

This article was downloaded by:

On: 24 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

Copolyesters of ϵ -Caprolactone, Isosorbide and Suberic Acid by Ring-Opening Copolymerization

Saber Chatti^a; Hans R. Kricheldorf^b

^a Pôle Technologique Sidi Thabet, Institut National de Recherche et d'Analyse Physico-Chimique (INRAP), Sidi Thabet, Tunisia ^b Institut für Technische und Makromolekulare Chemie, Hamburg, Germany

To cite this Article Chatti, Saber and Kricheldorf, Hans R.(2006) 'Copolyesters of ϵ -Caprolactone, Isosorbide and Suberic Acid by Ring-Opening Copolymerization', *Journal of Macromolecular Science, Part A*, 43: 7, 967 – 975

To link to this Article: DOI: 10.1080/10601320600740397

URL: <http://dx.doi.org/10.1080/10601320600740397>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Copolyesters of ϵ -Caprolactone, Isosorbide and Suberic Acid by Ring-Opening Copolymerization

SABER CHATTI¹ AND HANS R. KRICHELDORF²

¹Institut National de Recherche et d'Analyse Physico-Chimique (INRAP),
Pôle Technologique Sidi Thabet, Sidi Thabet, Tunisia

²Institut für Technische und Makromolekulare Chemie, Hamburg, Germany

Biodegradable copolyesters were prepared by copolymerization of ϵ -caprolactone (ϵ CL) with a cyclic polyester consisting of isosorbide and suberic acid (CPIS). Four initiators were compared: Sn(II)2-ethylhexanoate (SnOct₂) in combination with benzyl alcohol, 2,2-dimethyl-2-stanna-1,3-dioxepane (DSDOP) lanthanum and yttrium tris(isopropoxide). For SnOct₂ (combined with benzyl alcohol) and DSDPO temperature and time were varied. The highest molecular weights were obtained at the highest temperature. However, the compositions of the copolyesters varied largely. Whereas SnOct₂ favored the incorporation of CPIS, DSDOP favored incorporation of ϵ CL. A similar difference was found for La(OiPr)₃ favoring ϵ CL and Y(OiPr)₃ favoring incorporation of CPIS. ¹³C NMR spectroscopy proved that SnOct₂ yielded blocky sequences and mixtures of homo-polyesters. A greater extent of transesterification and a tendency towards random sequences was observed for DSDOP catalyzed copolymers. All reaction products contained crystallizing blocks of ϵ CL units. The melting temperatures decreased with the extent of transesterification.

Keywords ring-opening copolymerization, transesterification, biodegradable polyesters, isosorbide, ϵ -caprolactone

Introduction

Isosorbide is technically produced in large quantities from glucose (1). Hence, it is the only relatively inexpensive diol which is based on renewable resources and is not based on oil or coal chemistry. Furthermore, it possesses an interesting combination of useful properties. First, incorporation of isosorbide into polymers containing alkane or aliphatic ether building blocks will raise the glass transition temperature (T_g). Second, isosorbide is a rather thermostable monomer, and its polymers may be heated for a short time to 300°C without decomposition and even without significant racemization (or epimerization). Third, isosorbide is a chiral building block which is insensitive to racemization under acidic or basic conditions. For these reasons, numerous polymers containing isosorbide were synthesized and characterized over the past three decades (2–12). Most of the patents and publications pertinent to this field were summarized

Received January 2006; Accepted February 2006.

Address correspondence to S. Chatti, Institut National de Recherche et d'Analyse Physico-Chimique (INRAP), Pôle Technologique Sidi Thabet, 2020 Sidi Thabet, Tunisia. E-mail: sabchatti@yahoo.com

and discussed in a review article which appeared in 1997 (2). The present work deals with synthesis and characterization of biodegradable polyesters based on ϵ CL and isosorbide. This work served two purposes. First, a new synthetic approach should be studied, namely the copolymerization of monomeric cyclic ester (i.e. ϵ -caprolactone) with a cyclic polyester (poly(isosorbide suberate), **1**). Second, it should be elucidated to what extent incorporation of isosorbide raises the T_g of aliphatic polyesters.

