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Synthesis and characterization of oligo(lactone) methacrylates

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Oligo(lactone) methacrylates have been synthesized by oligomerization of L-lactide, D,L-lactide, ε-caprolactone and glycolide as well as by cooligomerization of the latter two with the former two. The oligomerization reaction was initiated by bisphenol-A-bis(2-hydroxypropyl methacrylate) and catalysed by a series of coordination-insertion catalysts of ring-opening polymerizations of lactones. The kinetics of the oligomerization of lactide at 130°C and the relatively narrow molecular weight distribution of the macromonomers, characterized by $M_w/M_n \approx 1.2$, suggest a living mechanism of the reaction. Optically pure macromonomers were obtained from L-lactide using Sn(II) octoate as a catalyst. Other catalysts, e.g. MgO, CaO, SnO_2 etc., caused racemization (17–37%). Relationships between the nature of the lactone units as well as the oligomerization degree of the macromonomers and the glass transition temperatures, melting points and degrees of crystallinity of the macromonomers were determined. © 1997 Elsevier Science Ltd.

(Keywords: macromonomer; methacrylate; oligo(lactone))

INTRODUCTION

Oligo(lactone) methacrylates are of interest for medical applications. Two principal methods to prepare macromonomers have been used for their synthesis.

(i) End-capping of oligo(lactone)s with suitable methacrylic derivatives[1–4].
(ii) Initiation of the lactone oligomerization by a methacrylic derivative with a suitable initiating group[3,5–10].

ε-Caprolactone and lactide were oligomerized by method (ii) utilizing a coordination–insertion mechanism with the aluminium monoalkoxide from triethylaluminium and 2-hydroxyethyl methacrylate (HEMA) as an initiator[3,5,6]. Macromonomers were obtained with a narrow molecular weight distribution, characterized by $M_w/M_n \approx 1.2$, indicating a living mechanism of the reaction. The living character of these lactone polymerization reactions was also concluded from the observed linear dependencies of the polymerization degree on the molar ratio of monomer and initiator as well as on the conversion of the reaction[5,6].

However, macromonomers prepared by the cationic ring-opening polymerization of various lactones with triethyloxonium hexafluorophosphate as an initiator, in the presence of HEMA at 25–80°C[7], showed a relatively broad molecular weight distribution, with M_w/M_n in the range of 1.7–2.5.

Catalysis of the ε-caprolactone polymerization with stannous octoate ($SnOct_2$), alkyl tin compounds or alkyl titanates in the presence of hydroxyalkyl (meth)acrylates required higher reaction temperatures, e.g. 100 to about 140°C[8].

We have found these reaction conditions to be a convenient technique for the preparation of oligo(lactide) methacrylates from various hydroxyalkyl methacrylates, e.g. HEMA, bisphenol-A-bis(2-hydroxypropyl methacrylate) (BisGMA) and 2-hydroxy-3-(2,4,6-tri-iodophenoxy) propyl methacrylate. The copolymerization of some of these macromonomers as well as the properties and the degradation behaviour of composites from the macromonomers have been reported[9,10]. Besides $SnOct_2$, MgO and N-vinylimidazole were also tested as catalysts of the lactide oligomerization at 130°C. In all cases, the increase of the number-average of the molecular weights, M_n, of the macromonomers during the reaction time as well as the relatively narrow molecular weight distribution ($M_w/M_n = 1.2–1.3$) of the reaction products after $\geq 95\%$ conversion of lactide indicated a living mechanism of the oligomerization reaction[9].

Dunsing and Kricheldorf[11] doubted the living character of the polymerization of L-lactide with MgO as a catalyst at 150°C. They found the expected steady increase of the yield of poly(L-lactide) with the reaction time, but the molecular weights were independent of the yield. Furthermore, poly(L-lactide) obtained by Kricheldorf *et al.*[12] with $SnOct_2$ as a catalyst and benzyl alcohol as a coinitiator at 120°C, possessed a relatively broad molecular weight distribution ($M_w/M_n \geq 2$), which is also inconsistent with a living mechanism. M_n of the poly(L-lactide)s actually increased with increasing L-lactide/alcohol ratio, but the polymerization degree P_n determined by ^1H nuclear magnetic resonance (n.m.r.) end group analysis, was considerably higher than P_n calculated for a quantitative initiation by the alcohol. An incomplete precipitation of oligomers when separating

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the lactide from the reaction mixture was cited by the authors as a reason for the discrepancies.

Therefore, we have studied the kinetics of the lactide oligomerization initiated by BisGMA, using gel permeation chromatography (g.p.c.) measurements as a method of avoiding the difficult separation of lactide monomer from its oligomers. In this paper, the results of further kinetic tests relating to a living mechanism of the lactide oligomerization will be discussed. Also, the influence of the reaction conditions on M_w/M_n and the stereoregularity of the macromonomers as well as their thermal transitions will be reported.

