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An NMR study of chain transfer to diols containing both primary and secondary hydroxy groups in the polymerization of ε-caprolactone

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ε-Caprolactone has been polymerized in the presence of various diols, *viz.* propane-1,2-diol (PD), butane-1,3-diol (BD) and hexane-1,5-diol (HD). ^{1}H and ^{13}C NMR spectroscopy were used to evaluate the structures. The final products were found to be a function of the diol used. It was shown that reactions incorporating PD gave low conversions and/or low degrees of polymerizations when compared with those involving BD or HD. In polymerizations involving BD two ^{13}C resonances could be seen in the carbonyl region, assignable to the ester carbonyls adjacent to the oxymethine and oxymethylene groups derived from the residues of the diol units. Thus, both primary and secondary hydroxy groups were shown to be active in the transfer reaction. Selective decoupling was used to assign the down-field resonance to the carbonyl adjacent to oxymethylene and the up-field resonance to the carbonyl adjacent to oxymethine. However, in the case of the polymerization incorporating BD, approximately 10% of end groups were shown to be secondary alcohols, which are derived from the secondary hydroxy group of BD that does not transfer. In polymerizations involving HD only one carbonyl resonance, which could be assigned to an ester adjacent to the diol residue, was observed. From COSY spectra it was possible to assign a peak due to the ester of the secondary hydroxy. The fraction of secondary chain ends was thus observed to be greater, at *ca.* 13%, than in the BD polymerizations.

Introduction

The polymerization of ε-caprolactone (CL) by ring-opening insertion polymerization, mediated by metal alkoxides, is a well established synthetic tool. The method is used widely in the preparation of both high molecular weight and oligomeric poly(ε-caprolactone) (PCL). Much of the work in elucidating the mechanism and applying ring-opening insertion polymerization can attributed to Kricheldorf *et al.*,[1–3] Jerome *et al.*[4] and Penczek *et al.*[5–8] These authors showed that the polymerization does in fact proceed by an insertion mechanism. Metal alkoxides that work well include those based on tin, titanium, aluminium and rare-earth metals (for examples of rare-earth catalyzed polymerizations see references 9–11).

In the case of the synthesis of telechelic oligomers the chain-end functionality can be added in one of two ways. In the first method a metal alkoxide is prepared and is then used as an initiator. The molecular weight of the resultant oligomer is inversely proportional to the metal alkoxide concentration. Chain-end functionality, usually hydroxy, is then formed by hydrolysis of the metal alkoxide bond that is successively transferred to the chain end as the polymerization ensues. Thus, if one uses a metal alkoxide prepared from a diol the product is a dihydroxy functional oligomer. In the second, commercially significant, variant of this methodology the metal alkoxide is employed in catalytic amounts in the presence of the hydroxy species,[12,13] the concentration of which determines the final degree of polymerization of the polymer. In this method the hydroxy species acts as a transfer agent. That is, the hydroxylic proton is transferred to the alkoxy chain end with scission of the metal alkoxide bond and formation of a new metal alkoxide bond. The transfer step is shown in Fig. 1.

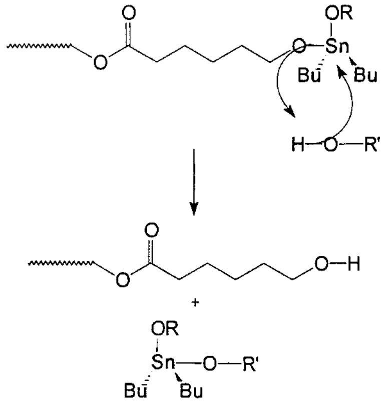

Fig. 1 Transfer of an alcohol (R′OH) to a tin catalysed ring-opening insertion of Cl.

