Polymer Bulletin 14, 491-495 (1985)

Polymer Bulletin

Polylactones

5. Polymerization of L,L-Lactide by Means of Magnesium Salts

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SUMMARY

Bulk polymerizations of L,L-lactide were conducted at 120 and 180°C, but mainly at 150°C. Magnesium oxide, ethoxide, acetate, stearate, and 2,4-pentane dionate were used as catalysts. Time conversion curves show that at least a temperature of 150°C and a reaction time of 72 h is required for maximum conversion. The highest yields (up to 96 %) were obtained with magnesium oxide. However, all initiators, in particular magnesium oxide, caused racemization which increased with reaction time and temperature. Polymerizations in solutions at temperatures around 100°C failed regardless of the solvent.

INTRODUCTION

Heavy metal compounds such as lead, tin or zinc oxide, $SnCl_4$, Sn(II)octoate or dibutyltin derivatives were frequently used as catalysts for the polymerization of L,L-lactide and lactones [1-9]. However, when poly(L-lactide) or copolyesters of L-lactid acid are designed for medical or pharmaceutical purposes, the polyesters need to be purified from there poisonous catalysts. On the other hand, magnesium and calcium ions participate in the metabolism of the human body, and thus, catalysts based on magnesium or calcium ions do not need to be removed from the polyesters prior to their application. Therefore, it was the purpose of this paper to investigate the usefulness of various commercially available magnesium compounds as polymerisation catalysts for L,L-lactide (results obtained with calcium salts will be reported in another part of this series). It should be mentioned that magnesium salts are known to catalyze the polymerization of lactones [1,10]. Yet detailed investigations on their usefulness in the case of L,L-lactide are lacking.

RESULTS and DISCUSSION

Five commercially available magnesium catalysts were investigated, namely magnesium acetate, stearate, 2,4-pentanedionate (acetylacetonate), magnesium ethoxide and magnesium oxide. Magnesium stearate and 2,4-pentanedionate may be considered as homogenous catalysts because they dissolved in the

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in the molten monomer, whereas all other catalysts were insoluble. In a first series of experiments polymerization of L,L-lactide was attempted in various solvents, such as dioxane, nitrobenzene or pyridine at 100°C. Magnesium stearate and magnesiumoxide were used as catalysts; yet all these experiments failed.

All further investigations were concentrated on bulk polymerizations of molten L,L-lactide. When magnesium stearate was used at 120°C, no polymer could be isolated after 8 h, and even after 96 h the yield only reached 35 % (Nos. 1-2, Tab. 1). At 150°C the yield increased to 65 % after 96 h. However, the time conversion curve (Nos. 3-12, Tab. 1) clearly indicates that the conversion levels off after 72 h, still far below the thermodynamically achievable maximum (ca. 97 %). Three observations support the hypothesis that the low yields result from desactivation of the catalyst (e.g. decarboxylation) and not from degradation of poly(L-lactide) due to back-biting of the active chain end. First, the viscosities increase steadily with increasing conversion. Second, longer reaction times favour racemization indicating side reactions due to proton transfer of the acidic C-α proton of the monomer. Third, a further increase of the reaction temperature strongly favours racemization and lowers the yield (No. 13, Table 1). The yields obtained with magnesium acetate (Nos. 14-18, Tab. 1) are slightly higher, yet the degree of racemization is also higher. Interestingly, the viscosities increase with conversion, indicating a living character of the chain growth. Also with magnesium 2,4-pentane dionate time-conversion curves were measured at 120, 150 and 180°C (Tab. 2). Again a reaction temperature of 150°C was found to be optimum and again the yields leveld off after 72 h, far below the theoretical maximum. Furthermore, racemization proceeded with increasing reaction time and temperature. Magnesium ethoxide (Nos. 13-16, Tab. 2) gave slightly higher yields; yet the extent of racemization was not higher, despite the greater basicity of the ethoxide groups.

Finally, three different grades of magnesium oxide were used as catalysts (Tab. 3). All three grades yielded similar results, and thus, do not need separate discussion. However, the results obtained with magnesium oxides differ from those of other catalysts in three aspects. First, yields up to 96 % were found, demonstrating that magnesium oxides are the most effective catalysts of this study despite its heterogeneous character Second, whereas the yield steadily increases with the reaction time,the molecular weights are independent on the conversion. In this respect the magnesium oxide catalyzed polymerizations of L,L-lactide resemble the radical polymerization of vinylmonomers, and not an anionic living polymerization. Third, the extent of racemization is greater than that of all other catalysts.

The present study enables two important conclusiones. First, Magnesium compounds are not suited as catalysts, if optically pure poly(L-lactide) or other polylactones with acidic protons are to be prepared. This is likewise true for calcium compounds as will be demonstrated in another part of this series. Second, when magnesium compounds are used as catalysts for D,L-lactide or optically inactive lactones, magnesium oxide (or hydroxide) is obviously the most effective catalyst.

