BUTTERWORTH HEINEMANN

*Polymer* Vol. 36 No. 19, pp. 3753–3759, 1995

0032-3861/95/$10.00 + 0.00

# Synthesis and characterization of high molecular weight poly(1,5-dioxepan-2-one) with narrow molecular weight distribution

**Anders Löfgren and Ann-Christine Albertsson***
*Department of Polymer Technology, The Royal Institute of Technology, 100 44 Stockholm, Sweden*
*(Received 24 August 1994; revised 19 September 1994)*

Ring-opening polymerization of 1,5-dioxepan-2-one (DXO) initiated with aluminium isopropoxide in tetrahydrofuran (THF) solution and in bulk has been investigated. An improved monomer purification procedure is presented which makes it possible to synthesize high molecular weight poly(DXO) with a narrow molecular weight distribution. The kinetic dependence on parameters such as polymerization temperature, the presence of Lewis bases and water impurities is discussed. The activation energies ($E_a$) of the solution polymerization with and without 1 molar equivalent of pyridine (relative amount of initiator) were found to be 42.2 and 44.0 kJ mol$^{-1}$, respectively. The addition of a Lewis base (pyridine) did not influence the polymerization kinetics and transesterification reactions to any great extent. Bulk polymerization proceeds rapidly to full conversion and leads to poly(DXO) with a controlled molecular weight and a narrow molecular weight distribution. The Mark–Houwink relationship in THF at 25°C was determined; values of constants were $K = 1.1 \times 10^{-4}$ dl g$^{-1}$ and $a = 0.766$.

**(Keywords: synthesis; poly(1,5-dioxepan-2-one); aluminium tri-isopropoxide)**

## INTRODUCTION

Aluminium alkoxide compounds are known to be very efficient in initiating the living polymerization of lactones and lactides[1–3]. A living polymerization behaviour has also been shown with an ether lactone monomer, 1,5-dioxepan-2-one (DXO, **1**)[4]. The polymerization mechanism (*Figure 1*) was shown to be analogous to that proven in the case of ϵ-caprolactone (ϵ-CL)[2] and it was indeed possible to synthesize well defined di- and triblock copolymers of ϵ-CL and DXO[4].

When aluminium isopropoxide ($Al(O^iPr)_3$) is used as initiator in DXO polymerization, only one of the three potentially active alkoxide groups is involved in the initiation and propagation steps[4]. This behaviour has also been reported with ϵ-CL and adipic anhydride as monomers[2,5], but this is in contrast to the polymerization of lactide where all three isopropoxide groups of the initiator participate[6]. The reason for this difference in the number of active sites has been thoroughly investigated by Ropson *et al.*[7–9] and has been found to be dependent on the steric arrangement of the monomer–initiator complex formed in solution.

The monomer, DXO, can be polymerized by a number of initiating systems[10,11] and a high molecular weight has been obtained[10]. These polymerizations are not, however, always easy to control and reproduce. Side reactions, such as intra- or intermolecular transesterification, often prevent the production of well defined poly(DXO) with, for example, a narrow molecular weight distribution (*MWD*) and functional end-groups. Poly(DXO) is an amorphous polymer with a glass transition temperature ($T_g$) at about −39°C[11]. Poly(DXO) is degraded in aqueous environments[10] and is an important and interesting polymer which could be utilized in the synthesis of new biodegradable materials for use in medical, agricultural or packaging applications. We became interested in the aluminium alkoxides as initiators for the polymerization of DXO since they allow a larger degree of control of the final materials synthesized.

The object of this work was to find a procedure which allowed for the controlled synthesis of poly(DXO) with a high molecular weight and a narrow molecular weight distribution.

## EXPERIMENTAL

### *Materials and methods*

Tetrahydrofuran (THF) and toluene were dried by distillation over a Na/K-alloy/benzophenone complex in an inert gas atmosphere. Pyridine was purified by drying over $CaH_2$ and subsequent distillation. Hexane (Shell) was used as received. Methylene chloride (Shell) was distilled over $CaCl_2$ before use. Diethylether (Riedel de Haen) was dried over sodium wire and distilled under reduced pressure before use. Aluminium tri-isopropoxide (Aldrich) was purified by distillation under reduced pressure and dissolved in dry toluene. The concentration of this solution was measured by complexometric titration of Al with a standard solution of ethylene diamine tetra-acetic acid.