Experimental

Materials

ϵ -Caprolactone (ϵ CL) was purchased from Aldrich Co. (Milwaukee, WI) and distilled over freshly powdered calcium hydride. Suberoyl chloride and dibutyltin dimethoxide were also purchased from Aldrich Co. and used as received. Isosorbide was purchased from ACROS Chem. (Gel, Belgium) and dried over P_4O_{10} *in vacuo*. $SnOct_2$ was purchased from Aldrich Co. and purified as described previously (13). $La(OiPr)_3$ and $Y(OiPr)_3$ were purchased from ABCR Chem. (Karlsruhe, Germany) and used as received. DSDOP was prepared from dimethyltin dimethoxide and dry 1,4-butanediol as described previously (14). CH_2Cl_2 was distilled over P_4O_{10} and dioxane over sodium.

Cyclic Poly(Isosorbide Suberate), CIPS (12), 1C

Dry isosorbide (45 mmol) was suspended in dry dichloromethane (800 mL) and a solution of suberoyl chloride (45.3 mmol) in dichloromethane (200 mL) was added dropwise. When a clear solution was obtained (after 2–4 h) dry pyridine (180 mmol) was added dropwise. After stirring for 48 h at 20–25°C the reaction mixture was concentrated to a volume of approx. 150 mL and precipitated into cold methanol. The isolated polyester had an inherent viscosity of 0.33 dL/g (in $CH_2Cl_2/20^\circ C$) and the MALDI-TOF mass spectrum exclusively displayed peaks of cycles (see Figure 1A).

Copolymerizations

ϵ -Caprolactone (20 mmol) and CPIS (10 mmol) were weighed into a cylindrical glass reactor equipped with a mechanical glass stirrer, gas-inlet and gas-outlet tubes. A catalyst (0.15 mmol) was added in the form of a 1.0 M solution in dry chlorobenzene. The reaction vessel was placed into an oil bath and rapidly heated to reaction temperature (Table 1). After cooling the product was dissolved in CH_2Cl_2 (approx. 50 mL) and precipitated into cold methanol. The isolated polyester was dried at 20°C *in vacuo*.

Measurements

The inherent viscosities were measured in CH_2Cl_2 using an automated Ubbelohde viscometer thermostated at 20°C. The 400 MHz 1H NMR spectra were recorded on a Bruker "Avance 400" FT NMR spectrometer in 5 mm o.d. sample tubes. The 100.4 MHz ^{13}C -NMR spectra were recorded with the same spectrometer in 10 mm o.d. sample tubes. $CDCl_3$ containing TMS served as solvent. The DSC measurements were performed on a Mettler Toledo WD 821 in aluminium pans under nitrogen at a heating rate of 10°C/min.

The MALDI-TOF mass spectra were measured with a Bruker Biflex III equipped with a nitrogen laser ($\lambda = 337$ nm). All spectra were recorded in the reflection mode with an