We have used this latter technique to prepare poly(ε-caprolactone-*g*-methyl methacrylate) materials.[14] In that work a poly(methyl methacrylate) with diol functionality at one chain end was prepared. This was then used as a transfer agent in the dibutyl tin oxide (DBTO) catalyzed polymerization of CL. The diol functionality was derived from a radical polymerization of methyl methacrylate in the presence of the chain transfer agent, 3-mercaptopropane-1,2-diol. Thus the end group contained both primary and secondary hydroxy groups. In order to show that both hydroxy groups were active in the transfer process, we determined the concentration of secondary hydroxy end groups in the resulting poly(ε-caprolactone-*g*-methyl methacrylate). Since this was found to be vanishingly low we concluded that in this case both primary and secondary hydroxy groups were transferred. To our knowledge no previous work on the transfer to similar diols has been reported. We have therefore embarked on a study using high field NMR spectroscopy, the results of which are reported here, of the transfer to diols containing both primary and secondary hydroxy groups in the polymerization of ε-caprolactone.

Results and discussion

Low molecular weight models for assignment of carbonyl resonances

The carbonyl regions of the ^{13}C spectra of CL synthesized under conditions in which chain transfer to hydroxy group

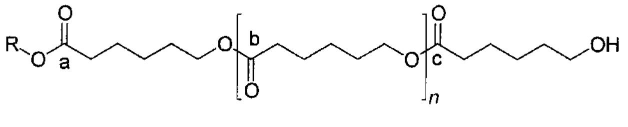

Fig. 2 A PCL with the carbonyl groups giving rise to resolved resonances in ^{13}C NMR spectra labelled (**a**, **b**, **c**). The polymerization was carried out in the presence of the alcohol, ROH.

dominates chain termination, contain three resonances that are derived from three different ester carbonyls.[15] The dominant resonance is due to the ester carbonyl of repeat units that lie within the bulk of the chain. The other two resonances are derived from ester carbonyls of an ultimate repeat unit together with those that are formed from esterification of the transferred hydroxy group. The carbonyls giving rise to this pattern of resonances are illustrated in Fig. 2.

The resonances of carbonyls **b** and **c** have been reported to occur at 173.9 and 174.1 ppm respectively.[15] The chemical shift of **b** is also a function of molecular weight.[15] The chemical shift of **a** is a function of R. Thus if transfer to different alcohol groups in the same transfer agent is possible then separate resonances for each carbonyl may be observed in medium field NMR spectra. In this work two different alcohol groups are present in the transferring diol. No data were available to enable the prediction of the position of the two chemical shifts to be expected from ester carbonyls derived from transfer to one or other of the two, primary or secondary, hydroxy groups in the diols. Therefore the model compounds shown in Fig. 3 were synthesized. Experiments to unambiguously assign the carbonyl resonances were then carried out.

In compound **1**, COSY unambiguously assigned the complex multiplet at 4.05–4.21 ppm to the oxymethylene protons and the multiplet at 5.15 ppm to the oxymethine protons. The proton-noise-decoupled ^{13}C spectrum showed carbonyl ester resonances at 173.75 and 174.02 ppm. The peaks were of equal intensity indicating that the NOES were the same for both carbonyl resonances. The observed spectrum for this region is shown in Fig. 4(a). The completely C–H coupled spectrum is shown in Fig. 4(b); as expected the spectrum is highly complex owing to multiple C–H couplings. Fig. 4(c) shows the spectrum with irradiation at δ 5.15, which corresponds to the resonance position for the oxymethine protons. Clearly, the up-field multiplet became less complex in this spectrum, while the down-field multiplet was unaffected. Irradiation at δ 4.125, the resonance position for the oxymethylene protons, produced the trace in Fig. 4(d). In this case the down-field multiplet became simplified. It was therefore possible to assign the peak at δ 173.75 to an ester carbonyl adjacent to the oxymethine group and that at δ 174.02 to an ester carbonyl adjacent to the oxymethylene group. The resonance from an ester carbonyl resulting from transfer to the primary hydroxy of PD was thus observed down-field of the carbonyl ester resonance resulting from transfer to the secondary hydroxy. Similar experiments with compounds **2** and **3** gave the assignments given in Table 1.