* To whom correspondence should be addressed

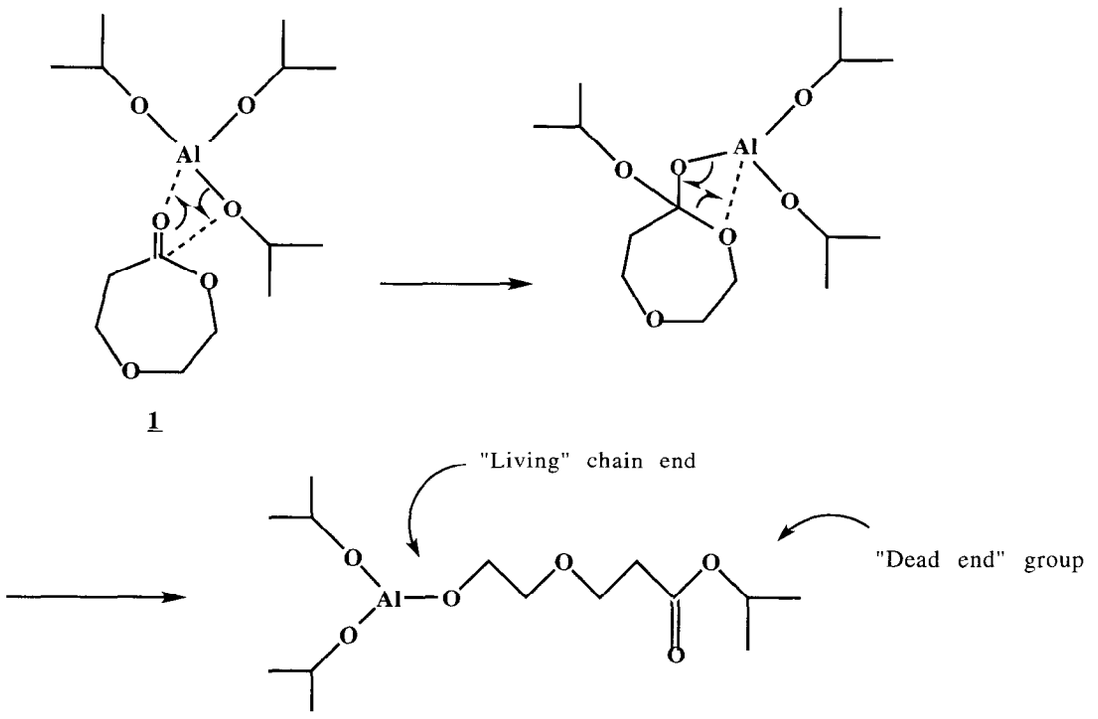



**Figure 1** DXO polymerization mechanism in the presence of aluminium isopropoxide

**Table 1** Polymerization of DXO in THF with $Al(O^iPr)_3$ as initiator

| Entry | [M]/[I] | Polymerization temperature (°C) | Polymerization time (h) | Pyridine[a] (eqv.) | Conversion (%) | $M_{n,th.}$[b] (g mol$^{-1}$) | $M_{n,exp.}$[c] (g mol$^{-1}$) | $M_{n,LS}$[d] (g mol$^{-1}$) | $MWD$ | $k_{app} \times 10^3$ (min$^{-1}$) |
|---|---|---|---|---|---|---|---|---|---|---|
| 1[e] | 130 | 0 | 2.5 | 0 | 98 | 15 000 | 22 700 | – | 1.10 | 45 |
| 2[e] | 470 | 0 | 18 | 0 | 85 | 47 000 | 43 600 | – | 1.10 | – |
| 3[e] | 430 | 0 | 19.5 | 0 | 16 | 8 000 | 8 700 | – | 1.10 | – |
| 4[e] | 630 | 0 | 18 | 0 | 32 | 22 200 | 16 900 | – | 1.10 | – |
| 5[e] | 173 | 0 | 3 | 1 | 60 | 12 000 | 14 700 | – | 1.10 | 5.6 |
| 6[e] | 173 | 0 | 3 | 2 | 67 | 13 400 | 17 400 | – | 1.10 | 7.8 |
| 7 | 517 | 0 | 42 | 0 | 95 | 57 000 | 69 000 | 59 000 | 1.15 | 2.2 |
| 8 | 600 | 0 | 42 | 1 | 85 | 59 200 | 73 800 | 63 000 | 1.10 | 2.6 |
| 9 | 517 | 25 | 24 | 0 | 72 | 43 200 | 54 000 | 47 000 | 1.10 | – |
| 10 | 430 | 25 | 16.5 | 1 | >99 | 50 000 | 44 500 | – | 1.20 | – |
| 11 | 517 | 25 | 69.5 | 0 | >99 | 60 000 | 60 500 | 55 500 | 1.30 | 13 |
| 12 | 517 | 25 | 67 | 1 | >99 | 60 000 | 59 700 | 56 500 | 1.30 | 17 |
| 13 | 861 | 25 | 21.5 | 1 | 97 | 97 000 | 126 600 | 118 600 | 1.15 | 2.6 |
| 14 | 517 | 40 | 17 | 0 | 98 | 59 000 | 66 500 | 60 500 | 1.30 | 24 |
| 15 | 517 | 40 | 17 | 1 | 99 | 60 000 | 62 000 | 61 000 | 1.30 | 30 |