EXPERIMENTAL

Materials

Bisphenol-A-bis(2-hydroxypropyl methacrylate) (BisGMA) was synthesized as described in ref. 13.

L,L- and D,L-lactide (Boehringer Ingelheim KG) were purified by recrystallization from ethyl acetate (distilled over calcium hydride), and dried over P_4O_{10} in a vacuum. Glycolide (Boehringer Ingelheim KG), ε-caprolactone (Fluka), $SnOct_2$ (Sigma Chemical Co.), 2,6-di-*t*-butyl-*p*-cresol (Ionol) (Merck-Schuchardt), *N*-vinylimidazole (NVI) (Riedel-de Haen AG), diglycidyl ether of bisphenol-A (DGEBA) (Leuna-Werke AG) and methacrylic acid (MAA) (Röhm Chemische Fabrik) were used as received. All other chemicals used were of analytical grade and used without further purification.

Synthesis of macromonomers by reaction of lactones with BisGMA

Mixtures of BisGMA, lactone, Ionol (0.3 wt% related to BisGMA) and catalyst in different ratios were stirred under air at 130°C for several hours until the lactone reacted almost completely. The conversions of the lactone were monitored by g.p.c. The synthesis of macromonomers was also carried out by parallel reaction of DGEBA, MAA and lactide in the presence of NVI as catalyst and of 0.1 wt% Ionol, with respect to the mass of DGEBA and MAA, at 110°C for 4 h.

Measurements

G.p.c. measurements were carried out in tetrahydrofuran (THF) on a Knauer device at a flow rate of $1\,ml\,min^{-1}$ with a combination of three HIBAR RT columns (PS1, PS4, PS20) (Merck) and detection with a differential refractometer (Knauer). The molecular weight was calibrated relative to monodisperse polystyrene. For determining the conversions of lactone, a calibration of lactone concentration against peak height was made.

The crude reaction product was dissolved in chloroform, precipitated in cold methanol and dried over calcium chloride at room temperature in a vacuum for determining M_n by ^1H n.m.r. spectroscopy.

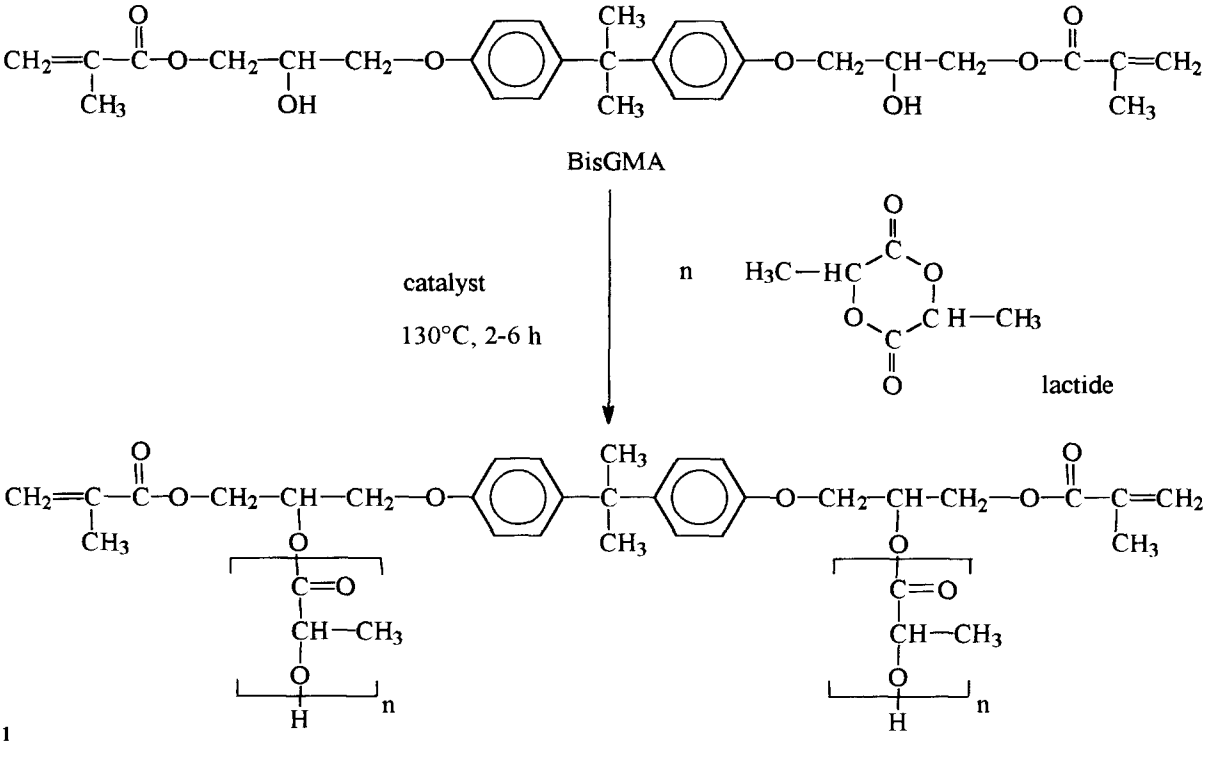
The ^1H n.m.r. spectra of the purified macromonomers were obtained on a Gemini 300 (Varian) at a frequency of 300 MHz. The intensity ratio of the CH signals of the lactide units at 5.1–5.2 ppm and of the CH_3 signals of the methacrylate group at 1.9 ppm was used to determine M_n.