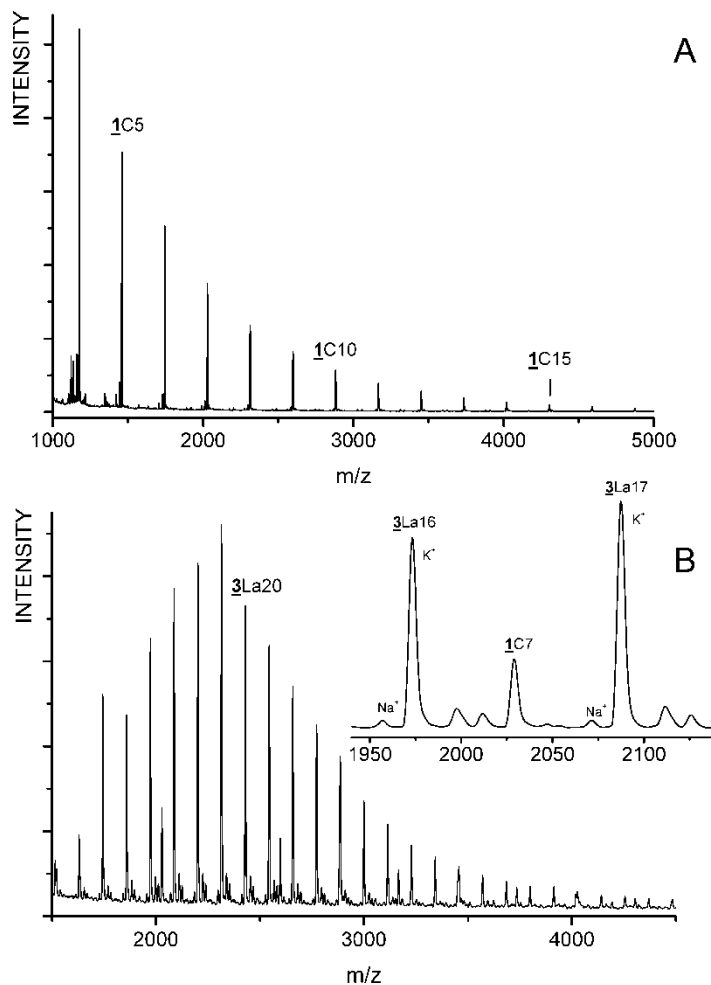


Figure 1. MALDI-TOF mass spectrum of: A) predominantly cyclic poly(isosorbide suberate) used as starting material; B) reaction product obtained by SnOct₂-initiated copolymerization at 80°C, No. 1, Table 1.

acceleration voltage of 20 kV. The irradiation targets were prepared from chloroform solutions with dithranol as matrix and K-trifluoroacetate as dopant.

Results and Discussion

All copolymerizations were conducted in bulk with a CPIS/ ϵ CL feed ratio of 1:2. Three parameters were varied: the catalyst, the temperature and the time as documented in Table 1. Four catalysts were compared: the tin-based catalysts SnOct₂ and DSDOP. Sn(II) salts were used by Kleine and Kleine as early as 1956 for ring-opening polymerizations of lactones (15). SnOct₂ has meanwhile become the most widely used catalyst for homo- and co-polymerizations of ϵ CL and lactide in both fundamental research and technical production of biodegradable polyesters. DSDOP is a cyclic tin alkoxide the structure of which is outlined in Scheme 1. This cyclic tin compound has proven to be

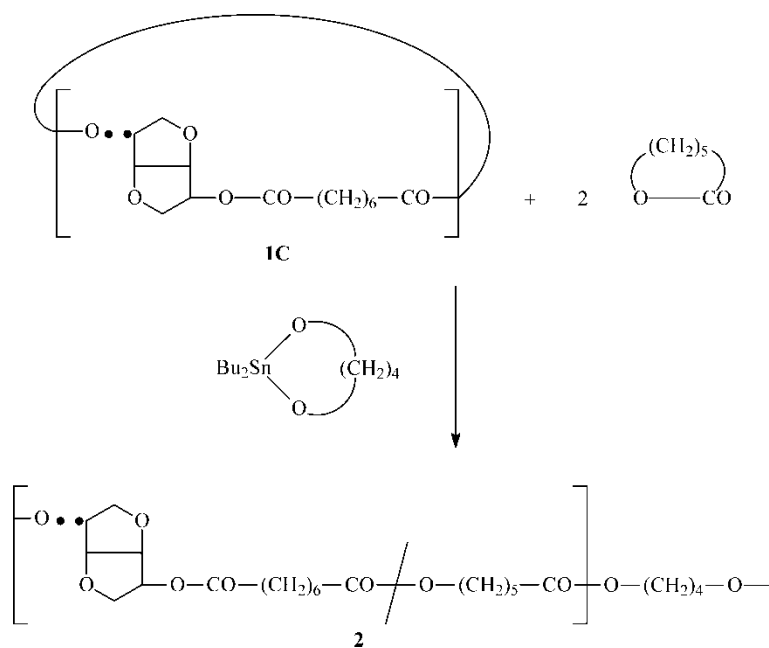
Table 1
Copolymerizations of CPIS and ϵ CL (feeds ratio = 1:2) conducted in bulk under various reaction conditions

