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Random Polyester Transesterification: Prediction of Molecular Weight and MW Distribution

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ABSTRACT: A statistical model has been developed for the prediction of molecular weight and molecular weight distribution in transesterification reactions of diols onto polyesters (ideally polycondensated with a polydispersity of 2). The model was checked out on a transesterification reaction of PEG or diethylene glycol on PLLA, which is a simple and noncatalytic route for obtaining blends of low-molecular-weight block copolymers PEG−PLLA and low-molecular-weight PLLA, which have biomedical interest. From this mathematical model, it is possible to predict the change in molecular weight and molecular weight distribution as a function of the different experimental variables. Reactions were characterized by ^{1}H NMR and GPC.

Introduction

The occurrence of transesterification and transamidation reactions in polyesters and polyamides has been known for many years.[1] Transesterification on polyesters is a useful reaction for blending noncompatible polyesters[2,3] and is also responsible for some chain extension effects.[4,5] This reaction commonly occurs in the molten state, which produces first block copolymers and finally random copolymers. On the other hand, it is a common side reaction undergone by polyesters[1,6] and is partially responsible for their degradation, especially in biodegradable poly(lactide) (PLA) derivatives.[5,7,8]

Transesterification of poly(ethylene glycol) (PEG) on poly(DL-lactic acid) (PDLA) has been described by Piskin et al.[9] as an interesting route for obtaining block copolymers PEG−PDLA. Poly(ether−ester) block copolymers of PLA and PEG are interesting materials because of their hydrophobic/hydrophilic block nature and their biocompatibility, and much work has been done in this field.[10−16] PEG is a water-soluble polymer which is accepted as a food or drug additive in most countries. PLA and copolymers of lactide and glycolide or ϵ-caprolactone have been investigated for application in implant materials such as medical sutures,[17] drug delivery systems,[17] and orthopedic devices.[18]

In this paper, we describe a simple model of transesterification of an oligomeric diol (PEG or diethylene glycol) onto a low-molecular-weight (LMW) polyester of biomedical interest: poly(L-lactic acid) (PLLA). LMW polymers and reactives were chosen such that it would be possible to analyze the final mixture of polymers and copolymers by ^{1}H NMR.

Experimental Section

Materials. L-Lactic acid (LLA), 90% aqueous solution, was purchased from Fluka. Poly(L-lactic acid) or Resomer (L104, $\bar{M}_w = 2000$ and polydispersity = 2) was supplied by Boehringer Ingelheim (Germany). Poly(ethylene glycol) 6000 (PEG 6000) ($\bar{M}_w/\bar{M}_n = 1.05$) was obtained from Merck and PEG 900 ($\bar{M}_w/\bar{M}_n = 1.05$) from Aldrich. Diethylene glycol was obtained from FEROSA (Spain).

Transesterification Reaction: Melt. The prepolymer PLLA was synthesized according to the procedures described by Fukuzaki et al.,[19] in the absence of a catalyst, at 200 °C, while a stream of nitrogen gas was passed through the polymerization mixture (~200 mL/min); the water formed during this reaction was removed by distillation. After a reaction time of 10−40 h, the appropriate amount of PEG 6000 as model diol was added, and the reaction was continued for 3−6 h.

Solution. Poly(L-lactic acid) used as starting material was a commercial Resomer L104. The transesterification reactions were carried out by using xylene as solvent in a closed flask at 150 °C (boiling point of xylene, 132 °C). Before closing the system, appropriate amounts of starting PLLA and diol (two reactions were carried out, with PEG 900 and diethylene glycol as model diols) were added into the flask under an oxygen-free N_2 atmosphere. At appropriate times, samples were taken by introducing a syringe through a septum tap.

Characterization. ^{1}H NMR spectroscopy was performed on a Bruker AC 250 or a Varian Gemini 200 spectrometer using $CDCl_3$ as a solvent. Sample concentrations were approximately 5% (w/v). To calculate the concentration of OH end groups in the PEG chains, trifluoroacetic anhydride was added to the solutions,[7] and the signal of the rapidly and quantitatively formed CH_2OCOCF_3 end groups was analyzed.