The optical rotations of macromonomers were measured in $CHCl_3$ at a concentration of $10\,g\,l^{-1}$, related to the content of oligo(lactone) at 20°C on a Carl Zeiss Jena polarimeter. Thermal properties of the macromonomers were measured with a differential scanning calorimeter (d.s.c.) 220 (Seiko Instruments) in aluminium pans under air at a heating rate of $10°C\,min^{-1}$.

RESULTS AND DISCUSSION

Catalysis of lactide oligomerization initiated by BisGMA

The oligomerization of both L-lactide and D,L-lactide can be initiated by BisGMA according to Scheme 1. In principle, a large number of transesterification catalysts appear to be suitable for acceleration of this reaction.



Scheme 1

Figure 1 shows the increase of the number-average of the molecular weights (M_n) during the oligomerization of L-lactide initiated by BisGMA at 130°C and accelerated with five different catalysts. Including additional catalysts tested, we found a decreasing activity in the series of catalysts: $SnOct_2 > SnCl_2 \cdot 2H_2O > NVI \approx MgO > ZnO \approx SnO_2 > Al_2O_3 > CaO \approx SnO \approx MgCO_3 > AlCl_3$.

Clearly $SnOct_2$, the most commonly used catalyst for the polymerization of lactide[14], has been found to be the most effective also for this oligomerization reaction. However, the use of $SnOct_2$ to prepare poly(lactide) for medical purposes has been questioned because of a possibly injurious effect of $SnOct_2$ on the human body[15].

Therefore, MgO should be preferred as a catalyst. It is of reasonable activity despite its insolubility in the reaction mixture. About the same reaction rate as with $[SnOct_2]/[BisGMA] = 0.02$ was achieved using about a twenty-fold higher molar ratio of MgO to BisGMA (*Figures 1* and *2*). Since MgO is more biologically acceptable, the oligomerization reaction may be carried out at this relatively high concentration of MgO.

NVI is a further catalyst of interest, for it is of

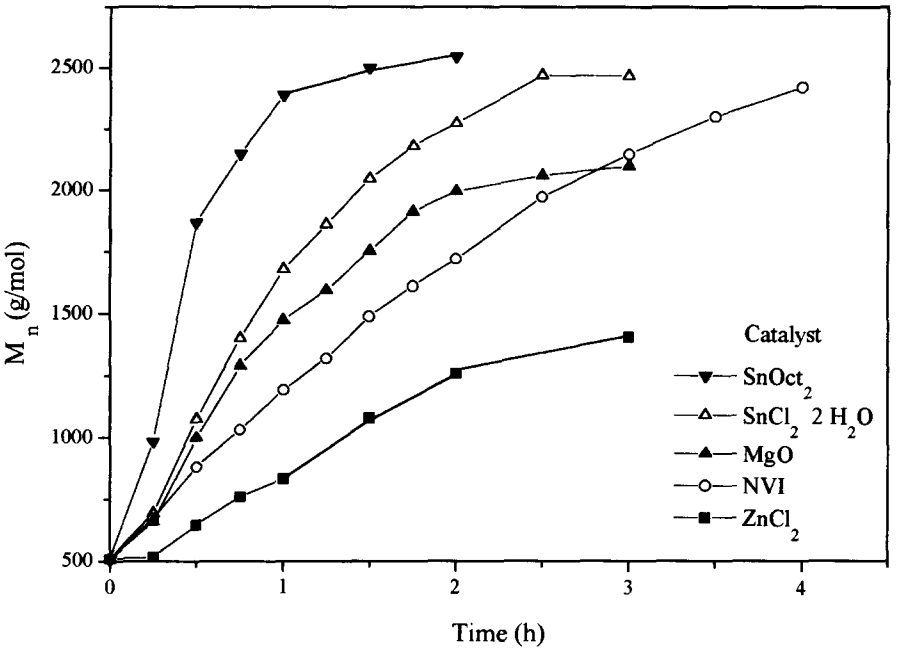


Figure 1 M_n of macromonomers from BisGMA and D,L-lactide (1/10 mol/mol) *versus* oligomerization time at 130°C ($M_{n,calc} = 2000\,g\,mol^{-1}$; molar ratio of BisGMA to catalyst 1/0.02)

