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Polymerization and copolymerization of β-butyrolactone by aluminium compounds *

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Abstract

Contrary to previous reports, mixed aluminium-zinc oxo-alkoxides $ZnAl_2O_2(OCHMe_2)_4$ initiate the polymerization of β-butyrolactone to the biodegradable polyester poly(β-hydroxybutyrate). The polymerization is very much slower than that of β-propiolactone, produces low molecular weight products, and does not have living kinetics. There is evidence for catalyst deactivation during the reaction, and the polymer is completely atactic. Copolymerizations with unsubstituted lactones are initiated by the oxo-alkoxide, by aluminium 2-propoxide and by (*meso*-tetraphenylporphinato)aluminium chloride. In all cases, the co-monomer dramatically reduces the rate of polymerization and the melting point of the product. Reactivity ratios for copolymerization where M_1 is ε-caprolactone have been determined to be $r_1 = 13 \pm 0.5$ and $r_2 = 0.4 \pm 0.04$. For the copolymerization with δ-valeroactone, the corresponding values are $r_1 = 7.4 \pm 0.5$ and $r_2 = 0.15 \pm 0.04$. These values imply that the copolymers contain only isolated units or short blocks of the β-lactone.

Introduction

Poly(β-hydroxybutyrate) (**1**; PHB) is a naturally occurring aliphatic polyester, produced by several bacteria as an energy store [1]. In recent years this polymer produced by fermentation has become commercially available. Its thermoplasticity allows it to be formed by conventional plastics processing machinery, and it is biodegradable to non-toxic products [2]. PHB, extracted from the bacterial cell, is a high molecular weight polymer, highly stereoregular, optically active, and crystalline. However, since it may be contaminated with other cell materials, notably proteins, it was desirable to produce samples synthetically.

PHB has a crystalline melting point of 195 °C, but at this temperature its thermal degradation during processing is significant. Since the processing temperature could

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* Dedicated to Professor C. Eaborn on the occasion of his 65th birthday. The work described here was submitted by MGP as part fulfilment of the requirements of a BSc degree at the University of Sussex. This "degree by thesis" was instituted in 1968 at the suggestion of Professor C. Eaborn.

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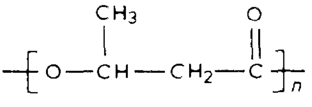
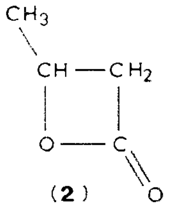
be reduced by copolymerization, synthesis of copolymers might provide useful models for biopolymer development.



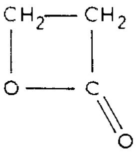
$$-\!\left[O-\overset{CH_3}{\overset{|}{C}H}-CH_2-\overset{O}{\overset{\|}{C}} \right]_n\!-$$

(**1** ; PHB)

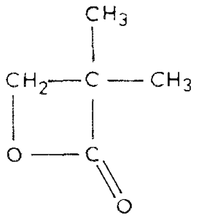


(**2**)

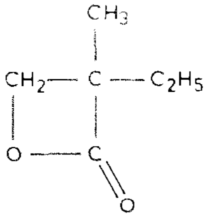
Direct synthesis of PHB *, via the self-condensation of 3-hydroxybutanoic acid, is not possible [3], partly because of the competing formation of the cyclic product, β-butyrolactone (**2**), but mainly because of the facile dehydration of the hydroxy acid to yield 2-butenoic acid. All reported syntheses of PHB have used the ring-opening polymerization of **2**. Unsubstituted lactones, e.g. **3**, are well known to polymerize with both cationic and anionic initiators [4,5], although low molecular weight products are common. The related disubstituted lactone, pivalolactone (**4**), is readily polymerized but 3-methyl substitution generally reduces the ease of polymerization of cyclic monomers [6], and **2** is very difficult to polymerize.



