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END-GROUP ANALYSIS OF POLY(ϵ-CAPROLACTONE) INITIATED WITH WATER, ETHYLENE GLYCOL, AND 1,4-BUTANEDIOL

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ABSTRACT

Low molecular weight poly(ϵ-caprolactone) (PC), produced using stannous octoate as catalyst and initiated with water, ethylene glycol, or 1,4-butanediol, was subjected to end-group analysis using gated decoupling (decgate) ^{13}C-NMR spectrometry. Within the main-chain ϵ-caprolactone repeat unit, the carbon resonances were assigned as follows: carbonyl, 173.9; α, 34.1; β, 25.5; γ, 24.6; δ, 28.3; ϵ, 64.3 ppm. The spectra of water-initiated polymers were consistent with a linear PC chain carrying one carboxylic acid end group and one hydroxyl end group. The presence of the terminal hydroxyl group yielded different chemical shifts for the ϵ-, δ-, γ-, α-, and carbonyl, but not the β-carbon of the ultimate repeat unit. The terminal acid group yielded different chemical shifts for the adjacent carbonyl, α-, β-, and γ-carbons. Spectra of diol-initiated polymers were consistent with a linear PC chain containing the initiator residue and carrying two hydroxyl end groups. The terminal hydroxyl groups caused the same chemical shift patterns within the ultimate repeat units as were observed in the water-initiated PCs.

INTRODUCTION

The use of biodegradable, aliphatic polyesters for implantable drug delivery devices [1–3], sutures [4, 5], and general tissue supports [6, 7] after injury or surgery has increased dramatically within the last two decades. The polymers traditionally of highest interest are derived from combinations of lactide, glycolide, and ϵ-caprolactone monomers, and they are generally polymerized to high molecular weight, forming linear, semicrystalline, thermoplastic materials.

The structures of these aliphatic polyesters have been extensively studied using ^{13}C-NMR spectroscopy. For example, Kricheldorf and coworkers investigated the synthesis and structure of ϵ-caprolactone/glycolide copolymers [8] and the transesterification of various poly(lactones) [9]. A considerably more detailed analysis of comonomer sequencing in copolymers of L,L-lactide and ϵ-caprolactone was reported by Kasperczyk and coworkers [10]. In addition to these studies, ^{13}C-NMR was also used to determine the various transesterification products from the polymerization of racemic mixtures of lactide [11].

Since these studies have dealt predominantly with high molecular weight polyesters, the emphasis has been on comonomer sequencing and transesterification during polymerization. Recently, investigators in our laboratory have been interested in biodegradable networks derived from functionalized, low molecular weight polyester prepolymers [12]. In this work, low molecular weight polyester diol and triol prepolymers have been synthesized from combinations of lactide, glycolide, and ϵ-caprolactone, and an appropriate polyol initiator. The resulting polyol prepolymers have then served as a starting point to various crosslinking chemistries such as urethane formation [13] and epoxy–anhydride curing reactions [14]. Due to the nature of this work, we have been particularly interested in the structure of these prepolymers with regard to end groups and initiator residues, in addition to the traditional backbone repeating structure.

The present study involves the use of gated decoupling (decgate) ^{13}C-NMR to identify the resonances of carbon atoms present in the terminal repeat units, i.e., those adjacent to the end groups, in low molecular weight poly(ϵ-caprolactone) (PC) chains. Molecular weight variance was utilized as a tool to bring about systematic diminution and hence identification of end-group resonances, and peak-area integrations were used to positively associate end-group resonances to their corresponding main-chain resonances. The investigation was applied to a series of water, ethylene glycol, and 1,4-butanediol-initiated homopolymers of ϵ-caprolactone that was synthesized via tin-catalyzed ring-opening polymerization.

EXPERIMENTAL

Materials

The following reagents were used without further purification: chloroform-*d* (99.8 atom%, 1% TMS) (Aldrich), 1,4-butanediol (BD) (Aldrich), ϵ-caprolactone (Union Carbide), ethylene glycol (EG) (Fisher), hexanes (Fisher), methylene chloride (Fisher), and stannous 2-ethylhexanoate (stannous octoate) (Sigma).