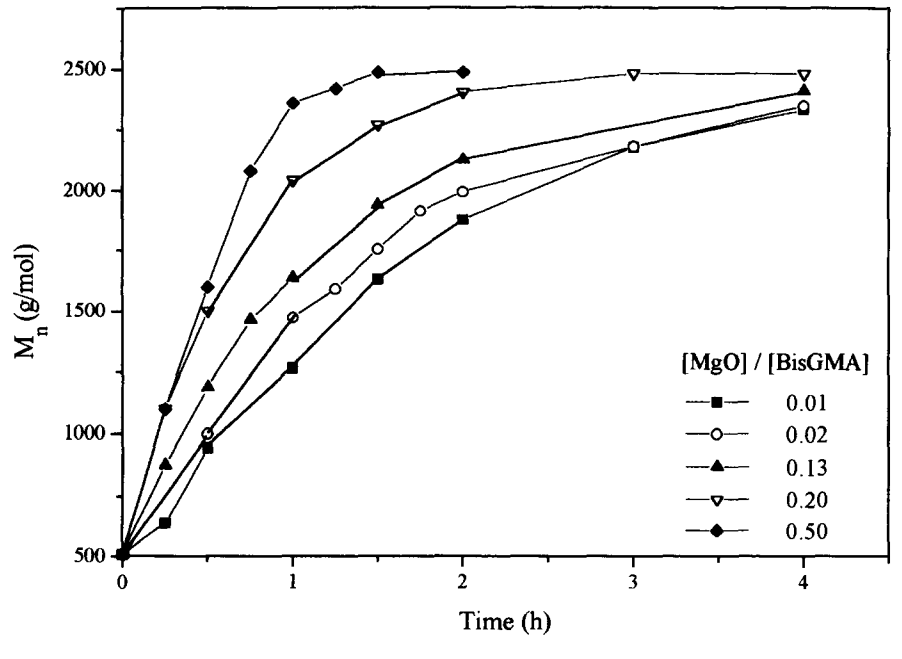


Figure 2 M_n of macromonomers from BisGMA and D,L-lactide (1/10 mol/mol) in dependence on the concentration of MgO as catalyst of oligomerization at 130°C

reasonably catalytic activity and it can be incorporated into the polymer network by crosslinking copolymerization with the macromonomer.

First of all, it is remarkable that the spontaneous free-radical polymerization of the dimethacrylate can be prevented even at a reaction temperature of 150°C by carrying out the oligomerization reaction under air. Further, the latter can be accomplished advantageously without any solvent, resulting in directly applicable macromonomers in contrast to catalysis of the lactide oligomerization by aluminium alkoxide[6].

Kinetics and the living mechanism of lactide oligomerization

It is well known[16] that the polymerization of lactide catalysed by the metallic compounds mentioned above, proceeds according to a coordination–insertion mechanism, with living character.

The reaction will be of the living type if the following conditions are fulfilled:

(i) M_n of the macromonomer is predictable according to the following equation (1)

$$M_n = M_{BisGMA} + \frac{[\text{lactide}] \times M_{lactide} \times X_{lactide}}{[\text{BisGMA}]} \quad (1)$$

where M_{BisGMA} and $M_{lactide}$ are the molecular weights of BisGMA and lactide, respectively, and $X_{lactide}$ is the conversion of lactide.

(ii) The molecular weight distribution is relatively narrow with $M_w/M_n \leq 1.2$.

(iii) The oligomerization rate is of first order related to [lactide].

The linear increase of M_n of the macromonomers with increasing conversion of lactide according to equation (1) is shown in *Figure 3*. It is consistent with the living mechanism.

However, *Table 1* demonstrates that M_n values found by g.p.c. differ from those calculated according to equation (1) for 100% conversion by factors from 0.8 to 1.9. Calibration of M_n of these macromonomers by poly(styrene) standards results obviously in the systematic differences found. Therefore, M_n of some oligo(L-lactide) macromonomers was also determined by ^{1}H n.m.r. after separation of non-converted L-lactide. A good agreement between M_n calculated and M_n found by ^{1}H n.m.r. is shown in *Table 2*, for the macromonomers with $M_n \geq 4000\,g\,mol^{-1}$. Incomplete precipitation of the macromonomers with $M_n < 4000\,g\,mol^{-1}$ in methanol appears to be the reason that their molecular weights were found to be too high. This conclusion is