[a] Equivalents compared to a molar amount of Al
[b] Theoretical molecular weight = ([M]/[I])$MMx$, where [M]/[I] = initial monomer/initiator molar ratio, MM = molecular weight of the monomer and $x$ = monomer conversion
[c] Molecular weight measured by s.e.c. (universal calibration with PS standard)
[d] $M_{n,LS} = M_{w,LS}/MWD$, where $M_{w,LS}$ is the absolute weight-average molecular weight determined by light scattering
[e] Old monomer purification method

*Synthesis of 1,5-dioxepan-2-one (DXO)*

A typical synthesis was carried out as follows. A 67 g portion of 3-chloroperbenzoic acid (70%) (Aldrich) was dissolved in 400 ml of methylene chloride and the organic phase was separated and dried with $MgSO_4$ (anhydrous) (Merck). After filtration, the methylene chloride solution was cooled to 0°C in an ice/water bath. A 20 g portion of tetrahydro-4*H*-pyran-4-one (Fluka) was immersed in the peracid solution which was allowed to attain room temperature under stirring during a period of 15 h. After filtration, the methylene chloride phase was washed with sodium bisulfite and sodium bicarbonate to eliminate any remaining peracid and most of the 3-chlorobenzoic acid. The methylene chloride phase was then evaporated to give a slightly yellow oil. This was distilled under reduced pressure ($10^{-2}$ mbar), and gave 80% yield of DXO (55°C). The DXO monomer was recrystallized twice in anhydrous diethylether to remove any residual

3-chlorobenzoic acid. The 'old' monomer purification method involves drying by dissolving the DXO in dry toluene and removal of the toluene/$H_2O$ azeotrope twice, whereas in the new method drying is carried out over $CaH_2$ at 40°C with subsequent vacuum distillation.

*Polymerization procedure*

The recrystallized DXO was dried over $CaH_2$ under stirring at 40°C during a period of at least 12 h and was subsequently distilled under reduced pressure ($10^{-2}$ mbar) just before use. The monomer was charged into a dry (flamed under vacuum, nitrogen purged) round-bottomed flask equipped with a magnetic stirring bar in a glove box (MBraun MB 150B-G-I, Germany) under strictly anhydrous conditions. THF and initiator solution were introduced into the polymerization vessel through rubber septums by stainless steel capillaries or glass syringes. The reaction vessel was, at all times, kept under a positive pressure of dry nitrogen. The polymer was precipitated and washed in hexane and dried under vacuum at ambient temperature to constant mass.

The same procedure was used in the bulk polymerization but the THF solvent was omitted. Before the addition of initiator solution, the monomer was melted at 40°C and then left to attain ambient temperature. After complete polymerization, a small amount of THF was introduced to remove any residual monomer droplets stuck on the wall of the round-bottomed flask. After removal of this fraction, THF with an excess of 1 M HCl (compared to the initiator) was added to solubilize and terminate the polymerization.

*Size exclusion chromatography (s.e.c.)*

S.e.c. measurements were made at 25°C with three PLgel columns (5 $\mu$m, mixed C). A Waters model 510 apparatus was used with a differential refractometer (Waters 410) as detector and a WISP 712. THF was used as solvent, with a flow rate of 0.5 ml min$^{-1}$. A Copam PC-501 Turbo unit was used to record the data and make the calculations. A universal calibration[12] was made according to the relationship $[\eta]_1 M_1 = [\eta]_2 M_2$, where $[\eta]_x$ corresponds to the measured limiting viscosity number and $M_x$ to the absolute weight-average molecular weight of poly(DXO) (subscript 1) and polystyrene (subscript 2).

*Light-scattering measurements*

Molecular weight data estimated from light scattering were obtained by a Wyatt Technology Dawn-F laser photometer operating at a wavelength of 632.8 nm and connected to the s.e.c. apparatus. Wyatt Technology data acquisition and processing software (ASTRA 2.11) was used to calculate the molecular weights. The differential refractive index increment ($dn/dC$) of poly(DXO) in THF (25°C) was determined to be 0.065 ml g$^{-1}$.

*Viscosity measurements*

The intrinsic viscosity of dilute poly(DXO) solutions in THF was determined with an Ubbelohde viscometer immersed in a water bath held at +25°C. Flow times varied between 99 and 110 s. At least four or five readings were made at each of the four concentrations of each sample until variations in flow time were kept within 0.2% of the mean value. Limiting viscosity numbers were estimated by the simultaneous extrapolation of $\eta_{sp}/c$ and $(1/c)\ln\eta_{rel}$ *versus* concentration plots to infinite dilution[13].

*Differential scanning calorimetry (d.s.c.)*

D.s.c. analysis was performed with a Perkin Elmer DSC-7. The samples were heated to 80°C and then cooled at 20°C min$^{-1}$ to −100°C. After 2 min equilibration, the heating scan was recorded at 10°C min$^{-1}$ to 80°C. Perkin Elmer 7 series standard software was used for processing and calculation of the glass transition temperatures.