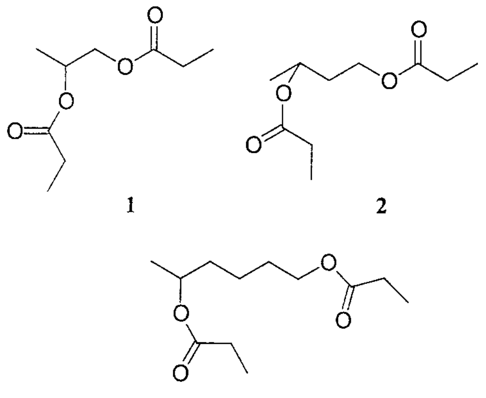

Fig. 3 Diesters used as models for the diol residues.

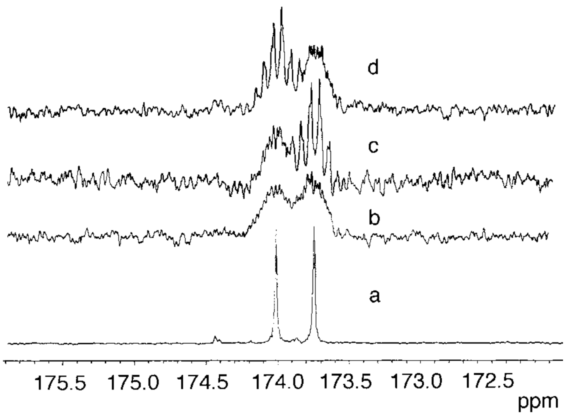

Fig. 4 Fully decoupled (a); C–H coupled (b); selectively C–H decoupled (irradiation at δ 5.15) (c) and selectively C–H decoupled (irradiation at δ 4.125) (d) ^{13}C NMR spectra of compound **1**, in the carbonyl region.

The other models that were required were those for the secondary hydroxy end groups, which are formed as a result of transfer to only the primary hydroxy group. Spectral data for the diols themselves were sufficient for these purposes. The observed ^{1}H and ^{13}C resonances for hydroxymethine sites and hydroxymethylene sites are given in Table 2.

NMR of PCLs: assignment of resonances and treatment of data

The main aim of this work was to examine the effect of changing the distance between primary and secondary hydroxy groups of diols involved in transfer during the polymerization of CL. The first aspect to be examined was the effect on the final conversion. The final % conversion of CL was determined from both the ^{1}H and ^{13}C NMR spectra. The ^{1}H NMR values were determined by comparison of the ^{1}H resonances due to the oxymethylene protons of CL (δ 4.17 (t)) and the converted oxymethylene ^{1}H resonances of the PCL ($\delta \sim 4.05$ (t) and ~ 3.60 (t)). An example of the signals in this region and assignment[15] of the resonances from the PCL polymer is shown in Fig. 5. Alternatively, the carbonyl resonances in the ^{13}C spectra may be used. The resonances of interest here are the carbonyl carbons from CL (176.1 ppm) and the four carbonyls of PCL (labelled as C1–C4 in Tables 4 and 6). While C–H decoupled ^{13}C NMR must not be assumed to be generally quantitative, these carbonyls are adjacent to similar

Table 1 Assignments of ^{13}C resonances in the ester carbonyl region of the model diesters. Calculated values are in parentheses

Compound	Oxymethine carbonyl (δ/ppm)	Oxymethylene carbonyl (δ/ppm)
1	174.02	173.75
2	174.34	173.88
3	174.44	174.04

Table 2 ^{13}C and ^{1}H NMR resonances associated with the primary and secondary hydroxy groups of the diols

	–CHOH (δ/ppm)		–CH$_2$OH (δ/ppm)	
Diol	^{13}C	^{1}H	^{13}C	^{1}H
PD	67.96	3.861	67.44	3.369/3.555
BD	66.43	3.991	60.04	3.730/3.780
HD	67.36	~3.78	61.86	~3.60

