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RANDOM COPOLYMERS OF 1,5-DIOXEPAN-2-ONE

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Key Words: DXO, ε–Caprolactone, δ-Valerolactone, L-lactide, Random Copolymerization, Reactivity Ratios)

ABSTRACT

Copolymers of 1,5-dioxepan-2-one (DXO) and ε-caprolactone (ε-CL), δ-valerolactone (δ-VL) or L-lactide (LLA) have been synthesized and characterized. High molecular weight copolymers were obtained using stannous-2-ethyl hexanoate as catalyst in bulk. Reactivity ratios for the copolymerization of DXO and δ-VL were determined at 110°C as r_{VL}=0.5 and r_{DXO}=2.3. At high conversion, depolymerization of δ-VL occurred, resulting in lower molecular weight and variations in the copolymer composition.

Physical properties, such as crystallinity and melting temperature of the DXO-copolymers proved to be strongly dependent on the choice of comonomer and on the molar composition of the copolymers. DXO appears to be incorporated into the poly-ε-caprolactone (PCL) crystals and to some extent into the poly-δ-valerolactone (PVL) crystals, resulting in a more gradual decrease in crystallinity with increasing amount of DXO.

INTRODUCTION

Polylactones, polylactides and copolymers based on them, have attracted much interest as biodegradable materials for various medical and pharmaceutical

applications, such as surgical sutures [1-2], orthopaedic materials [3], burn-covering materials [4] and in drug delivery systems [5].

Carothers *et al*. were the first to systematically explore the ring-opening polymerization of various lactones [6]. Since then much work has been done in this research area, not at least with copolymers of different compositions. Many studies have concentrated on polymers with ε-caprolactone (ε-CL), glycolide or lactide as at least one of the components.

Poly-ε-caprolactone (PCL) is a semicrystalline polymer (w_c=40-50%, T_m=63°C, T_g=-60°C), which crystallizes readily and cannot be quenched to a glass [7]. The crystalline structure of PCL has been well defined [8-9] and the mechanism of degradation has also been thoroughly investigated [10-11]. Due to its biocompatibility, its low glass transition temperature and its high permeability, PCL is one of the most frequently used compounds in biodegradable drug delivery systems [12-13].

A number of reports [14-15] have been presented about the use of the 6-membered ring, δ-valerolactone (δ-VL) in biomedical applications, particularly as a component of copolymers. The homopolymer, poly-δ-valerolactone (PVL), has physical properties similar to those of PCL (T_m=59°C, T_g=-67°C) [16], but the crystalline structure differs slightly [16-17].

Poly(lactic acid) (PLA) is one of the materials most frequently used in biomedical applications and there are several commercial products available in which PLA is a major component. Presence of the two stereocenters in dilactide (3,6-dimethyl-1,4-dioxane-2,5-dione) gives rise to four different dilactide-monomers, L-lactide, D-lactide, meso lactide and racemic mixture of lactide called D,L-lactide, which give rise to polymers with different properties. The monomer used in this work is L-lactide which gives a semicrystalline polymer (T_m=174°C, T_g=+60°C) [18]. The crystal structure of PLLA is pseudo-orthorhombic and the molecular conformation is a 10_3 helix [19].

The above-mentioned polymers are all semicrystalline, resulting in a heterogeneous degradation pattern, i.e. the amorphous regions tend to degrade first. This is usually a disadvantage as degradation is not linearly dependent on weight loss, so that quite often a severe loss in strength is observed with little loss in weight. It is therefore of great interest to be able to control extent of the crystallinity. Hence, the incorporation into polylactones and polylactides of a comonomer conferring greater flexibility and inhibiting crystallization could be a suitable way to modify the crystallinity and other physical properties, such as melting point and mechanical characteristics.

The seven-membered ether lactone, 1,5-dioxepan-2-one (DXO), might be suitable as such a monomer. DXO was first mentioned in the literature in 1960 [20-21], but more recently, we have found an improved method of synthesis [22]. Polymerizing DXO gives an amorphous polyetherester, with a T_g around -36°C [23]. However, the PDXO homopolymer has insufficient mechanical strength and must be crosslinked or copolymerized. We have reported studies of PDXO networks and of a number of copolymers [24-28].

Copolymerizing DXO with a semicrystalline lactone or lactide decreases the crystallinity of the resulting polymer. When copolymerizing DXO and ε-CL we found that the amorphous DXO-containing chain segments were to some extent included in the PCL-crystals [28]. This resulted in a more gradual decrease of crystallinity with increasing incorporation of DXO than if the crystals had been excluded any DXO-residues. Since there is a great similarity between the two monomers DXO and ε-CL, see Figure 1, this inclusion phenomenon is understandable.