## RESULTS AND DISCUSSION

The versatility of poly(DXO) as it is, in a crosslinked state or as a part of a copolymer or blend makes it a very useful component in the family of degradable polymers. This led us to investigate further the ring-opening polymerization of this ether lactone initiated by $Al(O^iPr)_3$. The results and conditions of the polymerizations are presented in *Table 1*.

To obtain more correct values of the true molecular weights, a universal calibration was performed based on light-scattering and viscosity measurements[12] of poly(DXO) with narrow *MWD*. The log–log plot of intrinsic viscosity *versus* molecular weight can be seen in *Figure 2*. The Mark–Houwink constants of poly(DXO) in THF solution at 25°C were determined to be $K = 1.1 \times 10^{-4}$ and $a = 0.766$.

*Influence of water impurities*

In earlier work[4], the monomer purification procedure used involved drying by azeotropic distillation of toluene under reduced pressure ($10^{-2}$ mmHg) and then recrystallizing twice from dry diethylether. This method gave homopolymers of low to moderate molecular weight with a narrow *MWD*. However, when attempts were made to synthesize poly(DXO) of higher molecular weights ($M_n > 35\,000$ g mol$^{-1}$), problems were encountered: either the polymerization was not initiated at all or it reached only a limited conversion. The reason for this behaviour was believed to be the presence of impurities in the system, which led to termination of the active sites. In cases where a limited conversion was observed, the molecular weights were lower or in reasonable accordance with the expected values, taking the degree of conversion into consideration. The conversion seemed to be very slow in these cases, but the *MWD*s were always narrow (entries 2–4, *Table 1*).

Termination of some of the active sites would indeed lead to a lower apparent rate constant ($k_{app}$) but it would also result in a higher molecular weight than expected. Since this was not the case, it was suspected that water was present and reacted with the $Al(O^iPr)_3$ to form the corresponding hydroxide salt and isopropanol according

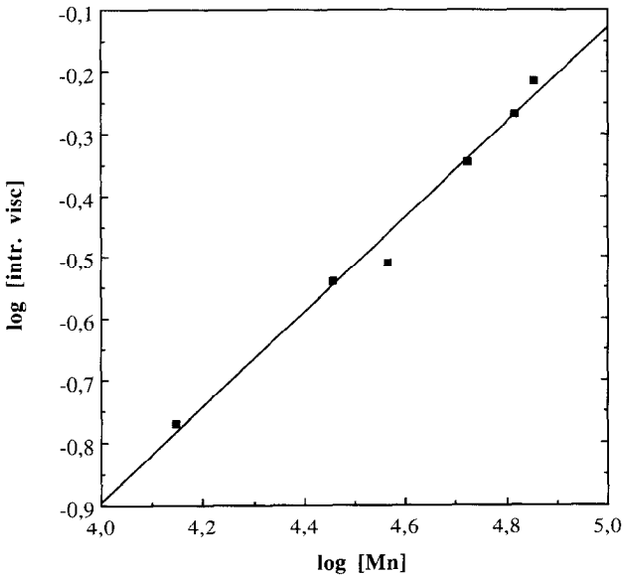
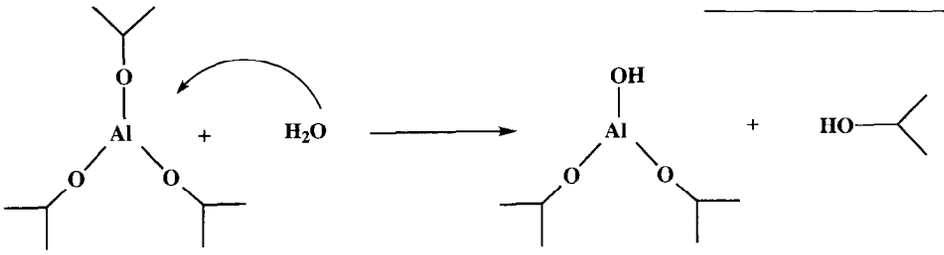


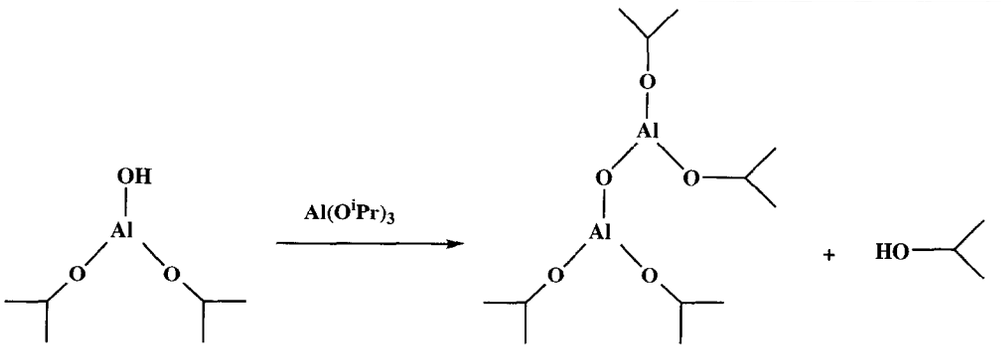

**Figure 2** Universal calibration plot for poly(DXO) in THF, 25°C

to the equation:

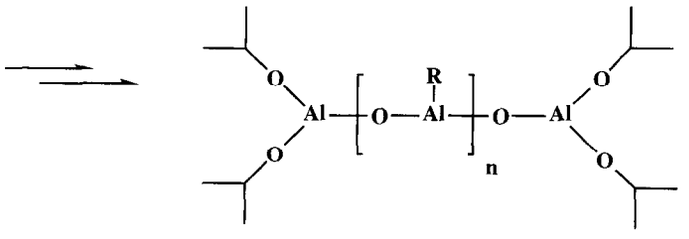



(1)

The $Al(O^iPr)_2OH$ formed might react further according to the equation:




(2)




R = $OCH(CH_3)_2$, O-$AlR_2$

In this way larger complexes resembling aluminoxane structures might form. Aluminoxanes have been investigated in a number of applications as catalysts[14,15] or cocatalysts[16].

The isopropanol can participate in exchange reactions with the remaining $Al(O^iPr)_3$ molecules. The effect of deliberate addition of isopropanol to the $\epsilon$-CL and lactide polymerization initiated with $Al(O^iPr)_3$ has been investigated by Jacobs *et al.*[1]. They found[1] that the alcohol had the effect of a dissociating agent, increasing the number of active sites according to the equation:

$$n_{th} = \frac{n^iPrOH + 3nAl(O^iPr)_3}{nAl(O^iPr)_3} \quad (3)$$

This would effectively lead to a lower molecular weight than expected in the case of only one active site, as earlier studies have shown for both $\epsilon$-CL[2] and DXO[4]. In addition to the lower molecular weight, a decrease in polymerization kinetics was observed.

Experiments were carried out with the deliberate addition of 0.5 and 1 molar equivalent (eq.) (with respect to $Al(O^iPr)_3$) of water, as shown in *Table 2*.

The results were very slow polymerizations which, in the 0.5 eq. case, reached almost full conversion after a polymerization time of 6 days. The polymer was precipitated in hexane which, after evaporation,

**Table 2** Polymerization of DXO with and without the addition of water ($Al(O^iPr)_3$, 25°C, THF solution $[M]_0 = 1.0$ M)

| Entry | [M]/[I] | Equivalent *a* $H_2O$ | $k_{app}$ ($\times 10^3$ min$^{-1}$) | Polymerization time (h) | Conversion[b] (%) | $M_{n,th}$ (g mol$^{-1}$) | $M_{n,LS}$ (g mol$^{-1}$) | *MWD* |
|---|---|---|---|---|---|---|---|---|
| 1 | 517 | 0 | 13 | 21 | 99 | 60 000 | 58 500 | 1.15 |
| 2 | 345 | 0.5 | 0.35 | 145 | 98 | 40 000 | 25 800 | 1.30 |
| 3 | 345 | 1.0 | 0.045 | 441 | 22 | 8 800 | 2 000[c] | 1.35 |

[a] Compared to amount of Al
[b] Determined by $^1H$ n.m.r. of crude polymer
[c] Determined from s.e.c.

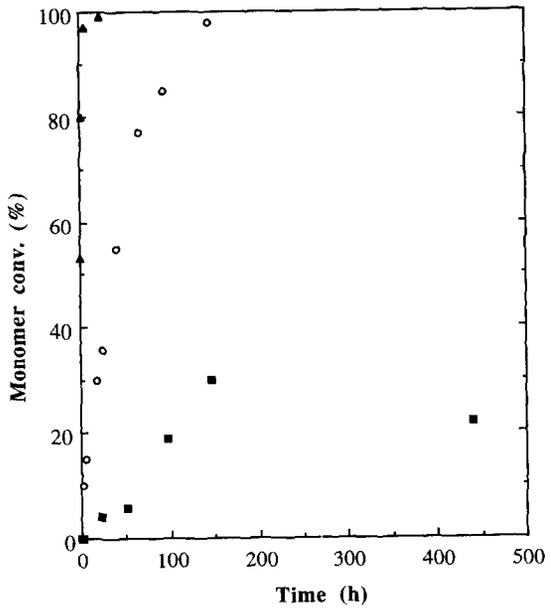



**Figure 3** Influence of added water in the polymerization of DXO initiated by $Al(O^iPr)_3$ in THF, 25°C. ▲, 0 eq. of added water; ○, 0.5 eq. of added water; ■, 1.0 eq. of added water