(**3**)



(**4**)



(**5**)

Inoue et al. [7] reported polymerization of **2** to a solid product, using diethylzinc and dioxygen as initiator, but gave few details of the reaction. Yamashita et al. [8] studied polymerization with a range of initiators, and claimed that anionic polymerization yielded only short-chain polymers (because of facile chain transfer by proton abstraction from the monomer), but that the initiator produced by partial hydrolysis of triethylaluminium with water, at a mole ratio of ca. 1/1, gave high conversions to a polymer with a limiting viscosity number of up to 0.5. The polymer from the racemic monomer was claimed to be crystalline, with X-ray *d*-spacings identical to those of natural PHB. Shelton et al. [9] also described polymerization initiated by diethylzinc or triethylaluminium in the presence of water or alcohol

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[*] Throughout this paper, a large number of trivial names have been used. Their systematic equivalents are:

trivial	systematic	
β-hydroxybutyrate	3-hydroxybutanoate	
β-butyrolactone (**2**)	3-butanolide	4-methyl-2-oxetanone
pivalolactone (**4**)	2,2-dimethyl-3-propanolide	3,3-dimethyl-2-oxetanone
18-crown-6	1,4,7,10,13,16-hexaoxacyclooctadecane	
β-propiolactone (**3**)	3-propanolide	2-oxetanone
δ-valerolactone (**6**)	5-pentanolide	tetrahydro-2*H*-pyran-2-one
ϵ-caprolactone (**7**)	6-hexanolide	2-oxepanone

co-catalyst, claiming that polymerization of a single enantiomer of the lactone gave an optically active crystalline polymer, although there was some racemisation and the molecular weight of the product was low. Teranishi et al. [10] also investigated polymerization of the lactones $\text{R}\overline{\text{CHCH}_2\text{COO}}$ (R = Me, Et, or CHMe_2); using typical cationic initiators, they were able to get only low yields of oily oligomers after long reaction times. With the alkyl-aluminium or -zinc initiators, they obtained high yields of a mixture of oligomers and crystalline polymer but the reaction times were typically 7–30 days. They suggested that the effective initiator was an alkoxide cluster of undefined structure.

The products of partial hydrolysis of alkylmetals are undoubtedly complex species, containing oxygen bridges and perhaps hydroxide groups. In attempting to produce better characterized initiators, Teyssie et al. [11] made mixed oxo-alkoxides of a range of metals, and showed that they efficiently initiated the polymerization of unsubstituted lactones. They claimed that these catalysts did not initiate the homopolymerization of **2**; instead any polymer formed was decomposed to 2-butenoic acid. In a similar study, Iida et al. [12] found that compounds of the general formula $(\text{EtAlO})_n$ were able to polymerize **2** slowly to give mixtures of crystalline and amorphous material.

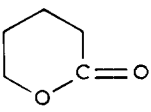
(*meso*-Tetraphenylporphinato)aluminium chloride also initiated the polymerization, although long reaction times were required to give good yields [13,14]. The reaction had living character, but the high initiator concentrations required for reasonable reaction rates led to polymers with low molecular weights. In the anionic polymerization of four-membered lactones by solutions of potassium metal in tetrahydrofuran (THF) containing 18-crown-6 [15], it was established that the initiator solution contained solvated electrons with crown-complexed K^+ counter-ions. This solution was able to initiate rapid polymerization of β-propiolactone (**3**) and of the 3,3-di-substituted compound **5**. From NMR studies, and other evidence, it was suggested that the reaction was initiated via cleavage of the C–C bond of the monomer to yield a carbanion which attacked a second monomer to produce a carboxylate active centre, which subsequently propagated. When this initiator was used to polymerize **2**, the rate of polymerization was several orders of magnitude lower and the molecular weight of the product very much reduced.

Because of the growing interest in bacterial PHB as a commercial polymer, we have studied the polymerization and copolymerization of (±)-β-butyrolactone (**2**). In this paper, we report the results of studies using several initiator systems, mainly of the oxo-alkoxide type.