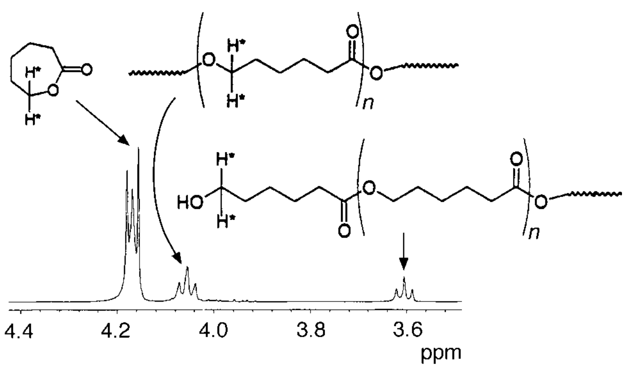

Fig. 5 ^1H NMR spectrum for the product of the TBO catalysed polymerization carried out at 80 °C in the presence of hexane-1,5-diol. An example of the resonances used to determine % conversion of CL.

groups containing identical numbers of hydrogens so that NOES are expected to be equal. This assumption is supported by the fact that carbonyl resonances observed for the model diester compounds (for example see Fig. 2) were indeed of equal intensity and were derived from groups of equal concentration.

A typical spectrum for the carbonyl region, showing all five resonances is shown in Fig. 6. The PCL resonances are labelled C1–C4 on progressing from high to low frequency. The two resonances common to all spectra are those at 173.6 ppm (C1) and 173.4 ppm (C2). C1 arises from carbonyl carbons on the ultimate repeat unit while the source of C2 is the in-chain caproate ester carbonyl.[15] The two ester carbonyls derived from transfer to each of the alcohol groups are observed at varying chemical shifts depending upon the diol used. By reference to the model diesters we were able to assign the up-field resonance (C4) to the carbonyl attached to an oxygen of the oxymethine group and the down-field resonance (C3) to the carbonyl attached to an oxygen of the oxymethylene group. The observed resonance positions and their signal assignments are given in Table 3.

It was also necessary to identify the ^1H resonances that arise from the hydroxymethine protons of secondary end groups. Such groups will arise if transfer does not occur to the secondary hydroxy group of the diol. Examination of the spectra of the free BD and HD diols showed that such oxymethine resonances should be expected at δ 3.99 and 3.78 ppm respectively (see Table 2). Peaks in this region could be observed in the relevant PCL spectra. However, these resonances, postulated as arising from end groups at relatively low concentration, cannot be unambiguously assigned in this manner. Therefore COSY measurements were also employed, so as to ensure correct identifications for these important peaks. The COSY spectra of PCLs prepared in the presence of BD and HD are shown in Fig. 7 and 8.

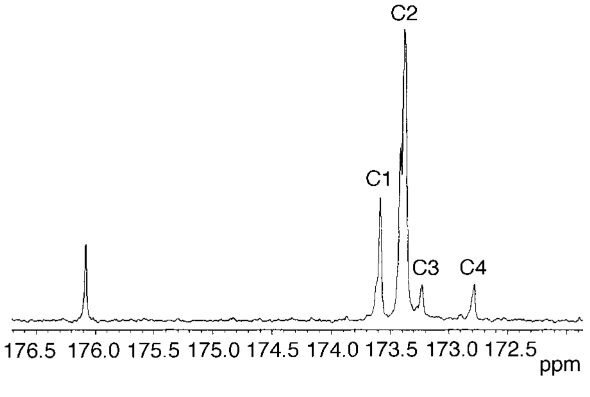

Fig. 6 The carbonyl region of a ^{13}C NMR spectrum of a PCL prepared at 80 °C with TBO catalyst.