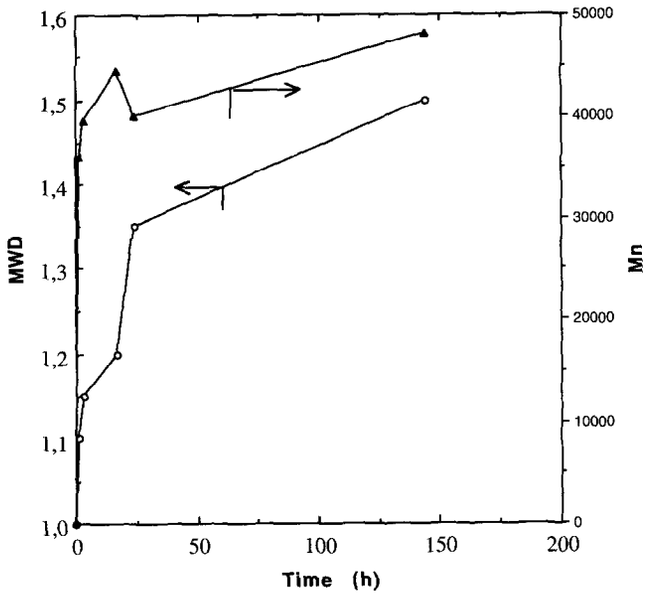



**Figure 4** Dependence of number-average molecular weight ($M_n$) and molecular weight distribution (*MWD*) on polymerization time. $[M]_0 = 1$ M, $Al(O^iPr)_3$ in THF, $[M]/[I] = 430$ polymerization temperature = 25°C

showed a small amount (1–2%) of oligomers as detected by s.e.c. The *MWD* had a value of 1.2 at the beginning of the polymerization, later increasing to a final value of 1.3. When 1 eq. of water was added, the polymerization proceeded even more slowly, never reaching high conversions even after 18 days. S.e.c. of the crude final product showed oligomers with a bimodal distribution. $^1H$ n.m.r. of the precipitated product showed fewer end-groups than could be expected from linear oligomers. It is thus probable that a mixture of cyclic and linear chains are formed. An illustration of the profound effect of added water on the polymerization rate can be seen in *Figure 3*.

It is difficult to state what influence the different species of aluminium alkoxides will have on the polymerization, and a more detailed investigation is needed to study further the influence of water impurities in polymerizations initiated by $Al(O^iPr)_3$.

*Influence of temperature and Lewis base addition*

When higher molecular weights are desired, the polymerization time must also be increased according to the first-order kinetics with respect to both monomer and initiator, which were determined in the earlier work[4]. A longer polymerization time makes transesterification reactions more probable, sometimes resulting in, for example, a broader *MWD*. An increase in the polymerization temperature might have the same effect, but can be beneficial if the increase in propagation rate is higher than the increase in transesterification rate. Polymerizations were therefore carried out at three different temperatures: 0, 25 and 40°C (entries 7, 11 and 14 in *Table 1*). As expected, the *MWD* increased slightly at the highest temperature (the *MWD* of entry 11 when full conversion had been obtained after 21 h was 1.15). To maintain the narrow *MWD* it is essential to terminate the polymerization after complete monomer conversion. If the living polymer solution is left standing, inter- and intramolecular transesterification reactions broaden the *MWD* and eventually oligomers are formed, especially at and above room temperature (see *Figure 4*).

As expected, the rates of polymerization are increased with increasing temperature, as seen in *Table 1*. The polymerization time to reach full conversion is lowered from *c.* 30 h at 0°C to *c.* 3 h at 40°C ($[M]/[I] = 517$).

Pyridine, a well known Lewis base, has shown some interesting effects when added to polymerizations promoted by aluminium alkoxides[4,17]. The higher polymerization rate and the reduction in transesterification reactions reported could possibly improve conditions in the poly(DXO) polymerization with $Al(O^iPr)_3$ as well. In *Table 1* (entries 5, 6, 8, 10, 12, 13, 15), the results of some polymerizations with added pyridine are reported. The effect on the kinetics was less than

expected and no significant change in *MWD* could be detected.

The absolute rate constant ($k$) can be derived from the first-order relationship:

$$k = \frac{k_{app}}{[I]} = -\frac{\ln([M]/[M]_0)/t}{[I]}$$

In the case of low to moderate molecular weight polymerizations of DXO in THF at 0°C, the absolute rate constant was found[4] to be 5.71 $min^{-1}$ $mol^{-1}$. The absolute rate constant ($k$) was found to be lower at higher molecular weights. For example, the $k$ value of a polymerization at 0°C with a monomer/initiator ratio of 517 ($M_{n,th}$ = 60 000 g $mol^{-1}$) was estimated to be $k$ = 1.11 $min^{-1}$ $mol^{-1}$. This could be attributed either to impurities or to some sort of coordinative interaction of the living chain end. An intra- or intermolecular interaction of the Al-alkoxide chain end to either the ester or ether linkage of the poly(DXO), leading to a more sluggish kinetic situation, can be imagined. The possibility of breaking this interaction by adding pyridine, which specifically coordinates to the Al atom and therefore might influence the situation by steric hindrance, was considered. Pyridine was therefore added to some of the polymerizations performed at 0, 25 and 40°C (entries 8, 10, 12, 13, 15 in *Table 1*) and the kinetics were evaluated and compared with those of corresponding cases without added pyridine (entries 7, 9, 11, 14 in *Table 1*). A slightly faster polymerization was observed in the case of added pyridine. Using data at different polymerization temperatures, it was also possible to derive the activation energy ($E_a$) of this polymerization, according to the Arrhenius equation. The activation energy is given by the slope of the straight line in a plot of $\ln k = f(1/T)$ (*Figure 5*).