Exp. no.	Initiator	Temp. ($^{\circ}$ C)	Time (h)	Yield (%)	CPIS ^a / ϵ CL	η_{inh}^b (dL/g)
1	SnOct ₂ + C ₆ H ₅ CH ₂ OH	80	20	63	1.0/0.9	0.30
2	SnOct ₂ + C ₆ H ₅ CH ₂ OH	120	20	56	1.0/1.6	0.27
3	SnOct ₂ + C ₆ H ₅ CH ₂ OH	120	4	79	1.0/1.8	0.29
4	SnOct ₂ + C ₆ H ₅ CH ₂ OH	160	4	70	1.0/2.2	0.28
5	SnOct ₂ + C ₆ H ₅ CH ₂ OH	200	4	81	1.0/2.3	0.46
6	DSDOP	80	4	83	1.0/8.0	0.15
7	DSDOP	80	20	79	1.0/3.2	0.32
8	DSDOP	120	20	83	1.0/2.9	0.40
9	La(OiPr) ₃	80	20	77	1.0/3.7	0.30
10	Y(OiPr) ₃	80	20	83	1.0/1.7	0.31

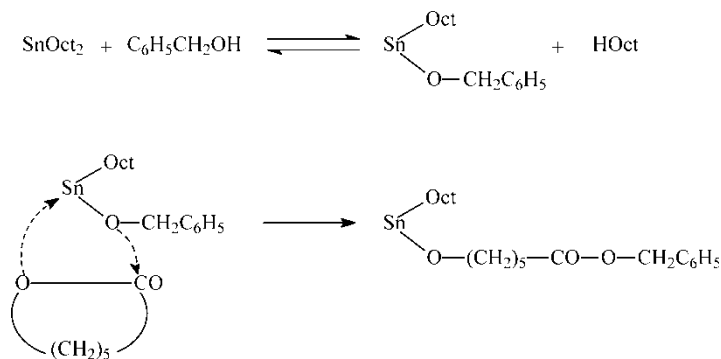
^aMolar composition of the isolated copolyesters as determined by ¹H NMR spectroscopy.

^bMeasured at 20 $^{\circ}$ C with c = 2 g/L in CH₂Cl₂.

a highly reactive initiator for ring expansion polymerizations of various lactones and cyclic diesters (16, 17). Lanthanum and yttrium tris(isopropoxides) are particularly reactive initiators for lactones and lactide allowing for their ring-opening polymerizations even at temperatures below 50 $^{\circ}$ C (18, 19).



Scheme 1. DSDOP-initiated copolymerization CPIS and ϵ CL.



Scheme 2. SnOct_2 /benzyl alcohol-initiated polymerization of ϵCL .