The purpose of this study is to show the effect introduction of DXO-units has on degradable polylactones and polylactides. By varying the molecular structure of the comonomer this effect should be more or less pronounced. The introduction of DXO-units could be a suitable tool to control various physical properties, such as crystallinity and melting behavior, for polylactones and polylactides. Other aspects, such as reactivity ratios and depolymerization, will also be discussed in this paper. The materials we have investigated are copolymers of ε-caprolactone and DXO, δ-valerolactone and DXO and L-lactide and DXO; respectively denoted P°CL-co-DXO), P(VL-co-DXO) and P(LLA-co-DXO).

EXPERIMENTAL

Materials

ε-caprolactone and δ-valerolactone were obtained commercially (Aldrich) and purified by vacuum distillation over calcium hydride (CAH2). L-lactide was also purchased (Boehringer) and recrystallized twice from dry toluene before use. Stannous-2-ethylhexanoate (Sn(oct)2) (Aldrich) was used as received.

1,5-dioxepan-2-one (DXO) was synthesized by Baeyer-Villiger oxidation of tetrahydro-4H-pyran-2-one (Fluka) as described in previous work [22]. Before polymerization, the monomer was distilled under reduced pressure (0.1 mbar) and recrystallized twice from anhydrous diethyl ether.

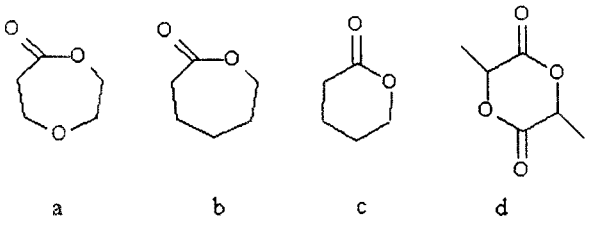

FIGURE 1. (a) 1,5-dioxepan-2-one, (b) ε-caprolactone, (c) δ-valerolactone, (d) lactide.

Polymerization Procedure

The purified DXO and stannous-2-ethylhexanoate and in some cases L-lactide were added to the polymerization flask in a glovebox under an inert atmosphere (Ar). The flask was equipped with a magnetic stirrer and sealed with a rubber septum. ε-caprolactone or δ-valerolactone were added through a syringe. The monomer/catalyst ratio was approximately 600 in all experiments. The polymerization flask was then immersed in a thermostated oil bath (110-120°C). After polymerization times of 20-24 hours, the product was dissolved in $CHCl_3$ and precipitated with cold petroleum ether. The polymer was isolated by filtration and dried under vacuum at room temperature. The copolymers were named CD 0-100 copolymers for copolymers made from ε-CL and DXO, VD 0-100 copolymers for those made from δ-VL and DXO, and LD 0-100 copolymers for those made from LLA and DXO; the digits signify the mole ratios of crystallizable comonomer in the initial reaction mixture.

Measurements

The ^{1}H-NMR spectra were obtained with a Bruker AC-250 or AC 400 FT-NMR spectrometer, using the deuterochloroform ($CDCl_3$) as the internal standard. Samples were dissolved in deuterochloroform in sample tubes, 5 mm in diameter.

SEC-measurements were made at 30°C with five μ-Styragel columns (100, 500, 10^3, 10^4, 10^5 Å). THF was used as solvent, with a flow rate of 1.0 ml/min. A Waters model 510 chromatography system was used with a differential refractometer (Waters 410) as detector. For data recording and calculations, a Copam PC-501 Turbo unit was used. Since PLLA homopolymer is not soluble in THF, the SEC-measurements for PLLA and P(LLA-co-DXO) were carried out at 25°C with $CHCl_3$ as solvent. Five Ultrastyragel columns (10^5, 10^4, 10^3, 500 and

100 Å pore sizes) and a Waters 6000A pump and RI 401-refractive index detector were used. The flow rate was 1.0 ml/min. Both SEC-systems were calibrated with polystyrene standards with narrow molecular weight distribution (MWD=1.06).

