Studies on the ring opening polymerization of caprolactone

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Abstract

The polymerization of ϵ-caprolactone(CL) with tetraphenyl-porphyrin(TPP)-diethylaluminium chloride(Et_2AlCl) or Et_2AlCl as initiator in toluene at 80° C gove a polymer with narrow molecular weight distribution.
The effects of the temperature and the concentration of catalyst on the polymerization rate and the molecular weight of polymer were studied.

Introduction

The polycaprolactone(CL) and its block polymer have been attracted much attention because of their peculiar combination of biodegradability and permeability as good materials for controlled release drugg delivery system [1].
The ring opening polymerization of CL using alkoxide [2,3], alkyllithium[4] as catalyst have been studied. Teyssie reported the living polymerization of CL with triisobutoxyaluminium[5] and bimetallic μ-oxoalkoxide[6] as catalyst. Inoue and his coworks have published a series of reports concerning the living polymerization of ϵ-lactone using porphyrin-diethylaluminium chloride(TPP-Et_2AlCl) as catalyst[7]. Recently Feng and coworkers have observed the living character of lactide(LA) polymerization using Teyssie's catalyst and then succesfully synthesized the AB diblock copolymer of PCL and PLA, and ABA triblock copolymer with PCL as A and PLA as B [8].
In this article we will report the preliminary results on the polymerization of CL catalyzed with either TPP-Et_2AlCl system (TPPAlCl) or $Et2AlCl$ at 80°C.

Experimental

Materials: 5,10,15,20-tetraphenyl porphyrin(TPP) was synhesized according to literature[9]. Et_2AlCl was purified by fractional distillation under reduced pressure in nitrogen atmosphere. ϵ-caprolactone, after dried with calcium hydride over night at room teperature, was distilled under nitrogen. The solvents such as toluene, tetrahydrofuran (THF) were purified by the usual methods.

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Prepration of TPPAlCl[10]: In a 50 ml pyrex flask equipped
with a rubber stopper for syringe, 0.1 mmol TPP was added
and purged with dry nitrogen thoroughly then 10 ml dry
toluene was introduced through a syringe. To this mixture
0.12 ml of Et_2AlCl as 1 M touene solution was added with
another dry syringe and then reacted at room temperature for
1 hr to obtain the catalyst solution.
    Polymerization: To the catalyst solution a given amount
of ϵ-caprolactone(CL) was added in a nitrogen atmosphere by
syringe. after a difinite time, a large excess of petroleum
ether was added to stop the polymerization and the poly-
caprolactone as precipitate was seperated by filtration.

Results and Discussion

    1. Polymerization of CL catalyzed by TPP-Et_2AlCl

    (1) Time-conversion and molecular weight of PCL
    The polymerization of ϵ-caprolactone by TPPAlCl at 80° C
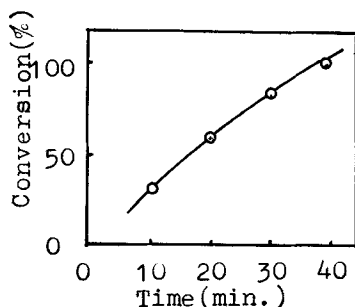proceeds rapidly as shown in Fig.1.

Fig.1 Time-conversion curve
for the polymerization of CL
with TPP-Et_2AlCl in toluene
at 80°C.
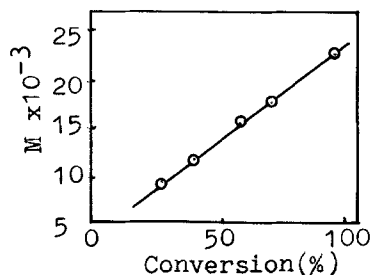 $[TPP]_o$: $[Et_2AlCl]_o$ = 1:2
    $[CL]_o / [TPP]_o$ = 290
    $[CL]_o$ = 2.3M

Fig.2 Relationship between
M_n and conversion% for the
polymerization of CL with
TPP-Et_2AlCl in touene at
80°C.
    $[TPP]_o$: $[Et_2AlCl]_o$ = 1:2
    $[CL]_o / [TPP]_o$ = 290,
 $[CL]_o$ = 2.3M

    The molecular weight of PCL increased linearly with the
increase of conversion as shown in Fig.2. The molecular
weight distribution M_w/M_n of the PCL was determined by GPC
to be 1.16, thus the ring opening polymerization of CL
catalyzed by TPP-Et_2AlCl is possible to proceed with good
living nature at 80°C and to polymerize futher with another
feed of CL. As the first step, a living prepolymer I of CL
was prepared as mentioned above at 80°C in toluene for 40
minutes with 96% conversion, M_n = 14600, M_w / M_n= 1.16. To
this prepolymer another portion of CL in same amount was
introduced. After 12 h at 80°C it is found that the new feed
of CL was polymerized to 100% conversion and obtained a

polymer with M_η = 29000, M_w/M_n =1.18. The GPC profile is shown in Fig.3.

(2) The effect of temperature on the polymerization

Fig. 3. The plot of GPC of the polymer obtained from twice feeds of CL. Peak I: prepolymer, M_η=14600, M_w/M_n=1.16; Peak II: final polymer, M_η=29000, M_w/M_n=1.18
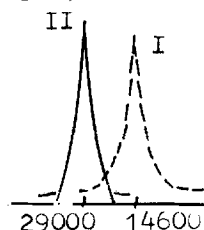
(M_η is determined viscometrically using THF as solvent at 25°C and calculated with the equation of $[\eta](dl/g)=1.09 \times 10^{-3} M^{0.6}$[11].)