It is well known that the efficiency of SnOct_2 as initiator increases when an alcohol is added as coinitiator. The reaction mechanism of SnOct_2 /alcohol-initiated ring-opening polymerizations of cyclic esters has recently been elucidated by two research groups (13, 20) as illustrated for benzyl alcohol in Scheme 2. In this work, benzyl alcohol was added as coinitiator because the aromatic protons of benzyl ester endgroups are easily detectable in the $^1\text{H-NMR}$ spectra of the reaction products. The temperature of the SnOct_2 -initiated polymerizations were varied from 80 to 200°C (Nos. 1–5, Table 1). The virgin reaction products were characterized by $^1\text{H-NMR}$ spectroscopy to determine the composition. The $^1\text{H-NMR}$ spectrum of Figure 2B demonstrated by comparison

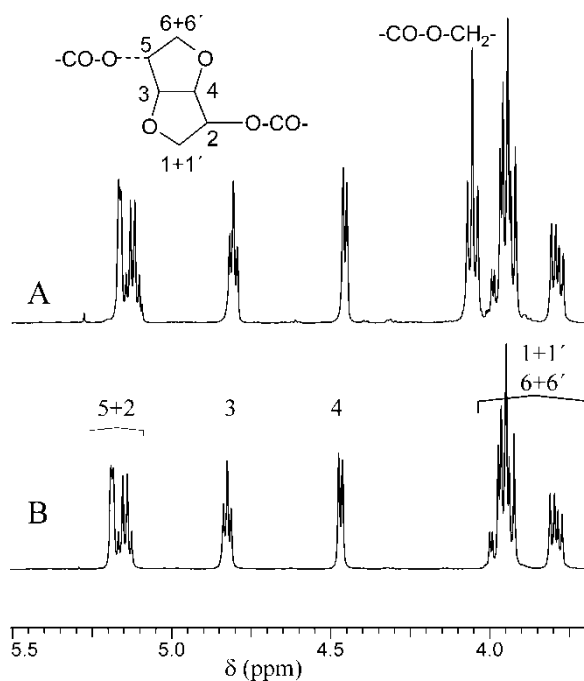


Figure 2. 400 MHz $^1\text{H-NMR}$ spectra of: A) reaction product obtained by SnOct_2 -initiated copolymerization at 80°C , No. 1, Table 1; B) poly(isosorbide suberate) used as starting material.

with that of the cyclic polyester **1** (Figure 2A) that a temperature of 80°C indeed sufficed for a partial polymerization of ϵ CL. However, the composition listed in Table 1 also indicates that not more than 50% of ϵ CL was in fact polymerized. With higher temperatures the content of ϵ CL units approached the feed ratio. However, the composition does not say anything yet about the extent of transesterification and the character of the comonomer sequences. Therefore, ^{13}C -NMR spectra were recorded with expanded reactions of the CO-signals because the CO-signals of copolyesters were known to be particularly sensitive to sequence effects (21–23). On the basis of the limited signal-to-noise ratio of these NMR spectra (see Figures 3 and 4), no indication of transesterification was found for the products of experiments 1–4 (Figure 3). In other words, it is not clear to what extent these reaction products are mixtures of homopolyesters or (multi)block copolymers. The MALDI-TOF mass spectra (m.s.) agree with this scenario. As illustrated by m.s. of Figure 1B, the most intensive peaks originate from benzyl alcohol-initiated poly(ϵ CL) (structure **3La** in Scheme 3). A series of weak peaks represents unreacted cyclic poly(isosorbide suberate), **1C**. After copolymerization at 200°C (No. 5, Table 1), the ^{13}C -NMR spectrum displays a new weak CO-signal (“f” in Figure 3) which represents a ϵ CL unit connected to isosorbide, and thus, indicates more intensive transesterification. The MALDI-TOF m.s. displays a multitude of new signals which also agree with the formation of cyclic and linear copolyesters.