X-ray diffraction (XRD) measurements were carried out on a Philips generator PW 1830, nickel filtered CuK_{α}-radiation (λ=1.542 Å), Warhus camera, and an Image Analysis System. The diffractograms were converted from light to intensity and corrections were made according to the procedure proposed by Kakudo and Kasai [29]. Equation 1 was used to calculate a measure of the degree of crystallinity of the samples

$$w_c = \frac{\Sigma I_c^{hkl}}{I_a + \Sigma I_c^{hkl}} \tag{1}$$

where I_a and I_c^{hkl} are the areas under the amorphous halo and the hkl-reflections, respectively.

Differential Scanning Calorimetry (DSC) measurements of melting endotherms were made on a Perkin-Elmer DSC-7 calorimeter calibrated using an indium pellet (T_m=156.6°C, ΔH_f=28.46 Jg^{-1}). The heating and cooling rates were 10°C min^{-1}. The heats of fusion obtained by DSC originate from the second heating and the degree of crystallinity is evaluated according to the expression proposed by Gray [30]:

$$w_c = \frac{\Delta H_f}{\left[\Delta H^0_{T_m^0} - \int_{T_1}^{T_m^0} (c_{pa} - c_{pc})dT\right]} \tag{2}$$

where ΔHf is the value of the measured heat of fusion, c_{pa} and c_{pc} are the specific heats of amorphous and 100% crystalline phases, respectively, T_m^0 is the equilibrium melting temperature and T_1 is an arbitrary temperature below the melting range. (c_{pa} - c_{pc}) is approximated with a third degree polynomial using the additional scheme of the constituents within the copolymers [31].

RESULTS AND DISCUSSION

Table 1 gives the mole ratio in the monomer feed, the resulting polymer composition and the molecular weights. The largest deviations from the expected

TABLE 1. Results of the Copolymerization of ε-CL, δ-VL or LLA with DXO in Bulk, Catalyzed by Stannous 2-Ethylhexanoate at 110°C

Sample	Mole ratio in feed	Copolym. comp.	<Mw> (g mol^{-1})	<Mn> (g mol^{-1})	H
i)	CL:DXO	P(CL-DXO)			
CD0	0:100	0:100	156 000	112 000	1.39
CD20	20:80	22:78	161 000	98 000	1.65
CD50	50:50	50:50	169 000	100 000	1.69
CD60	60:40	59:41	134 000	84 000	1.60
CD70	70:30	71:29	143 000	86 000	1.66
CD80	80:20	82:18	159 000	100 000	1.60
CD90	90:10	92:8	155 000	90 000	1.73
CD100	100:0	100:0	163 000	92 000	1.77
ii)	VL:DXO	P(VL:DXO)			
VD0	0:100	0:100	134 000	74 000	1.80
VD20	20:80	14:86	136 000	66 000	2.06
VD50	50:50	43:57	78 000	46 000	1.74
VD60	60:40	56:44	87 000	49 000	1.79
VD70	70:30	67:33	77 000	46 000	1.67
VD80	80:20	75:25	72 000	43 000	1.67
VD90	90:10	93:7	84 000	42 000	2.00
VD100	100:0	100:0	83 000	40 000	2.08
iii)	LLA:DXO	P(LLA:DXO)			
LD70	70:30	72:28	225 000	67 000	3.36
LD85	85:15	87:13	176 000	65 000	2.68
LD100	100:0	100:0	188 000	58 000	3.21

copolymer compositions were found with the VD copolymers. These copolymers were also the ones with the lowest molecular weight.

The reactivity ratio for copolymerization between CL and DXO were determined in earlier work as r_{CL}=0.6 and r_{DXO}=1.6 [28], and for copolymerization between LLA and DXO as r_{LLA}=10 and r_{DXO}=0.1 [24].

A large difference in reactivity ratio results in the fact that initially formed polymer chains are richer in more reactive species and form longer sequences than would be the case for a totally random copolymer. As the polymerization proceeds, the more reactive species is depleted and the less reactive species becomes the more abundant and is consequently incorporated. The resulting copolymer will have a more or less blocky structure, and this would be the case for the LD copolymers.

The tin catalyst used has, however, been shown to cause transesterification reactions and even racemization, especially at elevated temperatures or long reaction times [32-33], which will randomize the structure to some extent. Nevertheless, ^{13}C-NMR analysis in a previous study [25], indicated a blocky structure, i.e. tapered copolymers, despite transesterification reactions. The reactivity ratios for the CD copolymerization are close to unity, resulting in a random structure. Transesterification reactions will randomize the structure even more. The reactivity ratios for the copolymerization between δ-VL and DXO were determined in this work using the method of Kelen and Tudös [34], which allows quite high conversions. The composition of the reaction mixture was determined by ^1H-NMR. The reactivity ratios are calculated from a plot of Equation 3, see Figure 2.

$$\eta = (r_1 + \frac{r_2}{\alpha})\xi - \frac{r_2}{\alpha} \tag{3}$$

r_{VL} is taken from the intercept at ξ=1, and $-r_{DXO}/\alpha$ from the intercept at ξ=0, where α is a constant dependent on conversion. The plot gives the values r_{VL}=0.5 and r_{DXO}=2.3.

