39,44] Analysis of this situation in terms of the copolymerization kinetic scheme:

$$
\begin{aligned}
m_1^* + M_1 &\xrightarrow{k_{11}} m_1m_1^* \\
m_1^* + M_2 &\underset{k_{-12}}{\overset{k_{12}}{\rightleftharpoons}} m_1m_2^* \\
m_2^* + M_1 &\xrightarrow{k_{21}} m_2m_1^* \\
m_2^* + M_2 &\underset{k_{-22}}{\overset{k_{22}}{\rightleftharpoons}} m_2m_2^*
\end{aligned}
\qquad (14)
$$

(where M_1 stands for CL and M_2 for LA) requires $r_2 >> r_1$, what with the condition $k_{11} >> k_{22}$ gives: $k_{12} >> k_{11}$ and $k_{22} >> k_{21}$ (for the sake of simplicity we omit a reversibility of the LA propagation). Thus, both active species, i.e.: ...-C(O)CH-(CH_3)OAl and ...-C(O)(CH_2)$_5$OAl< react much more rapidly with LA than with CL. In a similar way kinetic behaviour of the styrene/butadiene system has been rationalized.[45]

Additional explanation needs low CL polymerization rate after LA exhaustion. It may be sufficient that $k_{12} > k_{11}$. However, intermolecular transesterification takes place and m_1* prefers to react with the foreign ...-$m_2m_2m_2$-... than with the parent ...-$m_1m_1m_1$-... homoblock, i.e. the cross-transesterification dominates, e.g.:

$$
\begin{aligned}
&\ldots - m_1^* + \ldots - m_2m_2m_2 - \ldots \rightarrow \ldots - m_2m_2^* \\
&+ \ldots - m_1m_2 - \ldots
\end{aligned}
\qquad (15)
$$

increasing concentration of active species m_2* Analysis of the ^{27}Al NMR spectra of the Al(O^iPr)$_3$/ CL/LA polymerizing mixture confirms these conclusions.[39] The final microstructure of the copolymer prepared starting from the equimolar CL/LA mixture, indicates the random arrangements of the lactidy] and ϵ-oxycapryloyl units, as deduced from the ^{13}C NMR spectra.[3,44]

These observations are also consistent with the course, described in the previous section, of the block CL/LA and LA/CL copolymerizations.

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6. RANDOM COPOLYMERIZATION OF ϵ-CAPROLACTONE WITH γ-BUTYROLACTONE INITIATED WITH $Al(O^iPr)_3$ TRIMER

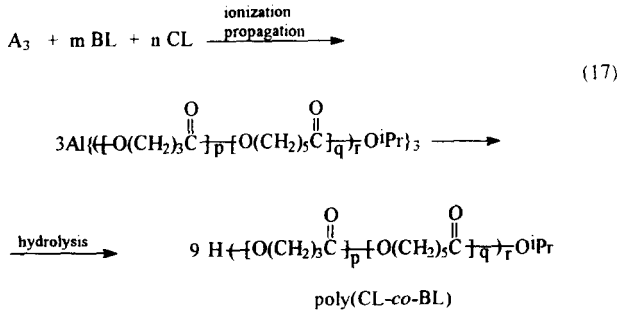
BL is able to form linear oligomers. In order to expect the possibility of high copolymer formation with other comonomers, it is sufficient that it can form a linear dimer.

In the copolymerization scheme (14) let the comonomers M_1 and M_2 stand for CL and BL, respectively (i.e. $k_{-22} > > k_{22}$[2]). BL can be introduced into the polymer chain in the cross-propagation processes, particularly when k_{21}[1]$>k_{-22}$. Apparently, this condition is met in the copolymerization with CL, initiated with A_3.

Although in the literature there are some data on the BL copolymerization,[29-32] our work reported the fully controlled process for the first time.[33] Poly(CL-*co*-BL)s, with molecular weights up to 3xl0^4 ($\bar{M}_n$) and containing up to 50mol% of the γ-oxybutyryl repeating units, were prepared. Their $\bar{M}_n$ could be calculated from the concentrations of the consumed comonomers ($[CL]_C$ and $[BL]_C$) and the starting concentration of the alkoxy groups in the initiator:

$$\bar{M}_n = (86.09[BL]_c + 114.14[CL]_c)/3[Al(O^i Pr)_3]_0 + 60.10 \qquad (16)$$

These theoretical $\bar{M}_n$ values were in close agreement with $\bar{M}_n$ measured by GPC (laser light scattering detection), osmometry and ^{1}H NMR end-group analysis.



Using ^{13}C INVGATE NMR we elucidated a microstructure of the resulting procedure. Signals of the carbonyl atoms are known to be particularly sensitive to sequence effects.[3,30] Fig. 2 shows the $^{13}C\{^1H\}$ NMR spectra (100 MHz with respect to ^{13}C) of PCL and poly(CL-*co*-BL). Triad CLCLCL absorbs at the lowest field ($\delta \approx$ 174). Integration in Fig. 2(b) gave an 8:1:1 intensity ratio for the peaks A:B:C, respectively. Remembering that 11 mol% of γ-butyryl units are introduced, the following assignments can be made: peak B (δ= 173.79 ppm) is due to the BLCLCL or CLCLBL triad, whereas peak C (δ = 173.24 ppm) to the CLBLCL triad. Since CLCLCL is structurally closer to BLCLCL than to CLCLBL, peak B corresponds rather to the CLCLBL triad. Thus, finally: peaks A, B and C can be related to CLCLCL + BLCLCL, CLCLBL and CLBLCL triads, respectively.