Model Polyesters

All polymerizations were carried out in the bulk under nitrogen using stannous octoate as catalyst at a concentration of 1.4×10^{-4} mole per mole of monomer. Table 1 lists the initiators, monomers, and reactant ratios used in the various polymerizations. The yield values shown are isolated yields and may suggest a lower monomer conversion than actual. Water-initiated reactions were carried out at 100°C, and ethylene glycol and 1,4-butanediol-initiated reactions were carried out at 120°C. Glassware was dried at 145–155°C for 24 hours, fitted with rubber septa, and cooled under a flow of dry nitrogen. Polymerizations (5–10 g) were conducted using 40 mL test tubes with 24/40 ground glass joints sealed with evacuated glass stoppers wrapped with Teflon tape.

A representative experimental procedure was as follows: The appropriate amount of monomer, initiator, and stannous octoate was added to a test tube. The test tube was purged with nitrogen and placed in a 100 or 120°C oil bath for 16 hours. The polymerization was quenched in an ice-water bath, and the polymer was dissolved in methylene chloride 25–35% (w/v), followed by precipitation into a tenfold excess of stirred hexanes. The hexanes layer was decanted, and the polymer was washed with hexanes (2 × 100 mL). The polymer was then redissolved, transferred to a specimen jar, dried for 24 hours in a 60°C oven, and then for 24 hours at 25°C in vacuo.

Measurements

Decgate and routine ^{13}C-NMR spectra of the model polymers were obtained on a Bruker AC-200 spectrometer using 5 mm o.d. tubes. Sample concentrations were approximately 25% (w/v) in chloroform-*d* containing 1% TMS as in internal reference. The pulse delay was set at 40 seconds for each experiment in order to insure complete relaxation of the polymer carbonyl carbons.

RESULTS AND DISCUSSION

To obtain the simplest ^{13}C-NMR spectra of poly(ϵ-caprolactone), water was chosen as an initiator because it contributes no resonances of its own and it yields a simple linear polymer structure consisting of one hydroxyl end group and one

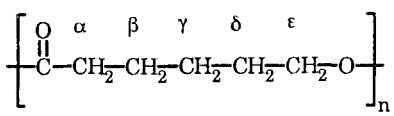
TABLE 1. Initiators, Monomers, and Reactant Ratios Used in Polymerizations

Run #	[M]	[I]	[M]/[I]	NMR DP	Yield, %
1	ϵ-Caprolactone	Water	2:1	3.4	84
2	ϵ-Caprolactone	Water	5:1	5.7	76
3	ϵ-Caprolactone	Water	48:1	19.1	31
4	ϵ-Caprolactone	EG	10:1	5.8	82
5	ϵ-Caprolactone	EG	48:1	27.4	83
6	ϵ-Caprolactone	BD	10:1	5.4	72
7	ϵ-Caprolactone	BD	48:1	34.3	84

carboxylic acid end group whose carbonyl carbon is shifted considerably downfield from the ester carbonyl groups. Figure 1 shows a typical ^{13}C-NMR spectrum of a water-initiated ϵ-caprolactone oligomer ([M]:[I], 2:1) with the main-chain carbon resonances correctly assigned. These assignments are the same as those given by Kasperczyk and coworkers [10], Duda [15], and earlier by Storey and coworkers [12, 13]. It should be noted that the γ-carbon has been placed at 24.6 ppm and the δ-carbon at 28.3 ppm. There has been some conflict in the literature concerning the ^{13}C-NMR assignments of these two carbons in the poly(ϵ-caprolactone) repeat unit. For example, Kricheldorf et al. [8] and Kricheldorf and Sumbél [16] reported exactly the opposite assignments, based upon analysis of glycolide/ϵ-caprolactone copolymers. The spectrum in Fig. 1 will serve as a representative model for further discussion of end-group resonances, and later in the paper it will be shown that these assignments are indeed correct, based upon quantification of end-group resonances.