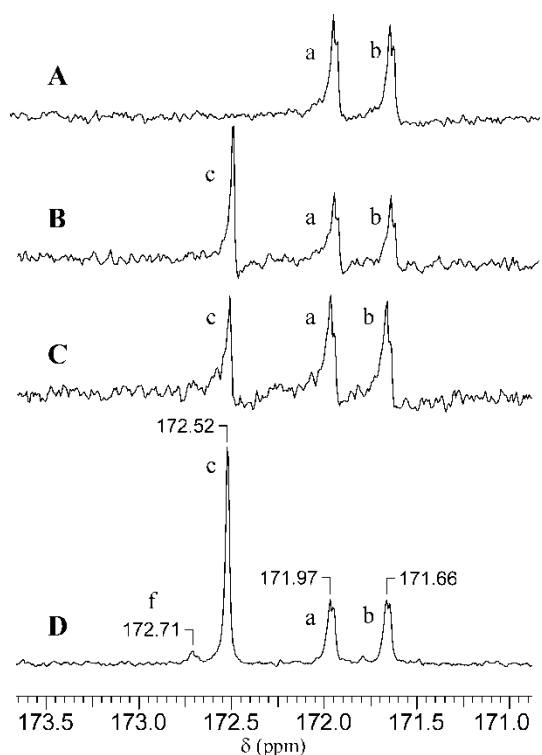


Figure 3. 100.4 MHz ^{13}C -NMR spectra (CO signals only) of: A) poly(isosorbide suberate); B) mixture of poly(ϵ -CL) and poly(isosorbide suberate); C) reaction product obtained by SnOct_2 -initiated copolymerization at 120°C, No. 2, Table 2; D) reaction product obtained by SnOct_2 -initiated copolymerization at 200°C, No. 5, Table 1.

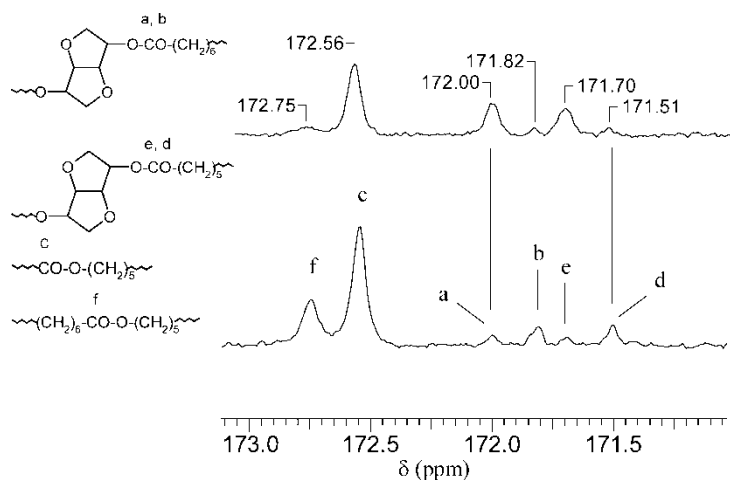
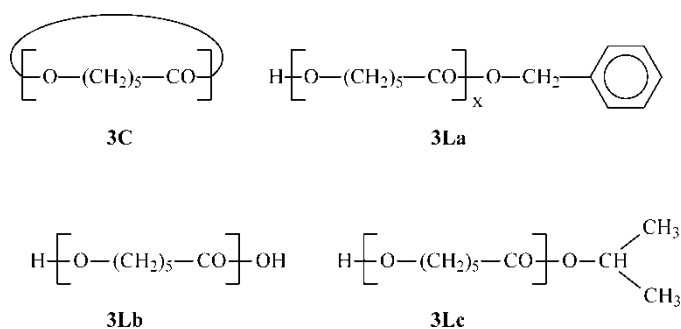


Figure 4. 100.4 MHz ^{13}C -NMR spectra of DSDOP-initiated copolymerizations: A) after 4 h/80°C (No. 6, Table 1); B) 20 h/120°C (No. 8, Table 1).

Furthermore, the highest viscosity was achieved in the 200°C experiment. Therefore, it may be concluded that this “high-temperature copolymerization” is the only successful experiment on the basis of the SnOct_2 /benzyl alcohol initiator.