Experimental

Monomers

(±)-β-Butyrolactone (**2**), δ-valerolactone (**6**) and ε-caprolactone (**7**) were obtained from Aldrich and β-propiolactone (**3**) from Fluka. All monomers were dried over calcium hydride, fractionally distilled under vacuum and stored at 0 °C under dinitrogen.



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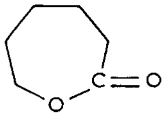

(**7**)

Other materials

All solvents were dried over sodium wire, then by calcium hydride, and distilled under vacuum from calcium hydride before use.

Zinc ethanoate was obtained from Sigma as a hydrate. It was heated under reflux with a large excess of ethanoic anhydride for a few hours, and the anhydrous salt was washed with dry toluene and dried under vacuum.

Initiators

Aluminium 2-propoxide was prepared from aluminium and propan-2-ol [16]. Zinc-aluminium 2-propoxides were prepared by the condensation of zinc ethanoate and aluminium 2-propoxide [11]. We found that the synthesis was rather sensitive to both reaction temperature and time, as has been observed by others [17]. The desired products, having empirical formula $ZnAl_2O_2(OCHMe_2)_4$ were orange glasses which exhibited green luminescence and were highly soluble in hydrocarbons: excessive condensation led to insoluble products. The 360 MHz ^1H and 20.15 MHz ^{13}C NMR spectra of the initiator in C_6D_6 showed the presence of five different $CHMe_2$ environments. The ^{27}Al NMR spectrum was featureless, suggesting that the aluminium atoms all have tetrahedral (rather than octahedral) environments. It is not possible to deduce precise structures for the initiators from these data, but the spectra are consistent with the presence of oligomeric species with several types of bridging and terminal $OCHMe_2$ groups: $OCHMe_2$ bridges between aluminium and zinc would be expected to give different signals, and in small oligomers there could be chemically different bridges of each type.

meso-Tetraphenylporphine was prepared by the reaction of pyrrole with benzaldehyde [18]. The product was treated with diethylaluminium chloride in dichloromethane [19] and the resulting solution was used to initate polymerizations; the pure initiator was not isolated.

Polymerizations

All polymerizations were performed either under vacuum or in dry dinitrogen. For most experiments, the reaction vessel was a 100 cm^3 flask fitted with a dinitrogen inlet and a suba-seal cap, transfers of material being made using dry hypodermic syringes. In some cases, rates of polymerization were measured by dilatometry. Polymerizations were terminated by reaction with hydrochloric acid and the polymer was extracted by precipitation of the organic layer into petroleum ether or, in cases where the polymer was of low molecular weight, by evaporation of the solvent.

Results

Homopolymerization of (±)-β-butyrolactone

Teyssie et al. [11] claimed that initiators based on mixed oxo-alkoxides of a range of metals did not initiate homopolymerization of **2**, although these compounds efficiently initiated polymerization of typical unsubstituted lactones, such as **3**, **6** or **7**. Since little evidence was given to support this claim, we have reinvestigated the use of the zinc oxo-alkoxide for polymerizations in toluene solution, using a monomer concentration of 0.83 *M* and a monomer/initiator ratio of 156/1. The formation of acid end-groups was assessed by titrations of samples of the reaction