Water-Initiated Poly(ϵ-Caprolactone)

A series of water-initiated PCs was synthesized using [ϵ-caprolactone]:[water] ([M]:[I]) ratios of 2:1, 5:1, and 48:1. In some cases the degree of polymerization was higher than theoretical, indicating inefficient initiation by water and/or loss of water toward the end of the reaction due to step-growth polymerization of the formed oligomers. Figure 2 depicts the gel permeation chromatograms for the 2:1 and 5:1 PCs. The polymer with the lower target degree of polymerization (2:1)



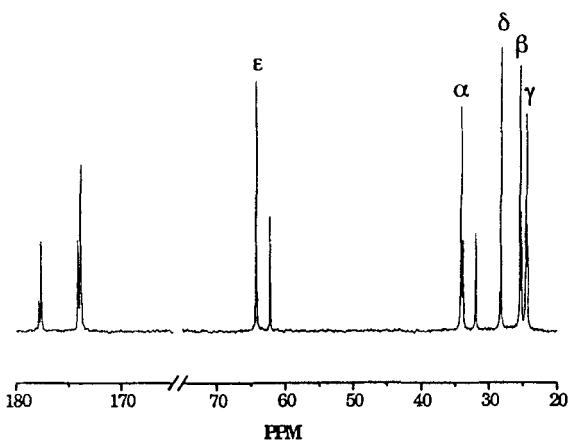


FIG. 1. Decgate ^{13}C-NMR spectrum of water-initiated poly(ϵ-caprolactone) with a [M]:[I] ratio of 2:1.

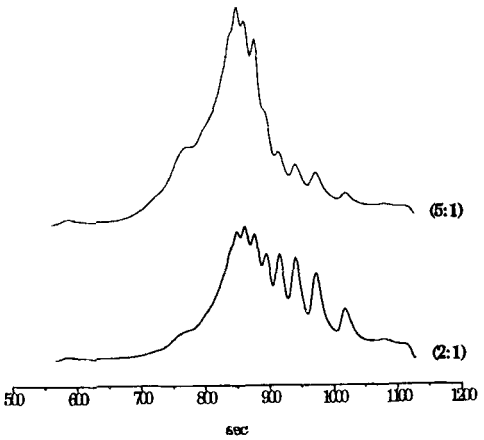


FIG. 2. Gel permeation chromatograms for water-initiated poly(ϵ-caprolactone) with [M]:[I] ratios of 2:1 and 5:1.

shows distinct peaks due to dimer, trimer, etc., and the distribution of degrees of polymerization is broad (MWD = 1.56). The 5:1 polymer shows an obvious increase in molecular weight, and the distribution is slightly more narrow (MWD = 1.45). The broad distribution of the 2:1 polymer is attributed to its relatively low degree of polymerization and the inefficient nature of water as an initiator.

As is typical of aliphatic polyesters, the carbonyl carbons exhibited the greatest sensitivity to chemical environment. Figure 3 depicts the decgate ^{13}C-NMR spectrum

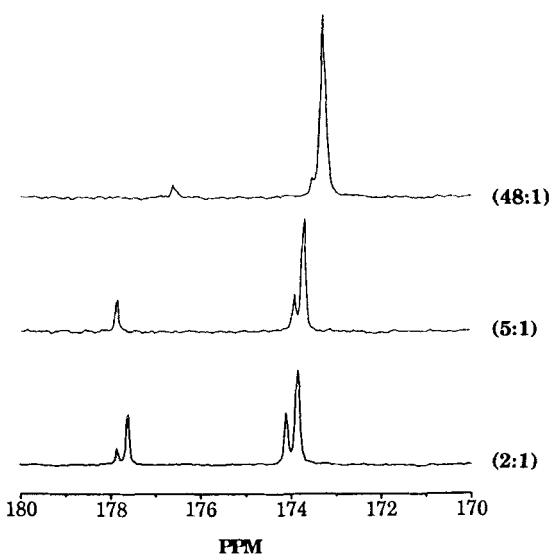


FIG. 3. Decgate ^{13}C-NMR spectra of the carbonyl region of water-initiated poly-(ϵ-caprolactone) with [M]:[I] ratios of 2:1, 5:1, and 48:1.