GPC measurements were performed by using $CHCl_3$ as the eluent. The GPC system consisted of a Waters 510 pump, a RI detector Waters 410 differential refractometer, and three columns of mStyragel of 10^4, 10^3, and 500 Å. The columns were calibrated with PMMA standards supplied by Waters Associates having a narrow molecular weight distribution.

Results and Discussion

Melt and solution reactions have been carried out. The melt reaction was achieved by polycondensating L-lactic acid from an aqueous solution at 200 °C and using a nitrogen flux of 200 mL/min. This reaction has previously been described[19] to give poly(L-lactic acid) with molecular weight ranging from 10^3 to 10^4. The degree of polymerization ($\bar{D}Pn$), which increases with reaction time to a standard value of approximately 100 after 20 h of polycondensation, was determined from the

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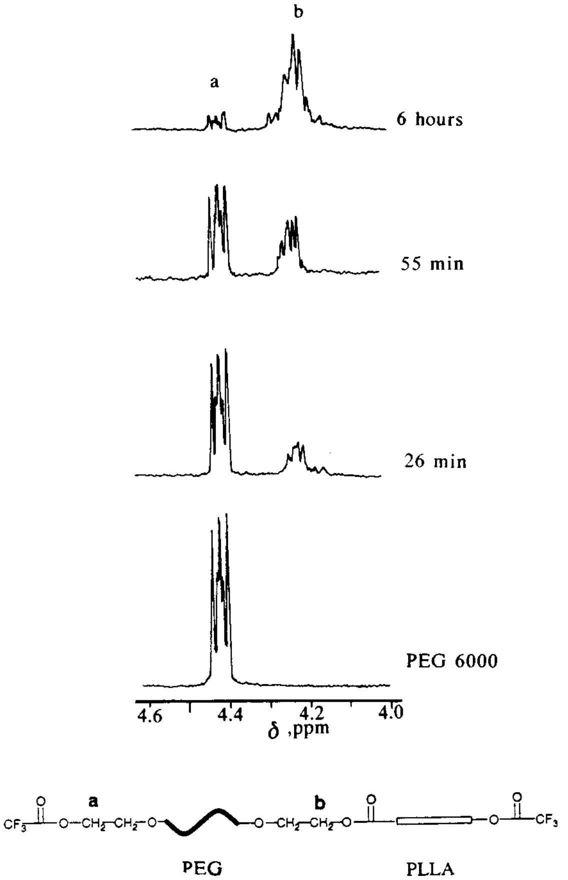


Figure 1. Methylene oxide signals of samples after various times of treatment in melt reactions.

integration ratio between the CH signal of the main chain (a, 5.1 ppm) and the CH of the terminal group (b, 4.3 ppm) in ^{1}H NMR spectra.

On the other hand, commercial PLLA of LMW (with an ideal polydispersity value of 2 for polycondensated material) was used in the solution reaction; xylene was chosen as solvent in order to reach temperature above 120 °C. In fact, the reaction was carried out at 150 °C in a closed flask, 18 °C above the boiling point of xylene at atmospheric pressure. The crude mixture of the different samples was analyzed by ^{1}H NMR as the melt reaction products.

Analysis of the copolymerization products was performed by ^{1}H NMR. The ^{1}H NMR spectra of the copolymers are quite similar to those reported by others for similar systems.[20,21] The signal of the terminal methylene protons of the PEG could be used to determine the conversion of the PEG hydroxyl end groups. However, the signal of the methylene protons of the free terminal unit overlaps with the signal of the PEG inner units of the main chain, but it can be shifted to δ 4.43 by derivatization to the trifluoroacetic ester formed. The CH_2 protons of the ethylene oxide unit linked directly to the PLLA blocks appear at δ 4.22. Figure 1 shows the methylene oxide signals of samples after various times of treatment in melt reactions.

Scheme 1 shows the proposed transesterification reaction. Using a difunctional PEG, it would be possible to find triblocks as well as diblocks in the final mixture after the transesterification reaction process. LMW PLLA will also be present. The diblocks/triblocks ratio depends on the conversion of the OH end groups of the PEG. At 100 % conversion, there will only be triblocks present, and, for instance, at 95% conversion, the mixture will contain about 90% triblocks and 10% diblocks (and 0.25% unreacted PEG). The melt reactions were carried out for 6 h, reaching a 90% conversion, whereas the solution reactions were carried out for 1 week in order to attain similar conversions, since the reaction temperature was much lower.