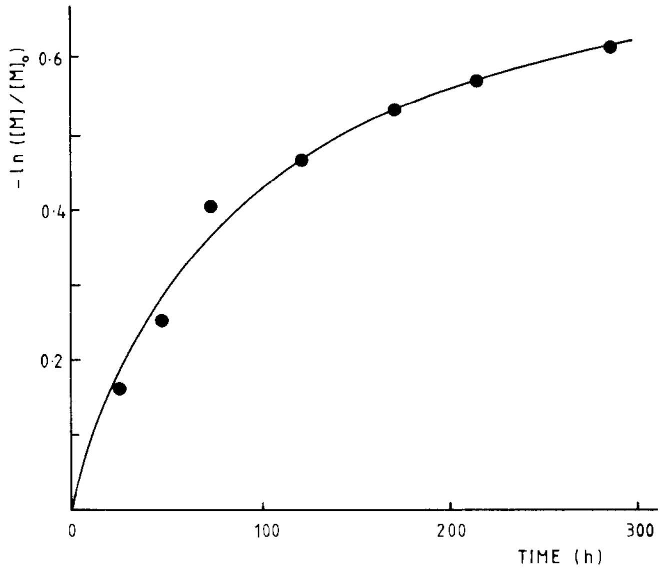

Fig. 1. Conversion-time data as a first-order plot for polymerization of **2** by the mixed oxo-alkoxide initiator at 40 ° C in toluene solution. $[M]_0$ 0.83 mol dm^{-3}.

mixture with KOH (the procedure being shown to be satisfactory by titration of standard solutions of 2-butenoic acid in toluene). **2** polymerized extremely slowly, the stated conditions gave conversions of ca. 45% after 14 days at 40 ° C. Figure 1

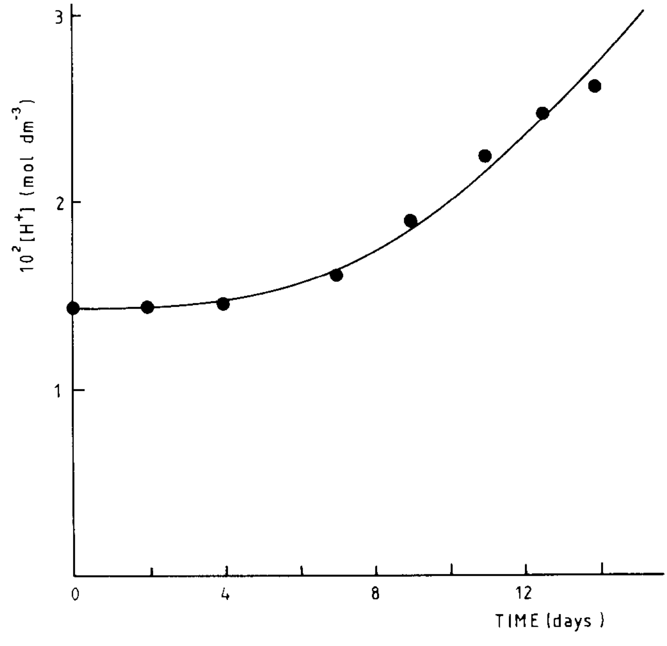

Fig. 2. Increase in acidity during polymerization; reaction conditions as for Fig. 1.

shows the conversion-time data represented as a first-order plot. Whereas polymerization of unsubstituted lactones usually has living character, and follows first-order kinetics, the reaction of **2** was more complex, the apparent first-order rate constant decreasing with increasing conversion. At the same time, the acidity of the reaction mixture increased as shown in Fig. 2, the acidity at the end of 14 days corresponding to conversion of ca. 1.4% of the original monomer to acid.

Characterisation of stereochemical sequences in PHB, using ^{1}H and ^{13}C NMR spectroscopy, has been reported by several groups [9,12,20]. We find that additional detail can be obtained at higher fields [21]; the spectra of the synthetic polymer are all consistent with an atactic structure.

The ^{1}H NMR spectrum of the synthetic PHB contained small peaks assigned to the CH_3 and CH resonances of a $CHMe_2$ end-group and to an OH end-group. By comparison of the end-group and main chain resonances the molecular weights of typical synthetic PHB samples were estimated to be ca. 5500.

Copolymerization reactions

The unsubstituted lactones **3**, **6** and **7** are all readily polymerized to high molecular weight, crystalline products by the oxo-alkoxide initiators and, more slowly, by aluminium 2-propoxide itself. We have investigated copolymerizations of these monomers with **2** using both the zinc-aluminium oxo-alkoxides and aluminium 2-propoxide as initiators. In the case of aluminium 2-propoxide, polymerizations were performed in toluene with an initiator concentration of 6.0×10^{-3} mol dm^{-3}, a monomer/initiator ratio of 133/1, and monomer feed ratios spanning the whole range of possible compositions. In the case of the oxo-alkoxides, the initiator concentration was 2×10^{-3} mol dm^{-3}, the monomer/initiator ratio 156/1, and the solvent either toluene or THF.