These results imply that there is a somewhat larger difference in reactivity in the VD-copolymer system than in the CD-system. For both systems it is the DXO-monomer that is consumed the fastest. However, considering the relatively small differences in reactivity and the fact that the catalyst $Sn(oct)_2$ causes transesterification reactions, the VD-copolymer system will, as for the CD, system-exhibit a somewhat randomized structure.

The definition of the reactivity ratio is the ratio of self-propagation and cross-propagation, see Equation 4.

$$r_1 = k_{11}/k_{12} \qquad r_2 = k_{22}/k_{21} \tag{4}$$

In the copolymerization of δ-VL (as monomer 1) and DXO (as monomer 2), the four different chain growth steps are shown schematically in Figure 3.

Substituting the experimentally determined reactivity ratios into Equation 4, and rearranging gives the relationships shown in Equation 5.

$$k_{12} = 2k_{11} \; ; \; k_{22} = 2.3k_{21} \tag{5}$$

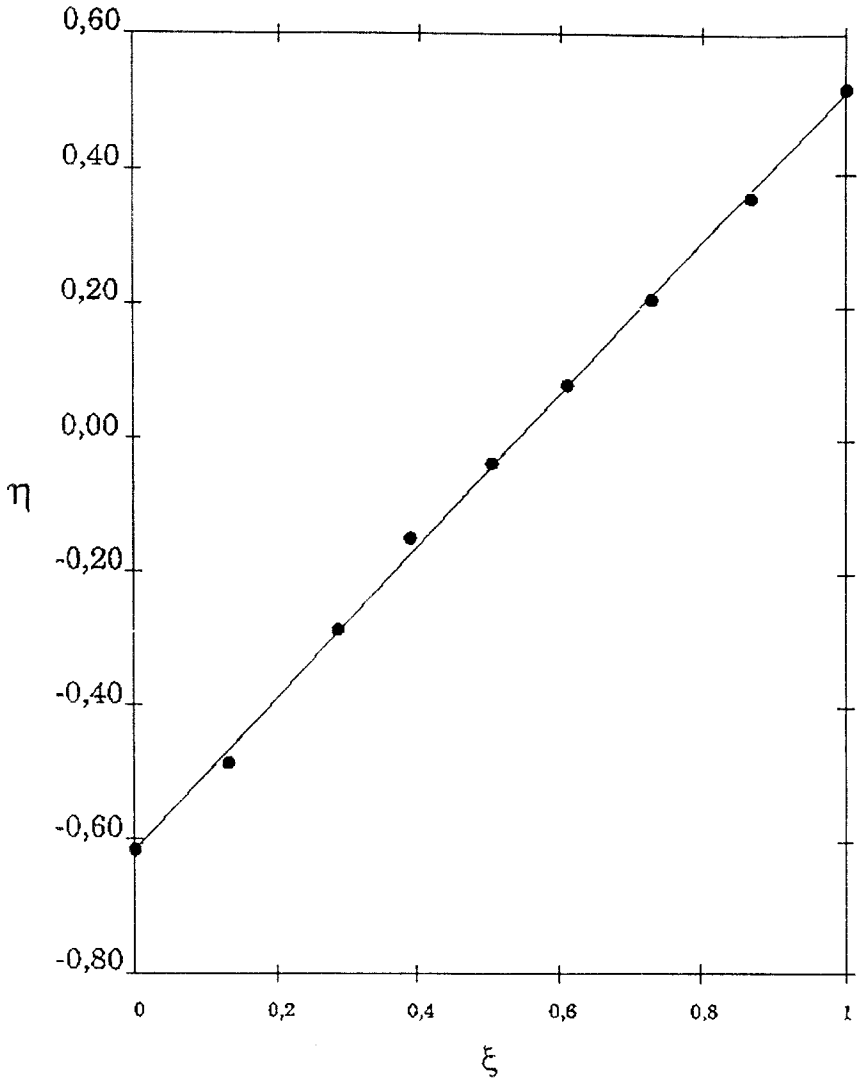

FIGURE 2. Reactivity ratio evaluation of the VD copolymer system r_{CL} = intercept at $\xi = 1$, $- r_{DXO}/\alpha$ = intercept at $\xi = 0$, where α is a constant dependent on the conversion.