Dibutyltin dialkoxides are known to be highly effective transesterification catalysts and initiators and the results obtained with DSDOP were indeed quite different from those obtained with SnOct_2 . A first characteristic difference are the high $\epsilon\text{CL}/\text{CPIS}$ ratios (Nos. 6–8). It seems that an efficient polymerization of ϵCL was combined with a partial degradation (resulting from back-biting) of CPIS. With higher temperatures, the compositions approached the feed ratio. Second, three new CO-signals (b, d and f) were detectable in the ^{13}C NMR spectra of all three samples (Figure 4), suggesting that intensive transesterification with a tendency towards random sequences had occurred. Taking into account that the highest viscosity was obtained at the highest reaction temperature, experiment No. 7 may be considered to be the most successful copolymerization of this work.

The copolymerizations attempted with $\text{La}(\text{OiPr})_3$ and $\text{Y}(\text{OiPr})_3$ gave the interesting result that the compositions of the reaction products showed opposite trends. A higher



Scheme 3. Reaction products of ϵCL observed in MALDI-TOF m.s.

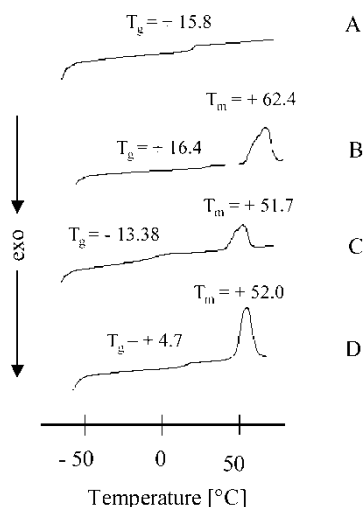


Figure 5. DSC heating curves (heating rate 10°C/min): A) poly(isosorbide suberate); B) mixture of poly(ϵ -CL) and poly(isosorbide suberate); C) reaction product obtained by SnOct₂ at 80°C (No. 1, Table 1); D) reaction product of the copolymerization initiated by SnOct₂ at 120°C (No. 2, Table 1).

content of ϵ CL units (relative to the feed ratio) was found for La and a lower ϵ CL content for Y. However, in neither case any indication of significant transesterification was found, so that no proof for the formation of true copolyester was found. The MALDI-TOF m.s. mainly displayed peaks of OH-terminated poly(ϵ CL) chains (**3Lb**) and of isopropanol-initiated poly(ϵ CL) chains (**3Lc**) Furthermore, weak peaks of unreacted CPIS chains were detectable. All MALDI-TOF m.s. together suggest that the linear poly(ϵ CL) chains “fly better” than the CPIS polyesters. Finally, the DSC measurements need a short comment. Two DSC heating curves of copolymerization products (Nos. 1 and 2) are displayed together with those of CPIS and a mixture of CPIS and poly(ϵ CL) in Figure 5. The most important result of these measurements is the observation that all samples display a melting endotherm (T_m) of poly(ϵ CL) blocks in their heating traces.

Table 2

Glass-transition (T_g) and melting temperatures (T_m) of various homo- and copolyesters

Polyesters	η_{inh}^a (dL/g)	T_g^b (°C)	T_m^b (°C)
CPIS	0.32	+16	—
Poly(ϵ -caprolactone)	0.35	-66	64.5
Copolyester No. 1, Table 1	0.29	-14	52.0
Copolyester No. 2, Table 1	0.27	+5	52.0
Copolyester No. 3, Table 1	0.29	-1	56.0
Copolyester No. 6, Table 1	0.15	-48	9.5 + 40.0 ^c

^ameasured at 20°C with $c = 2$ g/L in CH₂Cl₂.

^bDSC measurements with a rate of 10°C/min, 1st heating.

^cThe first endotherm was weaker and partially merged into the second endotherm in the second heating curve.

The weakest endotherm at the lowest temperature (between 30°C and 40°C) was observed for sample No. 8, corresponding to the highest level of transesterification and randomization. The T_m s of selected samples are listed in Table 2. This finding agrees with the MALDI-TOF m.s. which evidenced that all samples contain poly(ϵ CL) chains.