Figure 3 shows the dramatic effect of **2** on the yield of polymer after 1 h in copolymerization with **7**. In the absence of **2**, the conversion after 1 h was 100% but it fell rapidly as the concentration of **2** was increased. The oxo-alkoxides were more reactive initiators than aluminium 2-propoxide, and their activity was lower in THF than in toluene, implying that dissociation of the catalyst aggregates reduced the rate of polymerization. The aggregation of the initiator was lowered by addition of propan-2-ol (initiator/propan-2-ol 1/20) in a few experiments; in all cases, the yield of co-polymer was reduced markedly.

Figure 4 shows the effects of **2** on the same copolymerization after 24 h. The dramatic effect on the yield of co-polymer is still apparent. The oxo-alkoxides were usually more effective in toluene than in THF, but the aluminium 2-propoxide was now the more reactive initiator, suggesting that it is better able to survive the initiator deactivation reactions which reduce the activity of the oxo-alkoxides.

Figures 3 and 4 refer to copolymerizations with **7**; analogous results were obtained when **6** was the co-monomer, except that lower co-polymer yields were recorded for similar co-monomer concentrations. With **3** as co-monomer there was no detectable co-polymer after 1 h, and reduced yields were observed after 24 h with all of the initiators. In this case the yields were variable but the co-polymers were low molecular weight oils and difficult to recover quantitatively.

A number of attempts were made to copolymerize **2** with other lactones using (*meso*-tetraphenylporphinato)aluminium chloride. In toluene, at concentrations similar to those used for polymerizations with the oxo-alkoxides, reactions at 40 °C

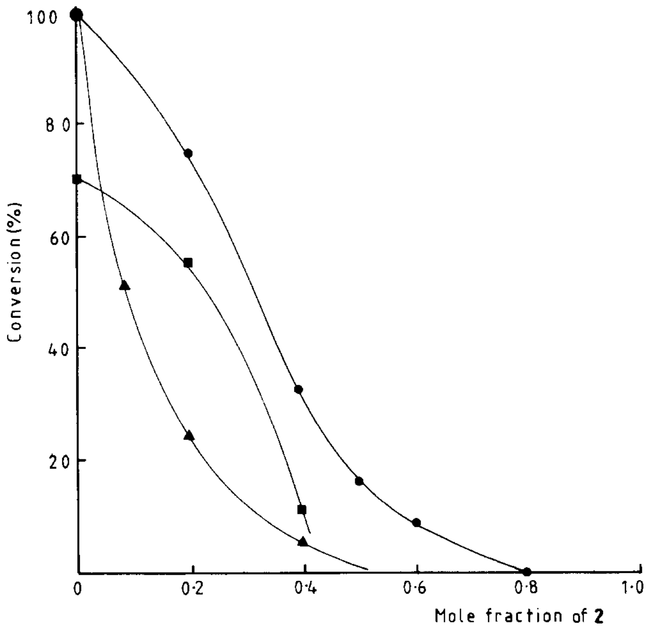

Fig. 3. Effect of concentration of **2** on yield of polymer after 1 h in copolymerizations with **7**. ▲ = initiated by aluminium 2-propoxide in toluene; ● = initiated by mixed oxo-alkoxides in toluene; ■ = initiated by mixed oxo-alkoxides in THF.