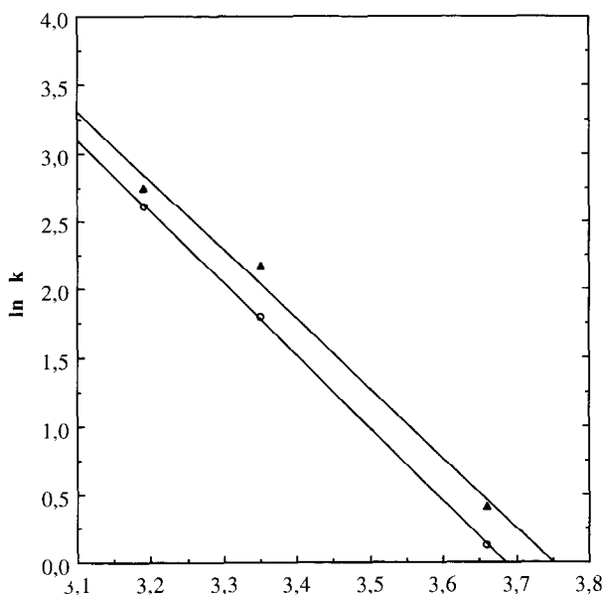



**Figure 5** Linear relationship between logarithm of absolute rate constant ($\ln k$) and inverse absolute polymerization temperature ($1/T$). The slopes yield values of activation energies for the solution polymerization of DXO with (▲) and without (○) addition of 1 eq. of pyridine

A small difference was observed and the values were calculated to be $E_a$ = 42.2 and 44.0 kJ $mol^{-1}$ with and without 1 eq. of pyridine, respectively.

The effect on *MWD* was not significant at any of the temperatures investigated. It was thus concluded that the slow propagation observed at large [M]/[I] ratios could be attributed to impurities such as water. It should be pointed out that the observed effect of pyridine in the case of $\epsilon$-CL was achieved with dialkylaluminium monoalkoxide as initiator and toluene as solvent[17]. If $Al(O^iPr)_3$ and $Et_2AlOR$ are compared, it is realized that the Al–O bond in $Al(O^iPr)_3$ should be of a more ionic character than in $Et_2AlOR$. This, together with the fact that toluene is a less polar solvent than THF, could explain the difference in the effect of addition of pyridine. Indeed, results obtained from the copolymerization of $\epsilon$-CL and DXO with $Al(O^iPr)_3$ in toluene confirm a small accelerating effect of pyridine in this solvent[18].

### *Bulk polymerization*

Polymerization of DXO in bulk initiated with $Al(O^iPr)_3$ was carried out at 25°C with the addition of 1 eq. of pyridine. Although no detailed kinetic measurements were made, it was clear that the bulk polymerization proceeded very quickly to full conversion. Only two attempts were made in this preliminary study, with the results shown in *Table 3*.

After less than 5 min the polymerization had reached a point where no further stirring with the magnetic stirring bar was possible. As can be seen in *Table 3*, full conversion was obtained in less than 1.5 h and the experimental molecular weights are in good agreement with the theoretical values. If the reaction medium is left for a prolonged time after full conversion has been obtained, transesterification reactions occur, as shown by the broad *MWD* at 12 h (entry 1, *Table 3*).

### *Thermal analysis*

The glass transition temperature ($T_g$) of a polymer depends on a number of factors, such as molecular weight, *MWD* and thermal history of the sample. D.s.c. studies of the synthesized poly(DXO) with narrow *MWD* were therefore made to look for any changes in the thermal behaviour compared to that of poly(DXO) synthesized by a non-living polymerization mechanism[10]. Results in *Table 4* indicate that although the

**Table 3** Bulk polymerization of DXO initiated with $Al(O^iPr)_3$ at 25°C in the presence of 1 eq. of pyridine

| Entry | Polymerization time (h) | Conversion (%) | $M_{n,th}$ (g $mol^{-1}$) | $M_{n,LS}$ (g $mol^{-1}$) | $M_{n,exp}$ (g $mol^{-1}$) | *MWD* |
|---|---|---|---|---|---|---|
| 1 | 12 | >99 | 20 000 | 18 400 | 19 400 | 1.55 |
| 2 | 1.5 | >99 | 30 000 | 36 000 | 30 200 | 1.17 |