Thus, independent of the end group, on the basis of this model, the growing polymer chain will react twice as fast with DXO as with δ-valerolactone. The same calculations for the CD-copolymer system (ε-CL as monomer 1 and DXO as monomer 2) gives Equation 6.

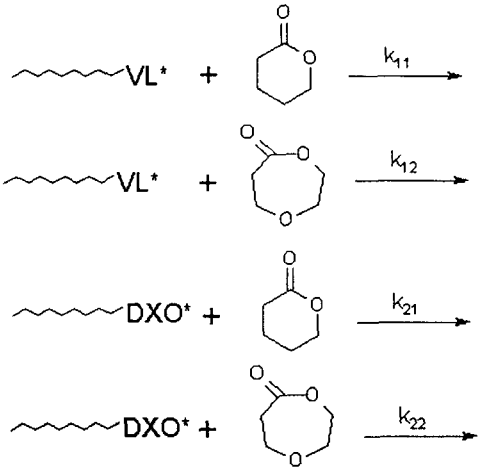

FIGURE 3. The four propagation reactions in the VD copolymer system.

$$k_{12} \approx 1.67k_{11} \; ; \; k_{22} = 1.6k_{21} \tag{6}$$

In this copolymer system, DXO will react 1.6 times faster than ε-caprolactone. A possible explanation of the somewhat lower reactivity for δ-valerolactone could be that this six-membered lactone is essentially strainless, compared with ε-CL, which is moderately strained [35].

A complicating factor with the copolymerization equations is any depolymerization that may occur, since one of the assumptions in the copolymer equation is that all propagation reactions are irreversible. In this respect, the polymerizations of δ-valerolactone and ε-caprolactone are quite different. The homopolymerization of δ-valerolactone has, in some cases, been found to form only low-molecular weight polymer with substantial amounts of monomer remaining in equilibrium with polymer [36]. Under the same conditions, the homopolymerization of ε-caprolactone produced high-molecular-weight polymer [37]. Copolymerization of δ-valerolactone with a monomer, less sensitive to depolymerization, should eliminate some of the problems, since this other comonomer would serve as a stable cap. Nevertheless, depropagation of δ-valerolactone has been found when copolymerizing δ-valerolactone and ε-caprolactone [38].

Depolymerization in the VD copolymer system would also explain the lower molecular weight and the deviations in copolymer composition from

predictions, as shown in Table 1. To investigate any possible depolymerization, conversion studies were performed. Thus, a series of polymerizations with an initial monomer composition of VL-DXO 50:50 were performed. After the desired polymerization time, the samples were precipitated to calculate the yield and subsequently analyzed by ^{1}H-NMR to determine the copolymer composition. The theoretically predicted copolymer compositions were calculated using the integrated form of the copolymer equation [39], and simple mass-balance considerations [40], see Equations 7-8.

$$x = 1 - \left[\left(\frac{f_1}{f_1^0} \right)^{\alpha} \left(\frac{f_2}{f_2^0} \right)^{\beta} \left(\frac{f_1^0 - \delta}{f_1 - \delta} \right)^{\gamma} \right] \tag{7}$$

where χ is the conversion, f_1 the instantaneous monomer composition and f_1^0 the initial monomer composition. The constants α, β, γ, δ have the values: $\alpha = r_2/(1-r_2)$; $\beta = r_1/(1-r_1)$; $\gamma = (1-r_1r_2)/(1-r_1)(1-r_2)$; and $\delta = (1-r_2)/(2-r_1-r_2)$.

$$\beta = r_1/(1-r_1);\ \gamma = (1-r_1r_2)/(1-r_1)(1-r_2);\ \text{and}\ \delta = (1-r_2)/(2-r_1-r_2). \tag{8}$$

$$\hat{F} = \frac{f_1^0 - f_1(1-x)}{x}$$

$\hat{F}$ is the cumulative copolymer composition.

The results are shown in Table 2.

The feed composition VL-DXO 50:50 initially produces copolymer with a 0.32:0.68 composition, and the δ-VL content then increases with time broadly as the theory predicts. However, this increase is less than theoretically predicted and after 16 hours reaction time (i.e. at high conversion) relatively large deviations between the actual and theoretically predicted compositions can be seen. At prolonged reaction time and at even higher yields, the δ-VL content in the copolymer decreases. These data suggest that at long reaction times and at high conversion, depolymerization of δ−VL occurs. This depolymerization is unexpected since the copolymerizations are carried out below the estimated ceiling temperature (180°C) of PVL [41].