Table 3 Observed resonances derived from ester carbonyls adjacent to the transferring diols

Diol	C3 (δ/ppm)	C4 (δ/ppm)
PD	173.0	172.8
BD	173.2	172.8
HD	n.a.	173.0

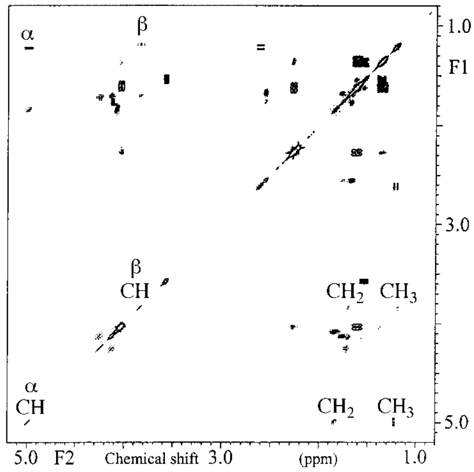

Fig. 7 COSY-45 spectrum for polymer formed in the presence of BD.

The important cross-peak connections to be made in these spectra involve couplings between methyl of the diol residue adjacent to the oxymethine protons of either a secondary alcohol (secondary alcohol end group) or esterified secondary alcohol (*i.e.* the residue of a diol that has transferred). Two couplings to methyl can be observed in both spectra. These are labelled α and β for the connections from ester methine and hydroxymethine respectively. Clearly the resonances at δ 3.84 (Fig. 6) and δ 3.73 (Fig. 7) in BD and HD respectively are coupled to the methyl protons at δ 1.19 (Fig. 7) and δ 1.15 (Fig. 8). The identity of these methine protons is confirmed by the presence of further coupling to adjacent methylene protons at ~δ 1.71 (BD) and ~δ 1.425 (HD) respectively. The ester oxymethine protons derived from diol residues that have undergone transfer show cross-peaks at δ 4.89 (Fig. 6) and δ 4.995 (Fig. 8). It can, therefore, be stated with confidence that the resonances at δ 3.84 and δ 3.73 are indeed due to secondary hydroxy groups that are derived from either BD or HD diol residues, which are located at chain ends.

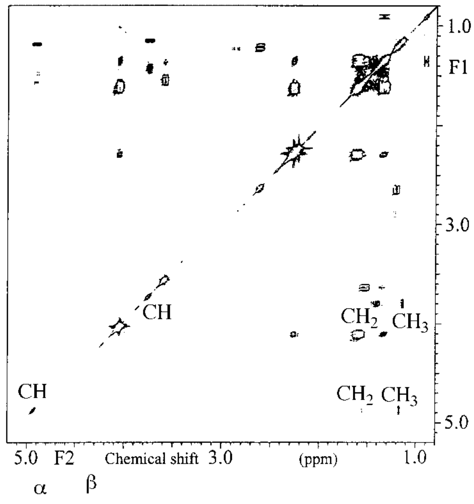

Fig. 8 COSY-45 spectrum for polymer formed in the presence of HD.

Table 4 M_n (SEC), DP (NMR) and % conversion data for polymerizations catalyzed by TBO

Diol	Reaction temp./°C	M_n (SEC)/ g mol^{-1}	DP (NMR)	% Conversion ^{1}H	% Conversion ^{13}C	% Secondary hydroxy end groups
PD	120	477	4.7	34	56	n.a.
BD	120	1690	12.1	100	100	10.0
HD	120	1660	11.0	100	100	12.7
PD	80	642	5.8	29	50	n.a.
BD	80	1390	10.8	80	93	8.6
HD	80	1028	11.2	100	100	14.0

Tetrabutoxy titanium (TBO) catalysis

Tables 4 and 5 contain the data derived from polymer systems formed *via* catalysis using TBO. The first observation to be made from these data is that none of the polymerizations attain degrees of polymerization (DPs) that are close to the theoretical value of 23. Secondly, both the DP and the final conversion of CL appear to be a function of the choice of diol. PD in particular is a rather poor choice of diol for these polymerizations. Both the degree of polymerization and final conversion of CL are significantly reduced at both reaction temperatures. No significant differences in DPs or in rates of polymerization were observed when the polymerizations were conducted in the presence of either BD or HD. The data imply that the PD–Ti complex, which forms as a result of transfer from the propagating PCL chain, is a less efficient initiator of CL polymerization than the similar complexes formed from transfer to either BD or HD. PD in these systems should in fact be regarded as a degradative chain transfer agent.