of each polymer in the series. It was observed for all of the water-initiated polymers that degree of polymerization caused a pronounced effect on chemical shift. In general, as the degree of polymerization increased, main-chain and end-group resonances shifted upfield. For the 2:1 polymer, two distinct regions can be observed, one at 173–175 ppm due to ester carbonyl groups and the other at 177–178 ppm due to carboxylic acid end groups. The most intense signal at 173.9 ppm was attributed to the main-chain carbonyl carbons; the companion signal at 174.1 ppm has been assigned to the terminal carbonyl carbon nearest to the hydroxyl end group. The two signals at 177–178 ppm are due to the carbons of carboxylic acid end groups that result from water initiation; the more intense signal at 177.6 ppm is due to carboxylic acid end groups of all chains with degrees of polymerization of two or higher. The weaker resonance at 177.9 ppm has been assigned to the carboxylic acid carbonyl group of 6-hydroxycaproic acid, which should be present in this polymer considering that its number-average degree of polymerization is 3.4. Since for every carboxylic acid end group there exists a hydroxyl end group, the sum of the integrated areas of the peaks at 177.6 and 177.9 ppm is approximately equal to the integrated area of the peak at 174.1 ppm.

The effect of the terminal hydroxyl group is most strongly evident in the ϵ- and δ-methylene regions of the poly(ϵ-caprolactone) spectrum. The ϵ-methylene carbon resonances fall between 61 and 65 ppm, i.e., the range characteristic of carbon bonded to oxygen. In Fig. 4 the 2:1 spectrum shows the main-chain ϵ-methylene resonance at 64.3 ppm and, in addition, a small complimentary resonance at 62.2 ppm that has been attributed to the methylene carbon bonded directly to the hydroxyl group at the end of the polymer chain. The latter assignment is supported by the gradual disappearance of this resonance in moving from 2:1 to higher (5:1) degrees of polymerization. Since no additional peaks were observed in this region, it seems apparent that the ϵ-methylene group closest to the carboxylic

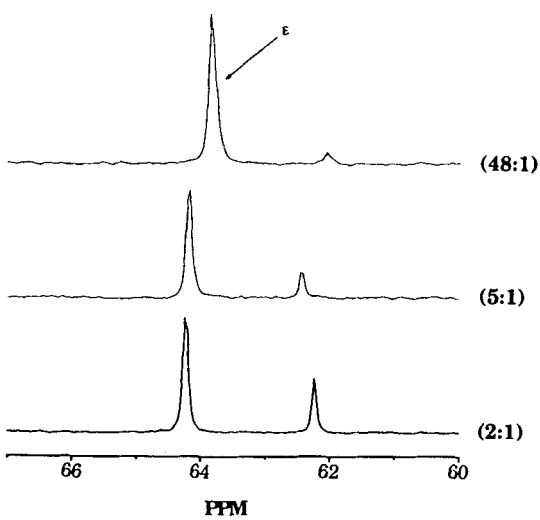


FIG. 4. Decgate ^{13}C-NMR spectra of the ϵ-methylene region of water-initiated poly-(ϵ-caprolactone).

acid end group is indistinguishable from the main-chain ϵ-methylene groups. This is sensible since it is separated from the acid group by five covalent bonds.

Perhaps the most interesting region of the poly(ϵ-caprolactone) spectrum is that for the δ-methylene group, whose main-chain resonance appears at 28.3 ppm. Also within this general region is a smaller peak at 32.0 ppm, which clearly diminishes in intensity as molecular weight increases (Fig. 5). As mentioned earlier, certain literature reports have assigned the 28 ppm region to the γ-methylene carbon instead of the δ carbon [8]. The reason, apparently, is that in copolymers of glycolide/ϵ-caprolactone the peak at 28.3 is the only one of the main-chain methylene resonances that does not show dyad sensitivity. Since the γ-carbon is approximately in the middle of the repeat unit, it is reasonable that it would be the least likely to be affected by different monomer units on either side. However, analysis of end-group resonances using decgate ^{13}C-NMR spectrometry offers convincing evidence that the peak at 28.3 ppm is in fact due to the δ-carbon.