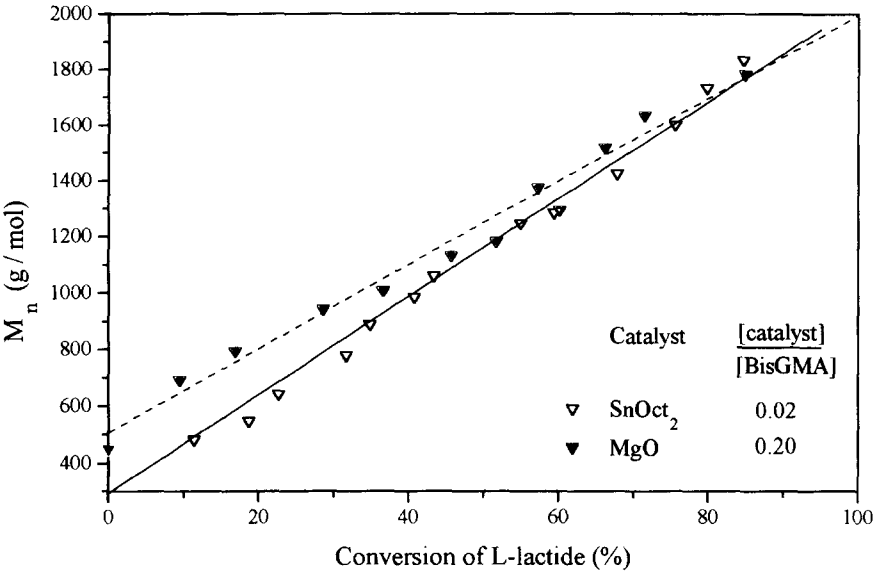


Figure 3 Relationship between M_n (g.p.c.) and L-lactide conversion at 120°C; [L-lactide]/[BisGMA] = 10

Table 1 Oligomerization of D,L-lactide initiated by BisGMA at 130°C

[D,L-lactide]/[BisGMA]	Catalyst	[Catalyst]/[BisGMA]	Oligomerization time (h)	M_n (g mol^{-1}) calc.	M_n (g mol^{-1}) found	M_w/M_n
4	–	–	7	1090	920	1.16
7	–	–	7	1520	1960	1.16
10	MgO	0.02	4	1950	2340	1.14
10	$SnCl_2 \cdot 2H_2O$	0.02	2.5	1950	2470	1.11
10	NVI	0.02	4	1950	2430	1.13
10	MgO	0.20	3	1950	2450	1.33
10	$SnOct_2$	0.02	2	1950	2350	1.24
17	$SnOct_2$	0.05	0.75	2960	4220	1.26
24	$SnOct_2$	0.05	1	3970	6200	1.10
31	$SnOct_2$	0.05	1	4980	7270	1.05

Table 2 Comparison of the calculated molecular weights of macromonomers with those experimentally found

[L-lactide]/[BisGMA] (mol/mol)	$M_{n,calc.}$ (g mol^{-1})	$M_{n,n.m.r.}$ [a] (g mol^{-1})	$M_{n,g.p.c.}$ [a] (g mol^{-1})	$M_{n,g.p.c.}$ [b] (g mol^{-1})	M_w/M_n [b] (g mol^{-1})
40	6280	6120	9320	10730	1.07
31	4980	5120	9830	8740	1.05
24	3970	4120	7180	7650	1.05
17	2960	3830	6480	4950	1.14
10	1950	3970	5280	2500	1.19

[a] Purified macromonomer
[b] Crude product

Table 3 Pseudo rate constants, k', for the reaction of L-lactide with BisGMA at different temperatures (molar ratio 10/1; $[SnOct_2]$/[BisGMA] = 0.02; [MgO]/[BisGMA] = 0.20)

Catalyst	Temperature (°C)	k' (min^{-1})	E_A (kJ mol^{-1})
MgO	122	0.00413	
MgO	128	0.00711	
MgO	137	0.01792	137.0
$SnOct_2$	120	0.00517	
$SnOct_2$	134	0.01003	
$SnOct_2$	142	0.01362	58.9

supported by comparison of M_n of the crude and purified products, both determined by g.p.c. (*Table 2*). Also Kricheldorf *et al.*[12] observed this fractionating effect, as already mentioned.

Condition (ii) is relatively well fulfilled in the oligomerization reaction of D,L-lactide with different catalysts. The molecular weight distribution characterized by the ratio M_w/M_n becomes narrower with increasing polymerization degree P_n from 10 to 31 of the macromonomer (*Table 1*). The latter has to be expected for a living polymerization, according to equation (2)

$$M_w/M_n = 1 + 1/P_n \quad (2)$$

The linear dependence of $-\ln([\text{lactide}]_t/[(\text{lactide}]_0)$, where $[\text{lactide}]_t$ and $[\text{lactide}]_0$ are the concentrations of lactide at reaction time t and at the beginning of the reaction, respectively, on the oligomerization time indicates that the reaction also meets condition (iii) (*Figure 4*).

The oligomerization rate of L-lactide initiated by BisGMA and catalysed by $SnOct_2$ is also first order with respect to catalyst, as shown by the linear dependence of $(\ln([\text{lactide}]_t/[\text{lactide}]_0))/t$ on the concentration of catalyst (*Figure 5*). The slope of the straight line is the rate constant, k, of the reaction corresponding to equation (3)

$$\frac{-\ln([\text{lactide}]_t/[(\text{lactide}]_0)}{[\text{catalyst}]\,t} = k \quad (3)$$

and equals 0.3241 mol^{-1} min^{-1}. This line does not go through the origin because BisGMA has been prepared using 0.8 mol% of NVI as a catalyst[13]. Therefore, there is some catalyst present additional to $SnOct_2$, for acceleration of the oligomerization of lactide.