Table 5 shows the relative peak sizes of components in the carbonyl region from the PCLs polymerized by catalysis with TBO. The degradative behaviour of PD in these systems is again noteworthy. At neither of the polymerization temperatures, 80 °C or 120 °C, are resonances due to esters adjacent to the diol unit observed. This again implies that initiation, following transfer to PD, by the PD–Ti complex is inefficient. The data imply that the majority of the PCL chains present are initiated by some process other than insertion into a PD alkoxide–Ti bond. The second point of note is that only one resonance due to carbonyls attached to HD units is observed. The spectra of all the polymerizations that include BD in the reaction mixtures show two peaks in this region of equal intensity. From reference to the spectra of the model diesters it is clear that two resonances should be present. It can thus be concluded that both the primary and secondary hydroxy groups of BD are active in transfer and in reinitiation. Two explanations are possible for the absence of the second peak in the polymerizations involving HD. Firstly, the down-field resonance due to a carbonyl attached to oxymethylene, derived from transfer to primary hydroxy, may be hidden within the dominant main chain resonance (C3). Alternatively, transfer may occur only to primary hydroxy sites leaving the secondary hydroxy group as a chain end. In the latter case it should be possible to observe the secondary alcohol end group. For example, in the product from a reaction conducted at 120 °C, a peak which could be assigned to the secondary alcohol oxymethylene protons was observed at δ 3.76. However, its integral when compared with that of the primary oxymethylene peak at δ 3.60 indicated that only 12.7% of chain ends could be accounted for in this manner. Table 4 indicates the fraction of secondary hydroxy end-groups formed in the polymerizations incorporating BD and HD. It can be seen from this table that, in BD polymerizations, *ca.* 10% of the end groups were formed from secondary residual BD units. Also, consistently higher secondary hydroxy contents were found in polymerizations involving HD than in those with BD.

Table 5 C1–C4 integrations for TBO catalysis

Diol	Reaction temp./°C	C4	C3	C2	C1
PD	120	n.a.	n.a.	0.58	0.42
BD	120	0.06	0.04	0.70	0.20
HD	120	0.08	n.a.	0.78	0.14
PD	80	n.a.	n.a.	0.71	0.29
BD	80	0.08	0.08	0.68	0.16
HD	80	0.05	n.a.	0.67	0.19

DBTO catalysis

The results from DBTO catalysis are shown in Tables 6 and 7. DBTO catalysis data echoed the results with TBO. Thus, in polymerizations involving PD, at a polymerization temperature of 120 °C, although the final conversion was high (in fact significantly higher than in the TBO catalyzed system), the degree of polymerization and M_n, as measured by SEC, was low. This again indicates that the PD–DBTO complex may not be an efficient reinitiator of polymerization. The high conversion and low degree of polymerization in this system may indicate the existence of a chain-breaking side reaction in this system. Significantly, when the reactions were carried out at the lower temperature of 80 °C, but for longer reaction times, much improved results were obtained. Thus the degrees of polymerization (as measured by NMR) and M_ns (SEC) were much higher. The DPs were still, however, well removed from the theoretical value. Examination of the ^{13}C spectrum showed that both of the expected oxymethylene and oxymethine ester carbonyls arising from esterification of both the secondary and primary hydroxy groups were present. Interestingly, the ^{1}H spectrum of the product from the PD polymerization carried out at 120 °C also showed resonances that could be attributed to free PD. The polymerizations involving BD and HD proceeded to high conversion and gave polymers of degrees of polymerization between 9 and 13, which are again below the expected value. With this catalyst, as with TBO, polymerizations involving HD appear to give a significantly higher fraction of secondary hydroxy. Also, the concentration of secondary hydroxy sites found in these polymerizations appears to be lower than in equivalent TBO polymerizations. No resonances that could be assigned to secondary hydroxy sites from the PD residue were observed.