The evidence is as follows: Within the terminal repeat unit, the δ-carbon, which is two bonds away from the hydroxyl group, should experience a stronger chemical shift, relative to the main-chain δ-carbons, than does the γ-carbon relative to its corresponding main-chain carbons. Thus the small peak at 32.0 ppm is most likely to be the terminal δ-carbon. In addition, if we identify some reference carbon whose assignment is not in question, say the ϵ-carbon, then the total number of δ-carbons, including main-chain and terminal carbons, must be equal to the total number of ϵ-carbons. Integration of the decgate spectrum shows that, indeed, the sum of the areas of the peaks at 28.3 and 32.0 is virtually identical to the sum of the areas of the two peaks assigned to the ϵ-carbons.

Figure 6 shows the β- and γ-carbon regions. The latter consists of three resonances, a main peak at 24.6 ppm that was assigned to the main-chain carbons and two smaller peaks at 24.4 and 24.7 ppm. The latter two represent the γ-carbons of

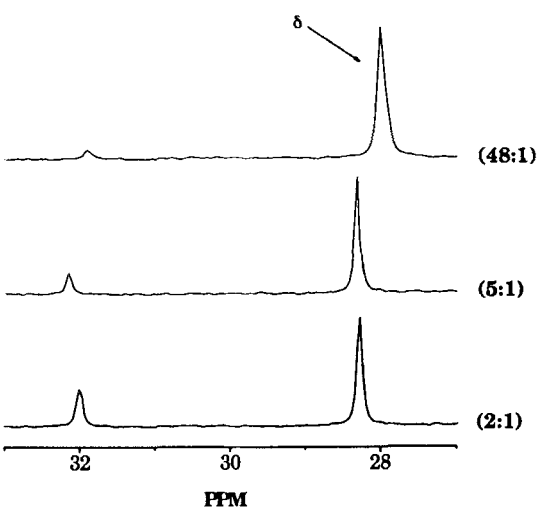


FIG. 5. Decgate ^{13}C-NMR spectra of the δ-methylene region of water-initiated poly(ϵ-caprolactone).

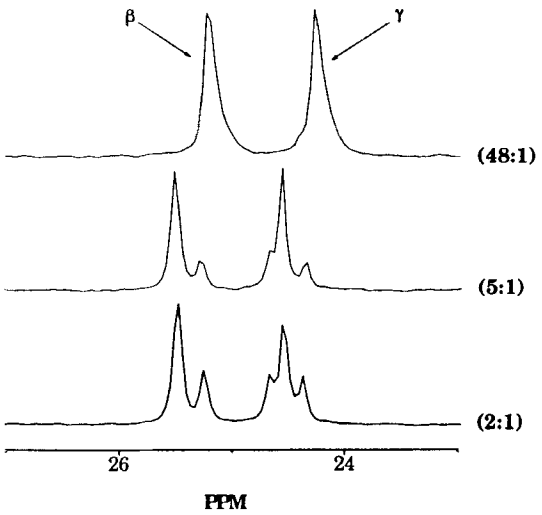


FIG. 6. Decgate ^{13}C-NMR spectra of the β- and γ-methylene regions of water-initiated poly(ϵ-caprolactone).

the first (adjacent to carboxylic acid) and last (adjacent to hydroxyl) repeat units; however, which is which has not been determined with certainty. The β-carbon region contains a major resonance at 25.5 ppm and a resonance at 25.3 ppm due to the β-carbon adjacent to the carboxylic acid end group. This carbon is apparently too far removed from the oxy end of the repeat unit to exhibit a unique chemical shift due to the hydroxyl group. The α-carbon region showed the second greatest sensitivity to chemical environment after the carbonyl carbons, and this region was also divided into two distinct subregions. Figure 7 shows a stack plot with molecular weight increasing from bottom to top. The main-chain α-carbons were assigned to the largest peak at 34.1 ppm, since as molecular weight increased, this peak grew at the expense of all the others. For the lowest molecular weight polymer (2:1), the peak just downfield of the main peak at 34.2 ppm is due to the α-carbon nearest to the terminal hydroxyl group. This peak is still present in the 5:1 spectrum, but much reduced. The signal at about 33.8 ppm is due to the α-carbon bonded directly to the carboxylic acid end group, and it shows the expected diminution with increasing molecular weight. It will be noted that the latter peak in the 2:1 spectrum is associated with a weak downfield shoulder that has been assigned to the α-carbon of 6-hydroxycaproic acid.