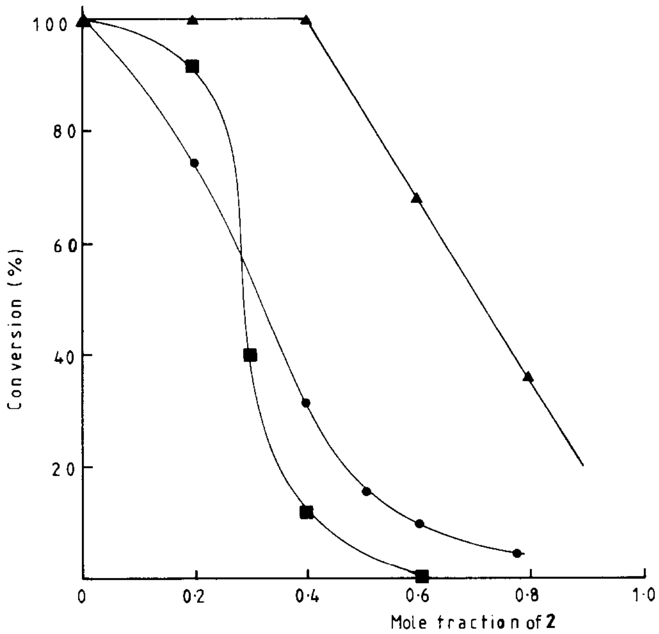

Fig. 4. Effect of concentration of **2** on yield of polymer after 24 h in copolymerizations with **7**. ▲ = initiated by aluminium 2-propoxide in toluene; ● = initiated by mixed oxo-alkoxides in toluene; ■ = initiated by mixed oxo-alkoxides in THF.

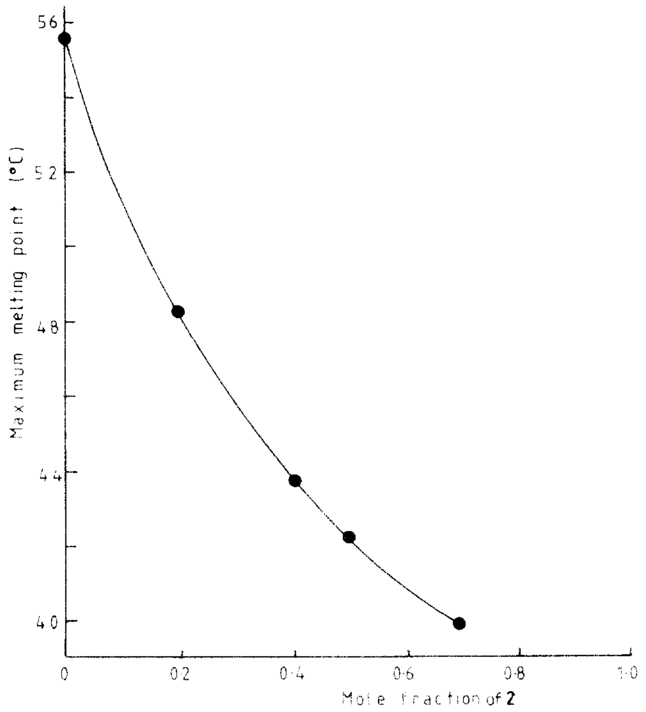

Fig. 5. Effect of concentration of **3** on melting point of polymer obtained after 24 h in copolymerizations with **7**.

yielded little or no co-polymer after reaction times of 24 h. When the experiments were carried out at much higher monomer concentrations (corresponding to the mixture of pure monomers with no added solvent), 90% yields of co-polymers of **3** with **2** were obtained after 14 days. The products were sticky oils, evidently of low molecular weight. Copolymerizations of **2** with **6** or **7** were unsuccessful. Since the rates were low, and it was difficult to free the products from the purple residues of the initiator, this investigation was not pursued.

Copolymer properties

The homo-polymers of **7** or **2**, as prepared with the oxo-alkoxide catalysts, were white, semi-crystalline solids, with m.p. ca. 55 °C, as determined by scanning calorimetry. Figure 5 shows the effect of the addition of **2** as co-monomer on the melting behaviour of the polymer from **7**. In all cases, the m.p. was much lower than that of the homo-polymer, implying that the product was indeed a co-polymer in which the incorporation of **2** restricted crystallisation. At the same time, the effect of the co-monomer was to lower the heat of fusion of the samples, implying lower crystallinity; with high levels of **2**, the co-polymers became greasy semi-solid materials. Similar results were obtained with other co-monomers.