The pseudo rate constants $k' = -(\ln([\text{lactide}]_t/[\text{lactide}]_0))/t$ of the oligomerization catalysed by MgO and $SnOct_2$, respectively, at three different temperatures each, and the activation energies, E_A, are listed in *Table 3*. The remarkably large difference between the activation energies of the reaction catalysed by MgO and $SnOct_2$ may be caused both by the heterogeneity with MgO and by the differences between the ability of the metal atoms to coordinate lactide.

Modification of macromonomer synthesis and cooligomerization of lactide

The addition of D,L-lactide and catalyst to a reaction mixture of DGEBA and MAA, the starting compounds of BisGMA, also resulted in the formation of the macromonomer. However, its molecular weight distribution was much broader, with $M_w/M_n = 1.48$, than that of the macromonomers discussed above (*Table 1* and *Figure 6*). The molecular weights of the macromonomers formed at the beginning of the reaction were relatively high, corresponding to the low concentration of BisGMA.

Furthermore, the reaction between DGEBA and D,L-lactide (molar ratio 1/5) without MAA was carried out with 0.33 mol% $SnOct_2$ as a catalyst at 135°C. After

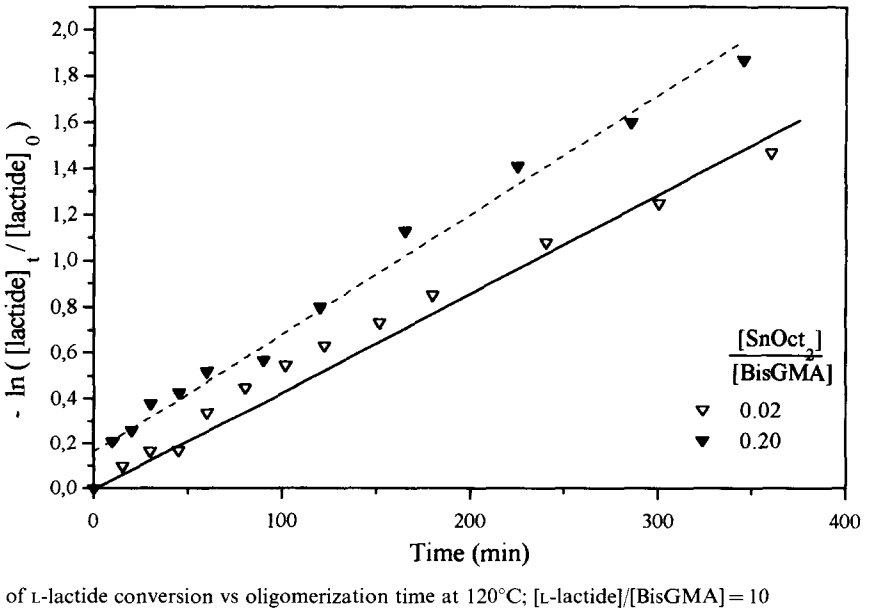


Figure 4 First order plot of L-lactide conversion vs oligomerization time at 120°C; [L-lactide]/[BisGMA] = 10

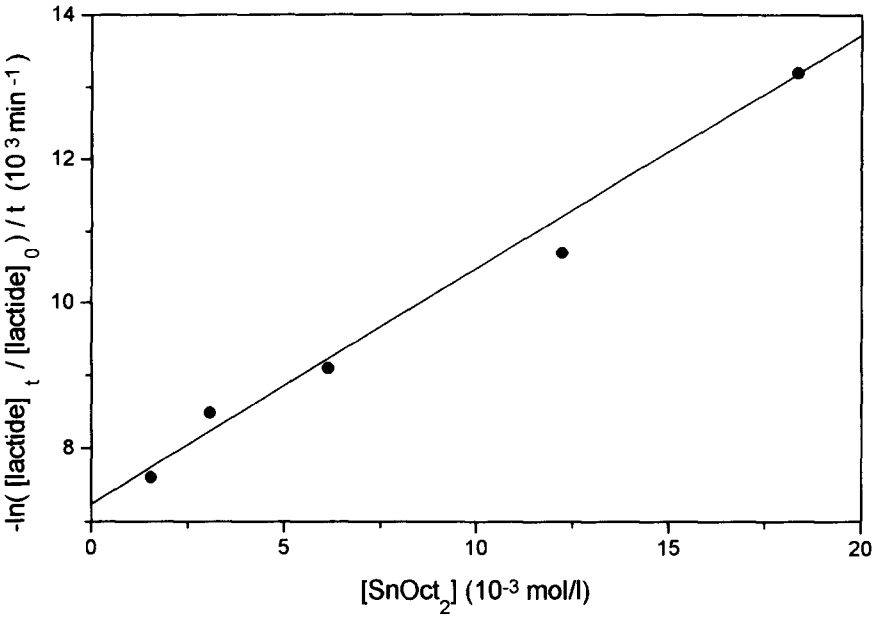


Figure 5 First order plot for the rate of oligomerization of L-lactide initiated with BisGMA (10/1 mol/mol)) and catalysed by $SnOct_2$ at 130°C