The samples from the conversion experiment were also analyzed by SEC to obtain the molecular weight of the copolymer and the results are shown in Figure 4.

TABLE 2. Effect of Conversion on Copolymer Composition in the Polymerization of δ-VL and DXO

Time (h)	Conversion (%)	Copolymer composition	Theoretical copolymer composition
0.5	9.1	0.319 : 0.681	0.320 : 0.680
1	18.9	0.326 : 0.674	0.330 : 0.670
2	44.8	0.368 : 0.632	0.360 : 0.640
3	60.9	0.379 : 0.621	0.386 : 0.614
5	83.9	0.436 : 0.564	0.438 : 0.562
16	95.6	0.467 : 0.533	0.480 : 0.520
25	96.0	0.434 : 0.566	0.481 : 0.519

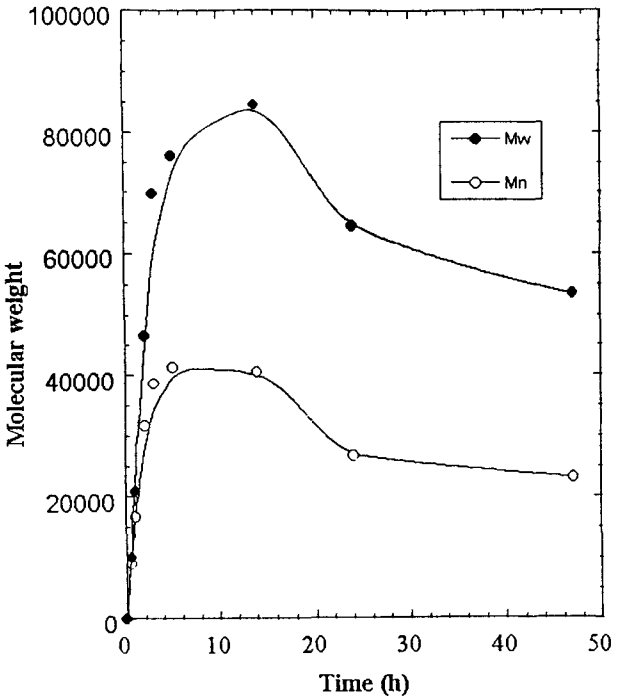

FIGURE 4. Molecular weight dependence on polymerization time for VD-copolymers. Filled circles: M_w. Open circles: M_n.

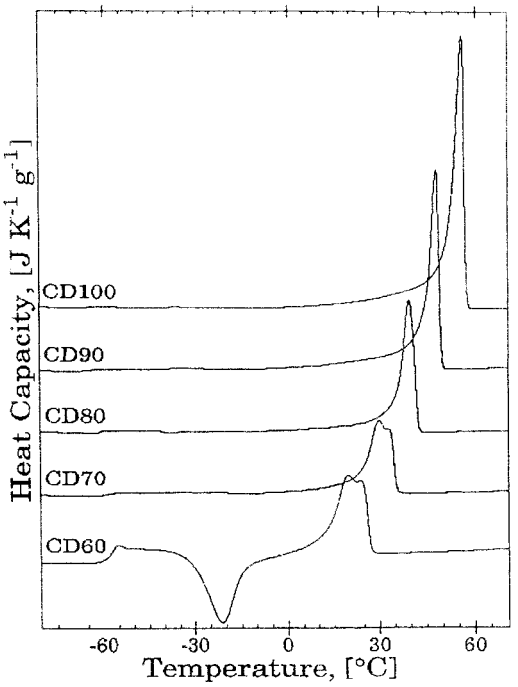

FIGURE 5. DSC-traces for the CD copolymer system

After 16 hours reaction time, there is a decrease in molecular weight which also gives a strong indication that depolymerization occurs.

The CD-copolymers were crystallizable when the amount of DXO did not exceed 40 percent, otherwise they formed an amorphous, sticky solid which could not be meltpressed into a film. The VD copolymers showed a negligible crystallinity when the DXO-ratio in the monomer feed was larger than 25%, while all LD copolymers exhibited crystallinity to some extent. Henceforth, only the crystallizable copolymers will be discussed.