A likely explanation for the fact that the carbonyl and α-carbons are sensitive to the hydroxyl end group, but that the β-carbon is not (in spite of the fact that it is closer) is that the former two are affected not directly through the C—C bonds of the chain, but through a hydrogen-bonded cyclic at the chain end.

Ethylene Glycol-Initiated Poly(ϵ-Caprolactone)

When ϵ-caprolactone was initiated with ethylene glycol and 1,4-butanediol, the resulting polymers exhibited nearly identical ^{13}C-NMR spectra to those of the

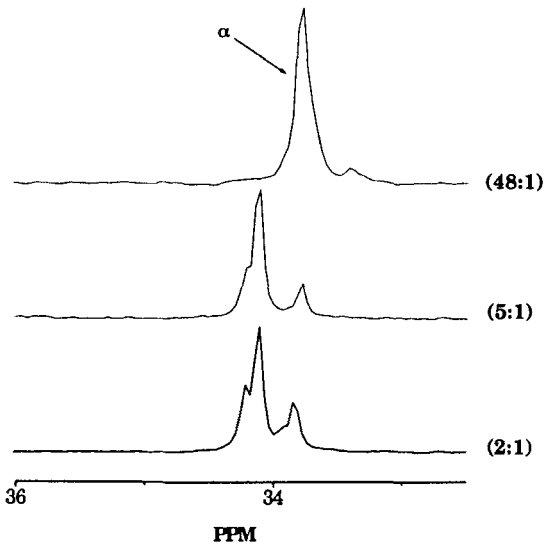


FIG. 7. Decgate ^{13}C-NMR spectra of the α-methylene region of water-initiated poly(ε-caprolactone).

water-initiated systems, except for the absence of resonances due to the carboxylic acid end groups. In both systems, [M]:[I] of 10:1 and 48:1 were used to serve as representative low and high molecular weight models, respectively. The carbonyl region of the ethylene glycol-initiated system (Fig. 8) shows signal splitting, in the lower molecular weight sample (10:1), that diminishes as the molecular weight is increased fivefold (48:1). The signal at 174.3 ppm is attributed to carbonyl carbons

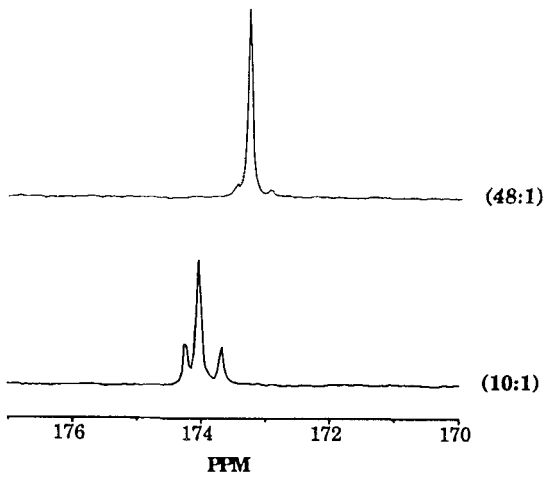


FIG. 8. Decgate ^{13}C-NMR spectra of the carbonyl region of ethylene glycol-initiated poly(ε-caprolactone).

contained in the hydroxyl end of the polymer chain, and the signal at 173.7 ppm can be assigned to carbonyl carbons adjacent to initiator molecules. In fact, the integration values of these two peaks are virtually identical.

The ϵ-methylene region (Fig. 9) from 60–65 ppm shows three distinct signals in the lower molecular weight prepolymer (10:1). The resonance at 64.5 ppm was assigned to the main-chain carbons. The two additional resonances are due to the ϵ-carbon bonded directly to the hydroxyl end group (62.5 ppm) and the ethylene initiator carbon (62.7 ppm). The integration values of these end-group resonances are approximately equal to each other, as predicted. In addition, as molecular weight increases from 10:1 to 48:1 and the concentration of end groups decreases, the resonances corresponding to initiator and end groups diminish.

The δ-methylene region (27–33 ppm) for this system exhibits the same end group effect as seen in the water-initiated system (Fig. 5).