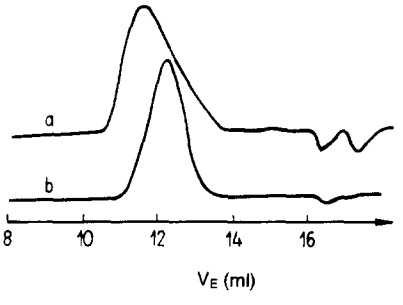


Figure 6 G.p.c. measurements of macromonomers prepared by reaction of D,L-lactide with DGEBA and MAA (10/1/2 mol/mol/mol) at 110°C (a), and of D,L-lactide with BisGMA (10/1 mol/mol) at 130°C (b), for 4 h catalysed by 0.8 mol% (a) and 2.0 mol% (b) NVI with respect to BisGMA

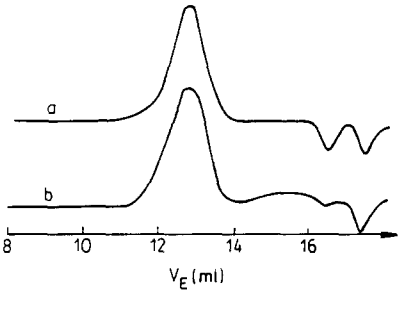


Figure 7 G.p.c. measurements of macromonomers prepared at 130°C from BisGMA, L-lactide and ε-caprolactone (1/7/3 mol/mol/mol) (a) and from BisGMA, D,L-lactide and glycolide (1/7/3 mol/mol/mol) (b)

90 min, lactide had reacted completely, forming a polymer with $M_n = 23\,000\ g\ mol^{-1}$ ($M_w/M_n = 1.09$). M_n corresponds to a content of about 3.2 mol% initiating hydroxyl groups in DGEBA as observable by high pressure liquid chromatography (h.p.l.c.)[13].

Macromonomers from ε-caprolactone and glycolide were also obtained by initiation with BisGMA. The former reacts distinctly slower than lactide, whereas the reaction rate with glycolide is higher than with lactide, as described already for the polymerization of these lactones[17].

Nevertheless, the large difference between the reactivity of glycolide and lactide causes only a relatively small non-uniformity of the cooligomers ($M_w/M_n = 1.32$) (*Figure 7*). This applies to cooligomers with ε-caprolactone in a similar manner ($M_w/M_n = 1.22$) (*Figure 7*).

Stereoregularity and properties of macromonomers

Like monomeric L-lactide, poly(L-lactide) may be optically active too. Its optical purity depends on the polymerization mechanism[18]. The coordination–insertion mechanism offers the possibility to synthesize enantiomerically pure poly(L-lactide), unless racemization occurs by deprotonation of L-lactide as a side reaction[19]. Of course, this reaction is promoted by high reaction temperatures as well as long reaction times. $SnOct_2$ is well known as an insertion catalyst, yielding stereochemically pure poly(L-lactide) by polymerization at 120°C[19]. Indeed, a specific optical rotation $[\alpha] = -158.5°$ which corresponds exactly to $[\alpha]$ of optically pure, high molecular weight poly(L-lactide), was found for the macromonomer obtained from BisGMA and L-lactide by catalysis of the oligomerization with $SnOct_2$ (*Table 4*).

The other catalysts studied and cited in *Table 4* caused racemization (17–37%) under the conditions of oligomerization used. These results support those results in ref. 19, that with increasing basicity of catalyst the racemization degree also increases.

Generally, optically pure, high molecular weight poly(L-lactide) is a highly crystalline polymer. The oligo(L-lactide) macromonomers from BisGMA showed a strong reduction of the relative degree of crystallinity calculated on the base of the melting enthalpy $\Delta H_m = 76.0\ kJ\ g^{-1}$, with a decreasing degree of oligomerization (*Table 5*). Partial crystallinity could only be observed for macromonomers with a molar ratio of L-lactide/BisGMA ≥ 17. As expected both the melting points (T_ms) and the glass transition points (T_gs) of the oligo(L-lactide) macromonomers increase with increasing degree

Table 4 Molecular weight and degree of racemization of oligo(L-lactide)s prepared with BisGMA and different catalysts (Bis-GMA/L-lactide = 1/10 mol/mol; $\frac{[\text{Catalyst}]}{[\text{BisGMA}]} = 0.02$; $M_{n,calc.} = 2000\,g\,mol^{-1}$)