**Table 4** Thermal data of poly(DXO), measured by d.s.c. (second heating)

| Entry | $M_{n,LS}$ (g mol$^{-1}$) | *MWD* | $T_g$ (°C) |
|---|---|---|---|
| 1 | 112 100[a] | 1.40 | −39.2 |
| 2 | 25 000 | 1.20 | −39.7 |
| 3 | 51 400 | 1.10 | −38.9 |
| 4 | 118 600 | 1.15 | −37.6 |

[a] Poly(DXO) made in bulk at 112°C with stannous-2-ethylhexanoate as catalyst

molecular weights were similar, the broader *MWD* of the poly(DXO) resulting from a stannous-2-ethylhexanoate-catalysed polymerization (entry 1, *Table 4*), gave a lower $T_g$ than the narrow *MWD* poly(DXO) made in this work (entry 4, *Table 4*). As expected, a reduction in the molecular weight leads to a lower $T_g$ (entries 2–4, *Table 4*).

## CONCLUSIONS

Aluminium isopropoxide is an effective initiator in the living polymerization of 1,5-dioxepan-2-one, and is capable of producing high molecular weight polymers with a narrow *MWD*, both in THF solution and in bulk.

Kinetics of the polymerization are highly dependent on water impurities, which also alter the molecular weight and broaden the *MWD* obtained.

Pyridine affects the polymerization kinetics and molecular weight distribution to a minor extent under the conditions used. An increase in the temperature of polymerization from 0 to 25°C or even to 40°C accelerates the polymerization but also leads to a slight broadening of the *MWD*.

Thermal analysis shows only small differences in $T_g$ values, but generally the narrow *MWD* resulting from the living polymerization initiated by $Al(O^iPr)_3$ yields polymers with a higher $T_g$ than polymers with a broader *MWD* resulting from, for example, stannous-2-ethylhexanoate-catalysed polymerizations.

## ACKNOWLEDGEMENTS

Dr Philippe Dubois (Centre for Education and Research on Macromolecules, University of Liège, Belgium) is thanked for great help in discussions and guidance during a short visit to our department. Bengt Erlandsson and Torbjörn Lindberg are thanked for their help with light-scattering and d.s.c. analyses, respectively. This work was financially supported by the Swedish Board for Technical Development (NUTEK).

## REFERENCES

1 Jacobs, C., Dubois, Ph., Jérôme, R. and Teyssié, Ph. *Macromolecules* 1991, **24**, 3027
2 Ouhadi, T., Stevens, C. and Teyssié, Ph. *Makromol. Chem.* 1975, (Suppl. 1), 191
3 Hofman, A., Slomkowski, S. and Penczek, S. *Makromol. Chem., Rapid Commun.* 1987, **8**, 387
4 Löfgren, A., Albertsson, A.-C., Dubois, Ph., Jérôme, R. and Teyssié, Ph. *Macromolecules* 1994, **27**, 5556
5 Ropson, N., Dubois, Ph., Jérôme, R. and Teyssié, Ph. *Macromolecules* 1992, **25**, 3820
6 Dubois, Ph., Jacobs, C., Jérôme, R. and Teyssié, Ph. *Macromolecules* 1991, **24**, 2266
7 Ropson, N., Dubois, Ph., Jérôme, R. and Teyssié, Ph. *Macromolecules* submitted
8 Ropson, N., Dubois, Ph., Jérôme, R. and Teyssié, Ph. *Macromolecules* 1993, **26**, 6378
9 Ropson, N., Dubois, Ph., Jérôme, R., Teyssié, Ph., Parente, V. and Bredas, J. L. in preparation.
10 Albertsson, A.-C. and Palmgren, R. *J. Macromol. Sci. – Pure Appl. Chem.* 1993, **A30** (12), 919
11 Mathisen, T., Masus, K. and Albertsson, A.-C. *Macromolecules* 1989, **22**, 3842
12 Atkinson, C. M. and Dietz, R. *Eur. Polym. J.* 1979, **15**, 21
13 Billingham, N. C. 'Molar Mass Measurements in Polymer Science', Kogan Page, London, 1977.
14 Pajerski, A. D. and Lenz, R. W. *Makromol. Chem., Macromol. Symp.* 1993, **73**, 7
15 Bloembergen, S., Holden, D. A., Bluhm, T. L., Hamer, G. K. and Marchessault, R. H. *Macromolecules* 1989, **22**, 1656
16 Kaminsky, W., Külper, K., Brintzinger, H. and Wild, F. *Angew. Chem. Int. Edn Engl.* 1985, **24**, 507
17 Dubois, Ph., Barakat, I., Jérôme, R. and Teyssié, Ph. *Macromolecules* 1993, **26**, 4407
18 Löfgren, A., Renstad, R. and Albertsson, A.-C. *J. Appl. Polym. Sci.* 1995, **55**, 1589