Reactivity ratios

Because of the ester groups between monomer residues, the ^1H NMR spectra of PHB contain no information derived from coupling between hydrogen atoms on different monomer residues, and all peak splittings are due either to coupling between hydrogen atoms in the repeat unit, or to stereochemical sequences. Because there are no asymmetric centres in the repeat units of the unsubstituted co-monomers, there are no stereochemical splittings in the NMR spectra of their polymers. The ^1H NMR spectrum of a co-polymer is thus expected to be simply the sum of the spectra of the two homo-polymers, modified by any stereochemical splitting in β-lactone sequences. This was the case for all the copolymers which were prepared, although all spectra showed peaks assignable to OH and $OCHMe_2$ end-groups. Accordingly, it was possible to use spectral integration (360 MHz) to determine the composition of co-polymers, and hence to determine the reactivity ratios for the copolymerizations.

Copolymer reactivity ratios were determined for the polymerizations of **2** (M_2) with **6** or with **7** (M_1), using the oxo-alkoxides as initiators in toluene solution. Reactivity ratios with **3** were not measured, as the low conversion co-polymers were of very low molecular weight and could not be isolated with sufficient reliability. All of the co-polymerizations were stopped at conversions of less than 10%. Reactivity ratios were calculated from the composition data by the method of Kennedy et al. [22], using eq. 1 [23], where the parameters η and ϵ are defined by $\eta = G/(\alpha + F)$, $\epsilon = F/(\alpha + F)$, and G and F are related to the instantaneous compositions of the monomer feed ($[M_1]/[M_2] = x$) and of the co-polymer ($d[M_1]/d[M_2] = y$) by $G = x(y-1)/y$ and $F = x^2/y$. The parameter α is defined by $\alpha = (F_{max} \cdot F_{min})^{0.5}$, with F_{max} and F_{min} being the highest and lowest observed values of F. For a binary co-polymerization which is adequately described by the copolymer composition equation, a plot of η against ϵ is linear and r_1 and r_2 can be determined from the slope, the intercept, and the value of α.

$$\eta = (r_1 + r_2/\alpha)\epsilon - r_2/\alpha \qquad (1)$$

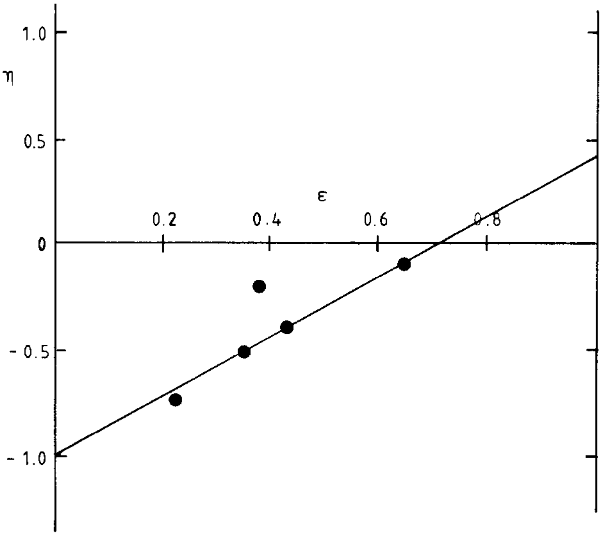

Fig. 6. Copolymer composition data for copolymerization of **2** and **7** with the mixed oxo-alkoxides, plotted according to eq. 1.

Figure 6 shows the plot of eq. 1 for the co-polymerization of **7** and **2**. From these data, $r_1 = 13 \pm 0.5$ and $r_2 = 0.4 \pm 0.04$ are derived. Similar plots for the co-polymerization with **6** and **2** give $r_1 = 7.4 \pm 0.5$ and $r_2 = 0.15 \pm 0.04$.