Analogously, for the copolymer containing 43 mol% of the oxybutyryl units (Fig. 2(c)): peak A (δ =174 ppm) can be ascribed to CLCLCL + BLCLCL, peak B (δ= 173.56 ppm) to CLCLBL + BLCLBL, peak C (δ= 173.32 ppm) to CLBLCL (C1) + BLBLCL (C2), and peak D (δ= 173.15 ppm) to CLBLBL (D1) + BLBLBL (D2) triads.

The ^{13}C NMR spectra analyses indicate a rather random structure of the CL/BL copolymers and the DSC data given in Fig. 3 support this conclusion. T_m decreases continuously with γ-oxybutyryl units content but T_g is only slightly affected by the copolyester composition. Interestingly enough, for 0.43 mol% of the γ-oxybutyryl units content, T_m of the copolymer is as low as 26°C. TGA analysis (Fig. 4) exhibits only a slight improvement of the poly(CL-*co*-BL) thermal stability with the BL-derived units increase.

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Fig. 2: *$^{13}C\{^1H\}$ spectra (>C = O group absorption range) of the isolated poly(CL-co-BL) containing (in mole fraction) 0 (a), 0.11 (b) and 0.43 (c) γ-oxybutyryl units. Chloroform-d as a solvent.*[33]

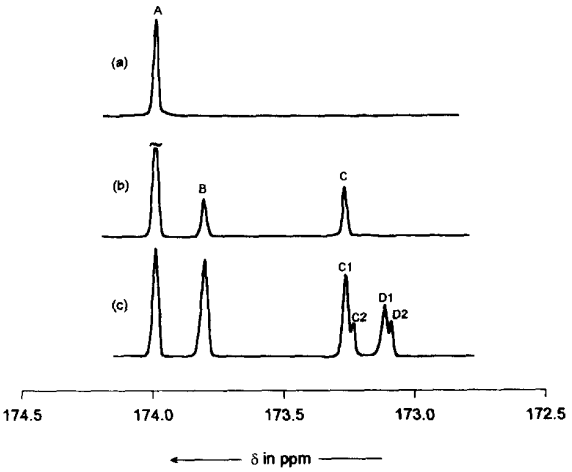


Fig. 3: *Dependence of melting points (T_m) and glass transition temperature (T_g) of poly(CL-co-BL) on the γ-oxybutyryl units content (DSC measurement, second heating run).*[33]

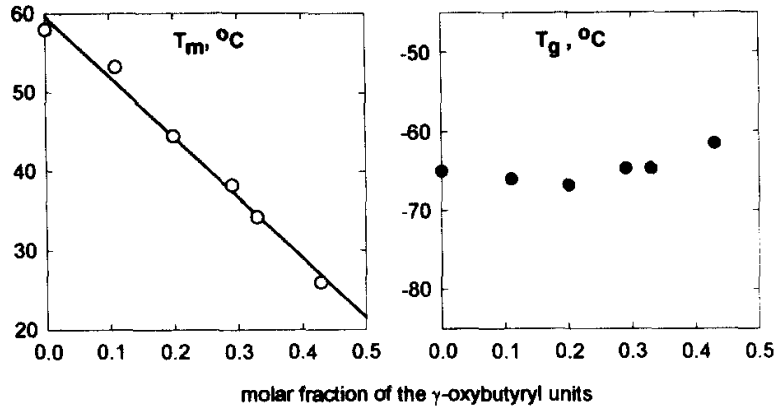
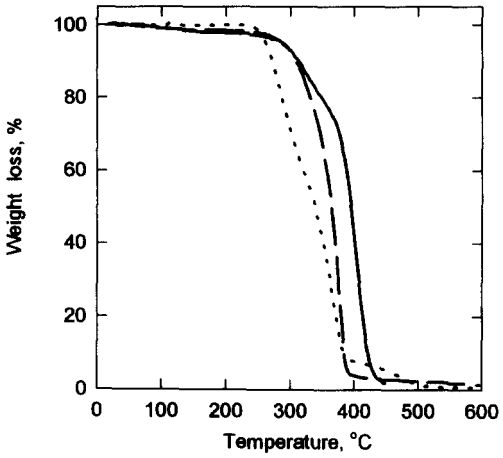


Fig. 4: *Thermogravimetric analysis of poly(CL-co-BL). Content of the γ-oxybutyryl units (in mole fraction): 0 [.....],0.11 [-----],0.43[—].*[37]



ACKNOWLEDGEMENTS

This work was supported in part by the Polish Committee for Scientific Research (KBN) Grant 3 T09B 105 11. P. D. and D. M. thank the Polish Academy of Sciences and the Belgian National Fund for Scientific Research (FNRS) for a grant to visit the Center of Molecular and Macromolecular Studies in Lodz. P. D. is 'Chercheur Qualifié' of the Belgian FNRS.

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