Figure 5 shows thermograms from the crystallizable copolymers. Increased content of DXO lowered the melting temperature as well as the enthalpies. Double peak endotherms were found for copolymers CD70 and CD60 which indicated a distribution of crystal sizes or the presence of two different morphologies. The DSC trace for the CD60 copolymer exhibited an exotherm prior to the endotherm, indicating kinetically inhibited crystallization.

The endotherms of the VD copolymers showed similar trends in melting temperatures, enthalpies and double peaks as the DXO content was increased, as did

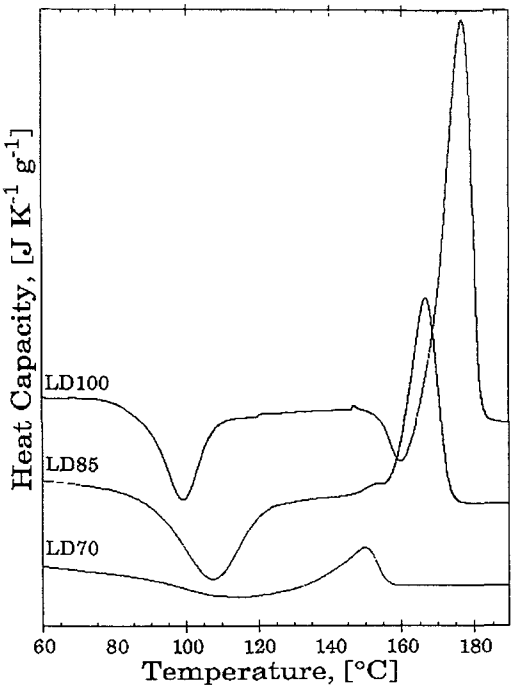

FIGURE 6. DSC-traces for the LD-copolymer system

the CD copolymers. However, the enthalpies and melting temperatures were generally lower for the VD copolymers compared with the CD copolymers. For example, the enthalpy of the VD 70 copolymer displayed a heat of fusion of 1.63 J g^{-1} and no detectable crystallinity as determined by XRD.

Figure 6 shows the DSC trace for the LD copolymers. All polymers in this system showed exotherms prior to the melting endotherm indicating polymers with inhibited crystallization ability. After annealing at 100°C for 24 hours, all exotherms disappeared, thus supporting this idea. The decrease in enthalpies with increased DXO content occurred faster for LD than for CD and VD copolymers.

We have reported earlier that in copolymers of CL and DXO approximately 40% of the DXO units are inserted in the PCL crystals [28]. This was determined using the melting point depression and the equation of Baur [42]. Goulet *et al*. have stated that this Baur-equation, despite the fact that it is derived from an exclusion model, can be used to estimate approximately the amount of insertion, if the two repeat units are similar [43], as are CL and DXO. Comparison of the molecular structures of VL and DXO, suggest that some degree of inclusion of DXO in the

TABLE 3. Morphological Properties of P(CL-co-DXO), P(VL-co-DXO) and P(LLA-co-DO)

Sample	% DXO in copolymer	w_C (DSC) [%]	w_C (XRD) [%]	T_g (DSC) [°C]	T_m (DSC) [°C]
CD50	50	0.4	-	-56.8	27.8
CD60	41	33	27	-57.8	27.2
CD70	29	38	34	-55.5	36.0
CD80	18	40	34	-61.0	42.8
CD90	8	48	38	-65.6	50.5
CD100	0	53	41	-65.9	57.6
VD70	33	1.0	-	-56.7	28.0
VD80	25	29	35	-56.1	37.7
VD90	7	35	46	-59.9	46.0
VD100	0	48	52	-63.4	57.5
LD70	28	11	30	23.1	154.1
LD85	13	46	38	41.1	170.8
LD100	0	66	50	58.5	183.8

PVL crystals would be possible. Both the homopolymer of PCL and the homopolymer of PVL attain a planar zig-zag conformation with a sequence length of about 17.0 Å and 15.7 Å, respectively [8-9]. The DXO sequence will, in planar zig-zag, measure about 17.0 Å, which is close enough for an inclusion. The PLLA-homopolymer on the other hand will attain a helix conformation (3_1 or 10_3). It has been shown that even a small amount of D-LA units incorporated in the PLLA crystals will disturb the crystallinity [44]. DXO units incorporated in the PLLA crystals would disturb the crystallinity even more because of the ether bond. Therefore, it is more likely that the DXO-units are excluded from the PLLA-crystals. Total exclusion has also been found for copolymers of CL and LLA [45].