Table 7 shows the results of ^{13}C spectroscopy in the carbonyl region. In the case of the PD (carried out at 80 °C) and BD containing polymerizations the carbonyls attached to both oxymethine and oxymethylene groups of the residual diol were observed. In each case both resonances were observed to have equal intensity. In the case of the HD containing polymerization only one resonance was observed. However, as discussed above for the TBO catalyzed polymerizations, this resonance is derived from an oxymethine carbonyl and therefore the second resonance must lie underneath the main chain resonance, C3. Thus, as with the TBO catalyzed polymerizations, both primary and secondary hydroxy groups are active in transfer and reinitiation. However, reference to the ^{1}H spectra, discussed above, indicates that, as in the TBO catalyzed system, the primary alcohol is more reactive in the transfer

Table 6 M_n (SEC), DP (NMR) and % conversion data for polymerizations catalyzed by DBTO

Diol	Reaction temp./°C	M_n (SEC)/ g mol^{-1}	DP (NMR)	% Conversion ^{1}H	% Conversion ^{13}C	% Secondary hydroxy end groups
PD	120	788	6.9	97	100	n.a.
BD	120	1474	12	89	95	10
HD	120	1445	11	78	90	13
PD	80	1782	14	100	100	0
BD	80	2109	11	100	100	9
HD	80	1782	14	96	100	14

Table 7 C1–C4 integrations for DBTO catalysis

Diol	Reaction temp./°C	C4	C3	C2	C1
PD	120	0.08	0.08	0.61	0.23
BD	120	0.05	0.05	0.57	0.22
HD	120	0.05	n.a.	0.80	0.15
PD	80	0.05	0.05	0.80	0.10
BD	80	0.06	0.06	0.74	0.14
HD	80	0.04	n.a.	0.80	0.16

reaction and this is reflected by the presence of secondary hydroxy end groups.

Conclusions

The purpose of this work was to further investigate, following on from our initial reports on the use of PMMA diols, the effect of using diols with both primary and secondary hydroxy groups as transfer agents for the preparation of PCL diols. As in our previous report[14] conditions were chosen that model those in operation on an industrial scale. Therefore water was removed from the system by passing a dried stream of nitrogen through the reaction mixtures at the reaction temperature. Water, in these insertion polymerizations, acts as another type of transfer agent. The occurrence of significant transfer to water would result in the formation of carboxylic acid end groups. Since these end groups were not observed in the NMR spectra we assume that the effect of residual water under these conditions is negligible. The presence of small amounts of water also has no effect on the final conversion of CL.

We have shown that under these conditions both 1,3 BD and 1,5 HD act as transfer agents in which both hydroxy groups are able to transfer the propagating chain end. However, the secondary hydroxy has been shown to be less reactive and this results in the presence of an appreciable number of secondary hydroxy end groups. A higher fraction of secondary end groups was found in the polymerizations involving HD than in those with BD. PD showed anomalous behaviour under some conditions. The results appear to indicate that PD may be involved in degradative chain transfer that may be a result of side reactions. However, at a polymerization temperature of 80 °C, PD gave polymer of a similar quality to that from polymerizations containing BD or HD. Thus there are structural differences in the final PCL product that are a function of the distance between the two hydroxy groups in the transferred diol. These observations strongly suggest that the structure of the catalytic site undergoing transfer is cyclic.

Experimental

Materials

CL (Aldrich, purity = 99.9+% (GC)), dibutyl tin oxide (DBTO) (Aldrich), titanium tetrabutoxide (TBO) (Aldrich), xylene (Aldrich), propane-1,2-diol (PD) (Aldrich, purity = 99.9+% (GC)), butane-1,3-diol (BD) (Aldrich, purity = 99.9% (GC)) and hexane-1,5-diol (HD) (Aldrich, purity = 99.9+% (GC)) were used as supplied. Since all of the reactants gave single peaks on analysis by GC further purification was deemed unnecessary.