Discussion

Unsubstituted or 2-substituted lactones are readily polymerized to high molecular weight polymers, by both anionic and cationic initiators. There is evidently little barrier to the polymerization of **2**, since the synthesis of PHB is easily achieved by bacteria via intermediates of higher stability than **2**. Polymerization of **2** was not, however, initiated by $[Et_3O]^+[BF_4]^-$ [24], and CF_3SO_3H gave only low molecular weight polymer. With polymerization initiated by $AlEt_3/H_2O$, conversion was high but again much of the polymer was of low molecular weight.

Teyssie et al. [11] used cryoscopic and NMR measurements to show that the oxo-alkoxide initiators exist in solution as aggregates of the general formula $[(RO)_2AlOZnOAl(OR)_2]_n$, where n is typically 2–8. Studies of the polymerization of cyclic ethers showed that the reaction proceeded by the insertion of monomer into an Al–OR bond, and that there were at least three types of active site, one giving oligomeric non-stereoregular products and the others producing high molecular weight, stereoregular or atactic polymers. The relative contributions of the various sites depended upon the degree of association of the cluster, and hence upon the solvent. The concentration of stereoselective active sites was about 4% of the total molar concentration of the initiator.

The polymerization of **2** is very much less efficient than that of unsubstituted monomers, gives respectable yields of low molecular weight products only after long reaction times, and displays no living character. The fact that the chains have one 2-propyl end-group and one hydroxyl end-group suggests a similar mechanism, involving monomer insertion into the Al–OR bond, but the lack of steric control suggests that steric hindrance at the active site is not important. The decay in rate of polymerization with increasing conversion suggests that there is some process for deactivation of the active sites, possibly the formation of acidic species by reaction of the polymer with the initiator. The increase in acidity observed in our experiments was small, but sufficient to deactivate the initiator. It is well established that acid end-groups are formed in the thermal decomposition of PHB, but the rate of this reaction at polymerization temperatures is too low to be significant. If the acid groups were formed by catalytic chain scission in the polymer, their concentration would indicate enough scission to destroy any high molecular weight polymer which might be formed. In a separate experiment, we dissolved a high molecular weight sample of bacterial PHB at a concentration equivalent to 100% conversion in a polymerization experiment, and treated it with the normal polymerization concentration of the initiator. After 14 days at 40 °C, there was no increase in acidity detectable within the limits of the titration experiment. This suggests that the initiator deactivating species may be formed in a side reaction of the monomer rather than of the polymer. However, in other experiments [24] we have found that the oxo-alkoxides are very powerful pro-degradants for bacterial PHB during melt extrusion at high temperatures.

The low reactivity of **2** is carried over into its co-polymerizations with unsubstituted lactones. Although it is possible to obtain high yields of co-polymer from reaction mixtures containing **2**, the yield of polymer, the rate of polymerization, and the melting point of the co-polymer all fall very rapidly as the content of **2** in the feed is increased. The co-polymers are typically of low molecular weight, as they are often greases rather than powders or rubbers. The observed reactivity ratios are unusual $r_1 > 1$ and $r_2 < 1$ implies that both types of propagating centre preferentially add the unsubstituted lactone, so that only isolated units or short blocks of **2** are produced at low conversions. In contrast to ^{1}H NMR spectroscopy, which is insensitive to monomer sequences in the polymer chain because of the isolating effect of the ester group, the ^{13}C NMR spectra are sensitive to the monomer sequences. ^{13}C NMR studies of the co-polymers will be reported elsewhere [21]; they show that the co-polymers do indeed contain more very short blocks than would be expected from purely random growth statistics. It appears that the inclusion of a single β-lactone unit leads at most to a short block, but that termination is then more favourable than cross propagation, leading to very low molecular weight chains and retardation of the polymerization.

Acknowledgment

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