1,4-Butanediol-Initiated Poly(ϵ-Caprolactone)

For 1,4-butanediol-initiated poly(ϵ-caprolactone), Fig. 10 depicts the carbonyl carbon region from 165–180 ppm. As expected, the large main-chain resonance is accompanied by a smaller resonance at 173.5 ppm due to the carbonyl carbon of the terminal repeat units. However, there is no unique carbonyl resonance corresponding to carbonyl carbons adjacent to initiator molecules. Unlike those of the ethylene glycol-initiated systems, the two additional methylene units in 1,4-butanediol cause the adjacent carbonyl carbons to resemble main-chain carbonyl carbons.

The ϵ-carbon region from 60–65 ppm is depicted in Fig. 11 for the 1,4-butanediol-initiated polymer. In addition to the large main-chain resonance, the resonance at 63.5 ppm was assigned to the 1 and 4 carbons of the 1,4-butanediol initiator residue, and the resonance at 62.1 ppm corresponds to ϵ-carbons bonded directly to the hydroxyl end group. The 2 and 3 carbons of the initiator could not be

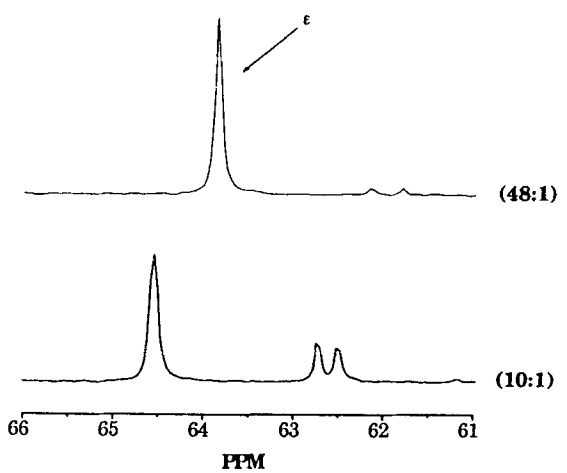


FIG. 9. Decgate ^{13}C-NMR spectra of the ϵ-methylene region of ethylene glycol-initiated poly(ϵ-caprolactone).

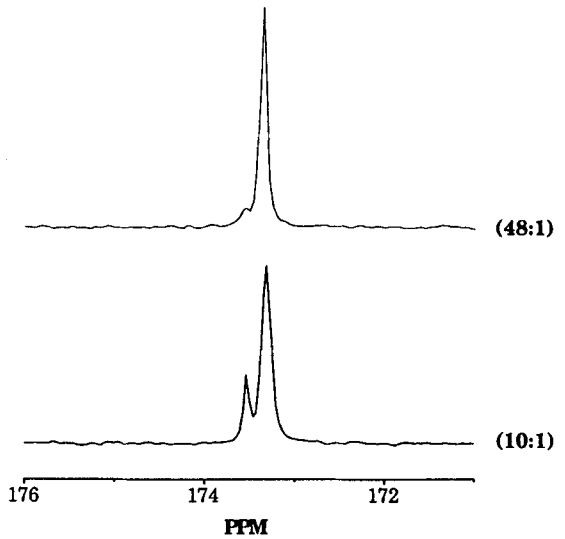


FIG. 10. Decgate ^{13}C-NMR spectra of the carbonyl region of the butanediol-initiated poly(ϵ-caprolactone).

observed, since they were apparently buried under the main-chain carbon resonances.

CONCLUSIONS

Gated decoupling (decgate) ^{13}C-NMR spectrometry was successfully employed to elucidate end-group signal assignments for poly(ϵ-caprolactone) oligomers initi-

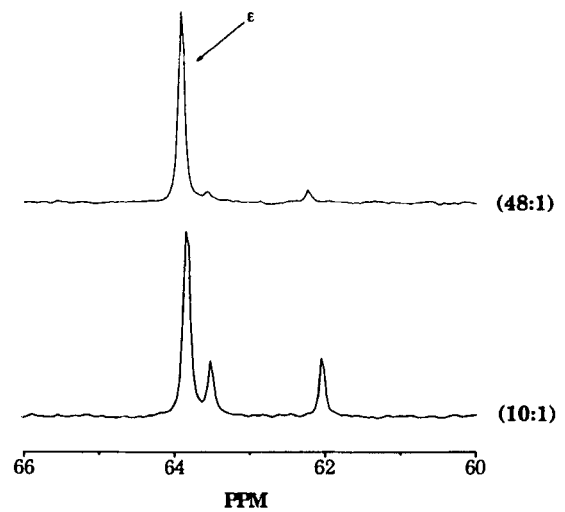


FIG. 11. Decgate ^{13}C-NMR spectra of the ϵ-methylene region of butanediol-initiated poly(ϵ-caprolactone).