Catalyst	Temperature (°C)	Time (h)	$M_{n,g.p.c.}$ ($g\,mol^{-1}$)	M_w/M_n	$[\alpha]^{20}$	Degree of racemization (%)
$AlCl_3 \cdot 6H_2O$	150	4.5	2120	1.26	−100.2	36.8
Al_2O_3	130	4.5	1960	1.23	−118.2	25.4
Al_2O_3	150	3.0	2090	1.25	−99.8	37.0
$MgCO_3$	130	5.5	1860	1.23	−116.5	26.5
$MgCO_3$	150	2.5	2140	1.21	−106.8	32.6
MgO	130	4.5	2350	1.24	−131.2	17.2
MgO	150	2.0	2150	1.29	−129.4	18.4
CaO	130	4.0	1780	1.24	−121.0	23.7
CaO	150	3.0	2200	1.28	−108.4	31.6
ZnO	130	4.0	2070	1.24	−131.6	17.0
ZnO	150	2.0	2330	1.24	−119.5	24.6
SnO_2	130	5.0	2060	1.24	−130.7	17.5
SnO	150	3.0	2120	1.26	−109.1	31.2
$SnOct_2$	130	2.0	2450	1.20	−158.5	0
NVI	130	5.0	2590	1.25	−109.2	31.1

Table 5 Thermal properties of macromonomers

Composition of macromonomers (mol/mol)	T_g (°C)	T_m (°C)	ΔH_m ($J\,g^{-1}$)	Relative degree of crystallinity (%)
BisGMA/L-lactide = 1/31	51.5	119.8	49.8	65.5
BisGMA/L-lactide = 1/24	37.8	104.8	14.0	18.4
BisGMA/L-lactide = 1/17	27.4	–	–	–
BisGMA/L-lactide = 1/10	16.5	–	–	–
Poly-(L-lactide)[18]	55–57	175–180	76.0	100
BisGMA/D,L-lactide = 1/31	22.6	–	–	–
BisGMA/D,L-lactide = 1/24	22.5	–	–	–
BisGMA/D,L-lactide = 1/17	21.9	–	–	–
BisGMA/D,L-lactide = 1/10	18.1	–	–	–
Poly-(D,L-lactide)[20]	55	–	–	–
BisGMA/CL = 1/31	−55.4	49.8	110.8	79.4
BisGMA/CL = 1/24	−55.0	43.2	101.8	73.0
BisGMA/CL = 1/17	−48.5	32.8	97.2	69.7
Bis-GMA/CL = 1/10	−56.2	12.1	69.9	50.0
Poly(ε-caprolactone)[20]	−63	63	139.5	100

of oligomerization (*Table 5*). In contrast to the macromonomer from L-lactide, the macromonomer with only ten ε-caprolactone units still exhibits partial crystallinity, caused by the large flexible monomer unit. Both the degree of crystallinity and T_m of oligo(ε-caprolactone) macromonomers increase with increasing degree of oligomerization. However, their T_g does not show any correlation with the degree of oligomerization in the range studied. Though the T_g of poly(D,L-lactide) and poly(L-lactide) are similar at 55°C, the T_g of their macromonomers differ at the higher degrees of oligomerization studied. Obviously, T_g of oligo(L-lactide) macromonomers is mainly influenced by the degree of crystallinity of the macromonomers.

The latter are hard and brittle solids, if the molar ratio of L-lactide to BisGMA is ≥5. Macromonomers with ε-caprolactone were highly viscous and liquid or waxy. Both types of macromonomers were easily soluble in THF. However, macromonomers with glycolide (10 moles per mole BisGMA) are insoluble in commonly used solvents. Solubility in THF has been achieved with cooligomers containing D,L-lactide and glycolide in a molar ratio ≥1.5.

CONCLUSIONS

The synthesis of uniform oligo(lactone) methacrylates, especially from lactide, is possible with BisGMA as an initiator of the lactone oligomerization in the presence of various coordination–insertion catalysts at 130°C in bulk, with relatively high reaction rates. These conditions have been found to be much more convenient for the synthesis of the macromonomers than the initiation by the diethyl aluminium alkoxide from a hydroxyalkyl methacrylate, because preparation of the initiator in a solvent and separation of the macromonomer from the solution are additionally necessary steps in the latter case. In spite of the higher reaction temperatures used

for our method of macromonomer preparation, the narrowness of the molecular weight distribution ($M_w/M_n \approx 1.2$) of the macromonomers obtained, corresponds to that for the aluminium alkoxide catalysed synthesis, i.e. to a living reaction mechanism. Additionally, the results of our kinetic studies of the lactide oligomerization catalysed by $SnOct_2$ and MgO, respectively, also clearly indicate the living mechanism of the reaction.

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