Conclusions

The present work had the purpose to serve as a first attempt to explore the copolymerization of a polydisperse cyclic polyester (CPIS) with a monomeric lactone (ϵ CL). The results demonstrate that such a copolymerization is in principle feasible, but composition, monomer sequence and physical properties depend very much on the initiator. DSDOP proved to be more efficient than the combination of SnOct_2 + benzyl alcohol in the polymerization of ϵ CL and in transesterification reactions. DSDOP also proved to be more efficient than $\text{La}(\text{OiPr})_3$ or $\text{Y}(\text{OiPr})_3$, although these rare earth alkoxides are the more efficient initiators of the ring-opening polymerization of L-lactide at low temperatures.

References

1. Flèche, G. and Huchette, M. (1986) *Starch/Stärke*, 38: 26.
2. Kricheldorf, H.R. (1997) *J.M.S.–Rev. Macromol. Chem. Phys.*, C37: 599.
3. Kricheldorf, H.R., Sun, S.-J., and Chang, T.-C. (1997) *J. Polym. Sci. Part A Polym. Chem.*, 35: 1611.
4. Kricheldorf, H.R. (1999) *Polym. Prep. ACS Polym. Div.*, 40: 568.
5. Sun, S., Schwarz, G., Kricheldorf, H.R., and Chang, T. (1999) *J. Polym. Sci. Part A. Polym. Chem.*, 37: 1125.
6. Espinosa, M., Cadiz, V., and Galia, M. (2001) *J. Polym. Sci. Part A. Polym. Chem.*, 39: 2847.
7. Charbonneau, L.F.; Khanarian, G.; Johnson, R.E.; Witteler, H.B.; Flint, J.A. US Pat. 6,063,495 to Hna Holding Inc. 2000.
8. Hayes, R.A. US Pat. 6,368,710 to DuPont, 2000.
9. Adelman, D.J.; Charbonneau, L.F.; Ung, S. US Pat. 6,656,577 to DuPont, 2003.
10. Adelman, D.J.; Green, R.N.; Putzig, D.E. US Pat. 0232960 to DuPont, 2003.
11. Lin, Q., Pasattie, J., and Long, T.E. (2003) *J. Polym. Sci. Part A., Polym. Chem.*, 41: 2512.
12. Kricheldorf, H.R., Chatti, S., Schwarz, G., and Krüger, R.-P. (2003) *J. Polym. Sci. Part A., Polym. Chem.*, 41: 3414.
13. Kricheldorf, H.R., Kreiser-Saunders, I., and Stricker, A. (2000) *Macromolecules*, 33: 702.
14. Kricheldorf, H.R. and Eggerstedt, S. (1998) *Macromol. Chem. Phys.*, 199: 283.
15. Kleine, J. and Kleine, H.H. (1959) *Makromol. Chem.*, 30: 23.
16. Kricheldorf, H.R. and Eggerstedt, S. (1999) *Macromol. Chem. Phys.*, 198: 283.
17. Kricheldorf, H.R. (2004) *J. Polym. Sci. Part A, Polym. Chem.*, 42: 4723.
18. McLain, S.J. and Drysdale, N.E. (1992) *Polym. Prep. ACS Polym. Div.*, 33: 174 and 463.
19. Stevels, W., Dijkstra, P.J., and Feijen, J. (1996) *Macromolecules*, 29: 6132.
20. Kowalski, A., Duda, A., and Penczek, S. (2000) *Macromolecules*, 33: 7359.
21. Kricheldorf, H.R. (1978) *Makromol. Chem.*, 179: 2133.
22. Kricheldorf, H.R., Mang, T., and Jonté, J.M. (1984) *Macromolecules*, 17: 2173.
23. Kricheldorf, H.R., Mang, T., and Jonté, J.M. (1985) *Makromol. Chem.*, 186: 955.