ated with water, ethylene glycol, and 1,4-butanediol. The quantitative nature of the decgate spectra allowed carbons within the ultimate repeat unit to be readily associated with their main-chain counterparts, thereby facilitating identification. For all of the polymers, there was no evidence of inclusion into the polymer structure of fragments of the stannous octoate initiator.

These three initiators were chosen to obtain the simplest ^{13}C-NMR spectra. Water was of particular interest as an initiator since it produces a linear poly(ϵ-caprolactone) carrying one hydroxyl and one carboxylic acid end group. Carbons within the terminal repeat unit at either end of the chain are thus subjected to strong chemical shifts compared to carbons of interior repeat units. The terminal carboxylic acid group yielded a unique carbonyl carbon and caused a chemical shift in the adjacent α-, β-, and γ-carbons. The presence of the terminal hydroxyl group afforded unique chemical shifts for the ϵ-, δ-, γ-, α-, and carbonyl carbons, but not the β-carbon of the ultimate repeat unit. The strong chemical shift imparted to the ultimate δ-carbon, combined with the quantitative nature of the decgate spectrum, was specifically used to confirm the assignments of the main-chain δ- and γ-carbons of the internal poly(ϵ-caprolactone) repeat units. The fact that the hydroxyl group caused shifts in the ultimate carbonyl and α-carbons, but not the β-carbon, provided strong circumstantial evidence for the presence of a hydrogen-bonded cyclic structure at the end of the chain, at least in chloroform solution.

The diol initiators were shown to produce a linear PC chain containing the initiator residue and two terminal hydroxyl groups.

ACKNOWLEDGMENTS

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REFERENCES

[1] M. Chasin and R. Langer, *Biodegradable Polymers as Drug Delivery Systems*, Dekker, New York, 1990.
[2] T. G. Park, S. Cohen, and R. Langer, *Macromolecules, 25*, 116 (1992).
[3] J. Kopecek, *Biomaterials, 5*, 19 (1984).
[4] C. C. Chu, *J. Biomed. Mat. Res., 15*, 795 (1981).
[5] S. Vainionpaa, P. Rokkanen, and P. Tormala, *Prog. Polym. Sci., 14*, 670 (1989).
[6] J. P. Vacanti, M. A. Morse, W. M. Saltzman, A. J. Domb, S. Perez-Atayde, and R. Langer, *J. Pediatr. Surg., 23*, 3 (1988).
[7] S. Shieh, M. C. Zimmerman, and J. R. Parsons, *J. Biomed. Mater. Res., 24*, 789 (1990).
[8] H. R. Kricheldorf, T. Mang, and J. M. Jonté, *Macromolecules, 17*, 2173 (1984).
[9] H. R. Kricheldorf and I. Kreiser, *J. Macromol. Sci.—Chem., A24*(11), 1345 (1987).

[10] M. Bero, J. Kasperczyk, and Z. J. Jedlinski, *Makromol. Chem., 191*, 2287 (1990).
[11] J. Kasperczyk and M. Bero, *Ibid., 192*, 1777 (1991).
[12] R. F. Storey, K. R. Herring, and D. C. Hoffman, *J. Polym. Sci., 29*, 1759 (1991).
[13] R. F. Storey and J. S. Wiggins, *Polym. Compos., 14*, 17 (1993).
[14] R. F. Storey and T. P. Hickey, *J. Polym. Sci., 31*, 1825 (1993).
[15] A. Duda, *Macromolecules, 27*, 576 (1994).
[16] H. R. Kricheldorf and M.-V. Sumbél, *Makromol. Chem., 189*, 317 (1988).

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