In Inoue's report they carried out the polymerization of ε-propiolactone or α-methyl propiolactone at room temperature with very slow rate such as 33 days necessary for 60% conversion in the polymerization of α-methylpropiolactone[7]. We found that the ring-opening polymerization of CL will increase remarkablely at higher temperature as shown in Table 1.
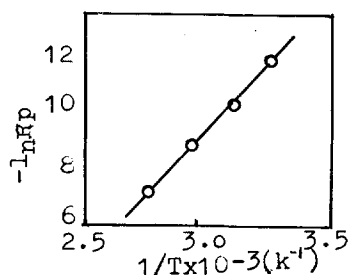
Table 1 The rate of polymerization of CL catalyzed by TPP-Et$_2$AlCl in toluene at different temperature

Polymn. temp.(°C)	20	40	60	80
Polymn.time(min.)	840	180	40	30
Conversion(%)	25.6	22.5	43.5	97.3
Rp(mol/l.s)x10	1.1	4.6	41	120

$[CL]_o$ =2.3 M, $[CL]_o/[TPP]_o$ =290, $[TPP]_o/[Et_2AlCl]_o$ =1/2

The values in Table 1 show that the Rp at 80°C is higher more 100 times than that at 20°C. From the plot of Rp-1/T(Fig.4) the overall activity energy E was calculated to be 21 KJ/mol according to the Arrhenius equation.
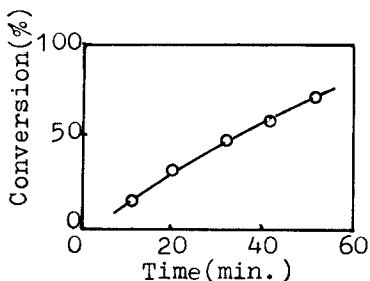
Fig. 4 The plot of $lnRp-1/T$

Fig.5 The relationship between conversion% and polymerization time of CL using Et_2AlCl as catalyst in toluene at $80^\circ C$. $[CL]_o = 2.2$ M, $[Et_2AlCl]_o = 1.5 \times 10^{-2}$ M

2.Polymerization of CL catalyzed by Et_2AlCl.

Although the ring-opening polymerization of CL has been studied extensively but only few studies on the polymerization of CL using diethylaluminium chloride alone as catalyst were reported. Cox[12] reported that a solid homopolymer was obtained by heating CL at $150^\circ C$ for 48 h using Et_2AlCl as catalyst. We observed that similar polymerization of CL occur in the presence of catalytic amount of Et_2AlCl at $80^\circ C$. Some preliminary results are summerized as follows:

(1) Living polymerization of CL catalyzed by Et_2AlCl

The relationship between the polymerizationtime and consion% was shown in Fig.5.

From Fig.5 we can see that the polymerization of CL catalyzed by Et_2AlCl alone proceeds rapidly with about 80% conversion in 1 h. The molecular weight of PCL increase linearly with increasing of conversion% as shown in Fig.6.
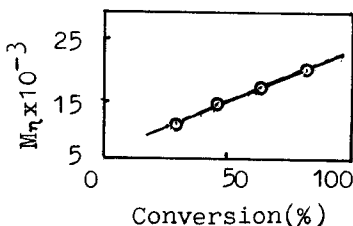

Fig.6 The relationship between molecular weight and coversion%, $[CL]_o = 2.2$, $[Et_2AlCl]_o = 1.5 \times 10^{-2}$ M. [11]
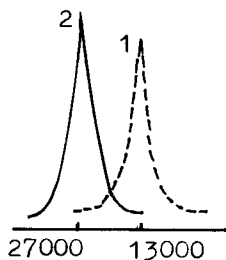

Fig.7 The GPC plot of polymer I and polymer II
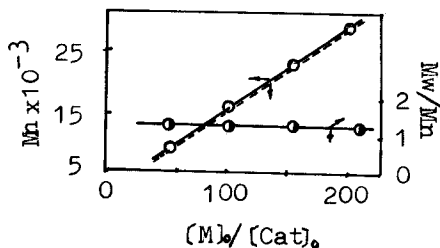peak 1, polymer I
peak 2, polymer II

Fig.8 The polymerization of CL catalyzed by Et_2AlCl in toluene at $80^\circ C$. The effect of $[M]_o/[Cat]_o$ on the M_n and M_W/M_n .

From the GPC analysis the molecular weight distribution M_w/M_n was calculated to be 1.20, so the ring-opening porization of CL catalyzed by Et_2AlCl also exhibits a living nature. It was further confirmed by the method of succeed feeding,i.e. the living prepolymer I (97% conversion, M_η =13000, M_w/M_n =1.20) was prepared first at 80° C then another feed of CL of the same amount as the first feed was added with dry syringe under nitrogen atmosphere. After 10-12 h, it was found that the second feed of CL has been polymerized completely and obtain a polymer II with M_η =27000, M_w/M_n =1.21.

The GPC profile of polymer I,II was shown in Fig.7

(2) The effect of concentration of catalyst on the molecular weight of PCL

The relationship between $[M]_o/[Cat]_o$ and M_n, M_w/M_n are shown in Fig.8. Where M_n and M_w/M_n determined from GPC with polystyrene as standard. The dotted line in Fig.8 was drawn from the calculated values according the equation of $M_n=[M]_o/[Cat]_o$. It is in good accordance with the experimental values(the solid line).Line 2 shows that the M_w/M_n is constant and always narrow, so it is reasonable to believe that the polymerization of CL with Et_2AlCl reveals the living character too.

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