Table 1: Reaction conditions and results of bulk polymerizations of L,L-lactide by means of Mg stearate and Mg acetate

No	Mg salt	Mon. / Init.	Temp. (°C)	Time (h)	Yield (%)	η_{inh} a)	$[\alpha]^{20}_{D}$ b)
1	Stearate	200/1	120	8	0	-	-
2	Stearate	200/1	120	90	35	0,15	-122
3	Stearate	200/1	150	4	3	-	-
4	Stearate	200/1	150	6	9	-	-
5	Stearate	200/1	150	8	12	0,11	-
6	Stearate	200/1	150	12	15	-	-
7	Stearate	200/1	150	16	18	0,15	-139
8	Stearate	200/1	150	21	34	0,18	-136
9	Stearate	200/1	150	24	36	0,19	-124
10	Stearate	200/1	150	48	55	0,25	-110
11	Stearate	200/1	150	70	65	0,26	-104
12	Stearate	200/1	150	96	65	0,28	-101
13	Stearate	200/1	150	96	37	0,22	- 41
14	Acetate	200/1	150	16	36	0,18	-107
15	Acetate	200/1	150	24	38	0,18	-108
16	Acetate	200/1	150	48	58	0,19	- 97
17	Acetate	200/1	150	72	71	0,20	- 88
18	Acetate	200/1	150	96	74	0,26	- 85

a) measured at c = 2 g/l in dichloromethane at 20°C
b) measured at c = 10 g/l in dichloromethane

EXPERIMENTAL

L,L-lactide was a gift of Boehringer-Ingelheim KG (W.Germany). It was recrystallized from dry ethylacetate, washed with ligroin and dried in a dessiccator over P_4O_{10} in vacuo.

MgO of technical grade and MgO p.a. were purchased from Merck & Co (Darmstadt, W.Germany) and were used without further purification. A third grade was prepared by dissolving the technical MgO in diluted p.a. HCL followed by precipitation with ammonium hydroxide. All other catalysts were purchased from Lancaster Synthesis Ltd. (Morecambe, England,) and dried over P_4O_{10} in vacuo at 60°C.

All polymerizations were conducted in 50 ml Erlenmeyer flasks with ground glass joints and silanised glass walls. Both catalyst and L,L-lactide were successively weighed into the reaction flasks under nitrogen. The reaction vessel was closed with a glass stopper and a steel spring and completely immersed into the thermostated oil baht. Finally, the reaction product was dissolved in methylenechloride, precipitated from cold methanol and dried at 60°C in vacuo.

Table 2: Reaction conditions and results of bulk polymerizations of L,L-lactide by means of MgO (three grades) at 150^{o}C

No	grade of$^{a)}$ purity	Mon./Init.	Time (h)	Yield (%)	$\eta_{inh}$$^{b)}$	$[\alpha]_D^{20}$$^{b)}$
1	technical	200:1	17	57	0,37	-114
2	technical	200:1	24	65	0,41	-110
3	technical	200:1	48	77	0,36	-104
4	technical	200:1	72	87	0,32	- 98
5	technical	200:1	96	97	0,32	- 99
6	purum-	200:1	48	72	0,40	-115
7	analyticum	200:1	96	96	0,38	-102
8	reprecipitated	200:1	48	85	0,30	-105
9	reprecipitated	200:1	120	94	0,34	-102

a) for characterization see EXPERIMENTAL
b) measured at c = 2 g/l in dichloromethane at 20^{o}C
c) measured at c = 10 g/l in dichloromethane

Table 3: Reaction conditions and results of bulk polymerizations of L,L-lactide by means of Mg-2,4-pentanedionate and Mg ethoxide

No	Magnesium Derivative	Mon./Init.	Temp. (^{o}C)	Time (h)	Yield (%)	$[\alpha]_D^{20}$$^{b)}$
1	Pentanedionate	200:1	120	24	17	-140
2	Pentanedionate	200:1	120	48	20	-134
3	Pentanedionate	200:1	120	72	41	-137
4	Pentanedionate	200:1	120	96	34	-134
5	Pentanedionate	200:1	150	24	49	-128
6	Pentanedionate	200:1	150	48	59	-127
7	Pentanedionate	200:1	150	72	68	-117
8	Pentanedionate	200:1	150	96	68	-114
9	Pentanedionate	200:1	180	24	25	- 95,2
10	Pentanedionate	200:1	180	48	30	- 84
11	Pentanedionate	200:1	180	72	48	- 81
12	Pentanedionate	200:1	180	96	31	- 63
13	Ethoxide	200:1	150	24	59	-132
14	Ethoxide	200:1	150	48	65	-115
15	Ethoxide	200:1	150	72	75	-113
16	Ethoxide	200:1	150	96	76	-112

a) measured at c = 10 g/l in dichloromethane

The viscosities were measured in an Ubblehode viscosimeter thermostated at 20°C. A concentration of 2 g/l in dichloromethane was used in all cases; η_{inh} is given in dl/g. The optical rotations were measured on a Perkin Elmer Md 243. The specific rotation $[\alpha]_D^{20}$ of optically pure poly(L-lactide) is -158 ± 1 in dichloromethane.

REFERENCES

1) J. Kleine, H.-H. Kleine; Makromol.Chem. 30 23 (1959)
2) W. Dittrich, R.C. Schulz; Makromol.Chem. 15 109 (1971)
3) R. Vasanthakumari, M.J. Pennings; Polymer 24 175 (1983)
4) Ethicon.Inc.Ger: Offen; 2.118.127 (28. Oct. 1971) Chem. Abstr. 76 73051w (1972)
5) D.M. Young, F. Hostettler and C.F. Horn; Ger. Offen 1.205 586 (11. April 1957) to Union Carbide Corp.
6) T.C. Snapp and A.F. Blood; US.Pat. 3645 941 (29. Feb. 1972) to Eastman Kodak Co.
7) H. Amann and H. Rauch; Ger.Offen 2056 729 (19. Nov. 1970) to DEGUSSA AG.
8) H.R. Kricheldorf, J.M. Jontê and M. Berl; Makromol.Chem. in press (Part 3 of this series)
9) D.B. Johns, R.W. Lenz and A. Luecke in "Ring-Opening Polymerization" (K.J. Ivin and T. Saegusa eds.) Elsevier N.Y. 1984, Vol. 1 pp. 461-521
10) E.I. DuPont; Brit.Pat. 1.101.766 (18. April 1966)

We thank Boehringer-Ingelheim for a gift of L,L-lactide and the Deutsche Forschungsgemeinschaft for financial support.

Accepted November 14, 1985

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