The morphological properties obtained by DSC and XRD of the three different kinds of copolymers are compiled in Table 3.

Figure 7 shows the crystallinity of the CD- and the VD copolymers. A common feature is the slightly sloped plateau in the curves obtained from the DSC data. The plateau was found between 5 and 40% DXO in the CD copolymer system and between 5 and 25% DXO in the VD copolymer system. This is interpreted as a result of DXO inclusion in the crystals. After the plateau, there was a rapid drop in

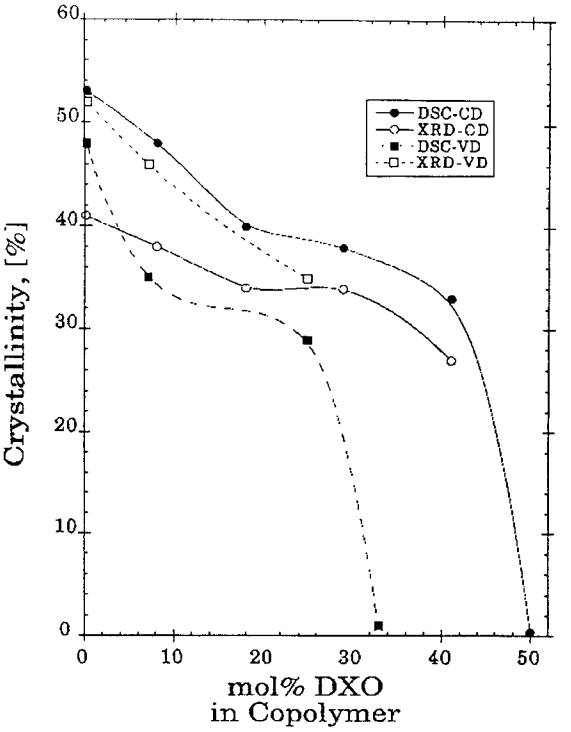

FIGURE 7. Measured crystallinity for the CD- and VD-copolymers using DSC or XRD.

Filled circles: Crystallinity for CD-copolymers obtained from DSC.
Open circles: Crystallinity for CD-copolymers obtained from XRD.
Filled squares: Crystallinity for VD-copolymers obtained from DSC.
Open squares: Crystallinity for VD-copolymers obtained from XRD.

the crystallinity, such that the crystallinity was not detectable at approximately 50% DXO in the CD copolymers and at approximately 33% DXO in the VD copolymers. The later onset of the CD copolymers was explained by the higher likelihood of inclusion of the DXO monomer in PCL when compared to PVL. The same distinct feature of a plateau could also be seen with the values of crystallinity obtained from the X-ray measurements for the CD copolymers, while the plateau was not as pronounced for the VD copolymers. The reduction of crystallinity upon insertion of DXO in the LD copolymer system was faster than that for the two other systems and no plateau-region was observed.

CONCLUSION

High molecular weight, random copolymers can readily be produced from bulk polymerization of DXO with various lactones and lactides, such as ε-CL, δ-VL and LLA, using $Sn(oct)_2$ as a catalyst. The reactivity ratios in the copolymerization between DXO and δ-VL were determined at 110°C as $r_{VL}= 0.5$ and $r_{DXO}= 2.3$. Thus, the growing chain end reacts twice as fast with a DXO monomer compared with a δ-VL monomer. In the copolymerization of DXO and ε-CL there was a somewhat smaller difference in reactivity, though DXO is still consumed most rapidly. However, due to transesterification reactions, both these copolymers exhibit a randomized structure. At high conversion in the copolymerization of DXO and δ-VL, depolymerization of the latter occurs, which results in lower molecular weight and deviations in the copolymer composition. For all three kinds of copolymers investigated in this paper, P(CL-co-DXO), P(VL-co-DXO) and P(LLA-co-DXO), both the crystallinity and melting point decreased with increasing DXO content. For (P(CL-co-DXO) and P(VL-co-DXO) the crystallinity exhibited a slightly sloped plateau. These results, together with a comparison of the sequence lengths, support the proposed inclusion of the amorphous DXO monomer in the crystalline lattice of PCL and PVL. This has been shown earlier for P(CL-co-DXO), using the melting point depression. P(LLA-co-DXO) showed no such behavior, and total exclusion of the DXO units was claimed. With a sufficient amount of DXO, the crystallization rate is diminished. The copolymer with 40% DXO and 60% ε-CL, exhibited an exotherm prior to the endotherm in the DSC-trace, indicating recrystallization.

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