Analysis

NMR spectra were recorded at 399.78 MHz (^{1}H) and 100.54 MHz (^{13}C) using a JEOL GSX400 instrument. Magnitude-mode 2D-COSY-45 spectra of polymers were measured using a spectral width of 2718.9 Hz and 56 acquisitions for each of 1024 increments were sampled into 1024 complex points. Data were processed for presentation and analysis using the software suite nmrPipe.[16] The arrays were zero-filled to 2048 × 2048 complex points and transformed in each dimension after application of a sinebell window function. Molecular weights and molecular weight distributions of the PCLs were measured by size exclusion chromatography (SEC) (calibrated against polystyrene standards) with Styragel® 5 mm mixed gel columns (Polymer Laboratories) and a UV detector system. Tetrahydrofuran was used as the eluent at a flow rate of 1.0 cm^3 min^{-1}. Sample concentrations were approximately 2 g dm^{-3}.

Synthesis of model compounds

In order to correctly assign the ^{13}C resonances derived from the carbonyl carbon of the diester unit, model compounds were prepared. Models for each diester unit were prepared by preparing the dipropionyl ester of each diol. Thus each diol (50 mmol) (PD, BD or HD), in turn, was mixed with propionic acid (100 mmol) and toluene-*p*-sulfonic acid (0.35 mmol). The mixture was heated using Dean–Stark conditions at 175 °C for approximately 24 h. The products were then distilled under vacuum. The ^{1}H NMR (400 MHz) and mass spectrometric (EI+) data for each diester were as follows.

Propane-1,2-diyl dipropionate (**1**): δ 1.14 (2 × t, 6H), 1.25 (d, 3H), 2.33–2.35 (2 × q, 4H), 4.07 and 4.18 (2 × dd, 2H), 5.15 (m, 1H); *m/z* 115 (**1** minus –O–COCH$_2$CH$_3$).

Butane-1,3-diyl dipropionate (**2**): δ 1.14 (t, 6H), 1.26 (d, 3H), 1.89 (m, 2H), 2.40–2.42 (2 × q, 4H), 4.12 (dd, 2H), 5.03 (m, 1H); *m/z* 133 (**2** minus –O–COCH$_2$CH$_3$).

Hexane-1,5-diyl dipropionate (**3**): δ 1.13, 1.14 (2 × t, 6H), 1.21 (d, 3H), 1.4–1.65 (3 × m, 6H), 2.30–2.32 (2 × q, 4H), 4.07 (t, 2H), 4.92 (m, 1H); *m/z* 157 (**3** minus –O–COCH$_2$CH$_3$).

Polymerizations

Polymerization mixtures were prepared from CL (6.3 g, 55 mmol), catalyst (0.1 mmol) (DBTO or TBO), xylene (12 cm^3) and the required diol (4.7 mmol). These mixtures were then heated under a stream of dry nitrogen at either 120 °C for 6 h or 80 °C for 7 days. This procedure would give a theoretical degree of polymerization (DP) of 23. The whole reaction mixture, including the xylene solvent, was then analysed by ^{1}H and ^{13}C NMR and SEC.

Assignment of carbonyl resonances in models

In order to assign the two resonances derived from the ester carbonyls of the primary and secondary esters the following procedure was used. A fully decoupled spectrum was first run; this located the two carbonyl resonances from each diester. Fully C–H coupled spectra were then obtained, displaying complex couplings for both sites, involving interactions with several protons. From ^{1}H COSY spectra ester methylene (–CH$_2$O–) and methine (–CHO–) proton resonance positions were identified and frequency values determined. The ^{13}C coupled experiment was repeated but with selective irradiation at the resonance frequency for the methylene protons of the primary ester. This caused the primary carbonyl response to be partially decoupled with simplification of the multiplicity. This procedure was repeated with irradiation at the methine frequency; in this case the secondary ester carbonyl response showed partial collapse.

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