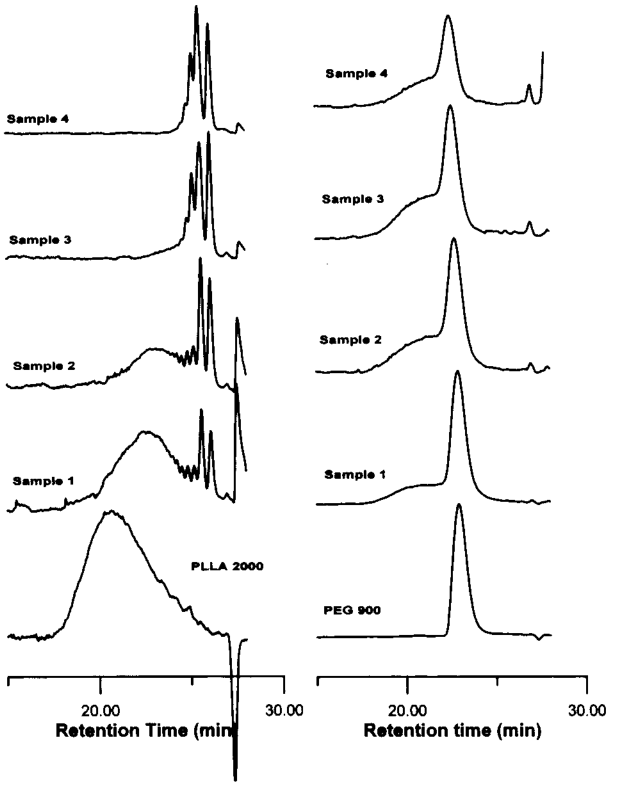
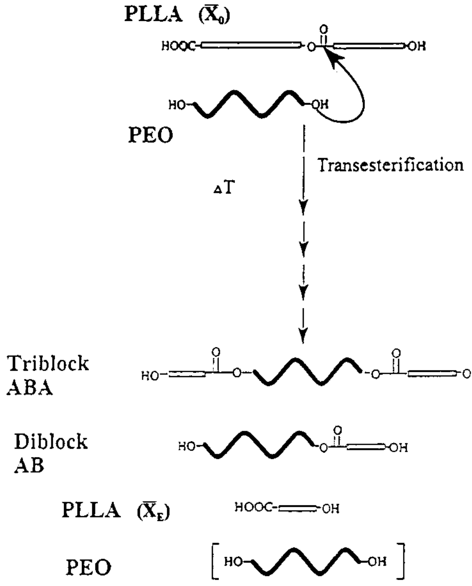


Figure 2. GPC traces of the solution reactions with diethylene glycol (left side) and PEG 900 (right side) as reactive diols.

Scheme 1. Possible Components of the Reaction Medium after the Thermal Treatment



GPC was used only as a qualitative method due to the inherent problems associated with the technique in the analysis of block copolymers and mixtures of LMW compounds.[22] The GPC traces shown in Figure 2 for the solution reactions confirm the transesterification reaction and show qualitatively the evolution of the reaction versus time. With increasing conversion (right side of the figure), a shoulder is observed in the PEG 900 peak at lower retention time, which can be associated with the di- and triblocks. Moreover, LMW species increase with the extension of the reaction, as can be clearly observed in the reaction with diethylene glycol (left-hand side). In this case, the number of reactive hydroxyl groups is much higher, and PLLA is degraded with time to very short oligomers. The different GPC peaks traces (very well resolved) should be assigned to di- and triblocks with 1−4 lactic units and to free lactic dimer and trimer species.

Mathematical Description

To simplify the mathematical description, the following treatment ignores the effects of the polycondensation and also ignores the transesterification produced by the OH end groups of the PLLA itself (assuming that the transesterification by OH-PEG is much faster than both processes). In an ideal step growth polymerization reaction, the classical treatment considers[23]

$$\begin{aligned} N_i^{\mathrm{p}} &= N_0 x^{i-1}(1-x)^2 \\ M_{\mathrm{n}} &= \frac{m}{1-x} \\ \bar{M}_{\mathrm{w}} &= m\frac{1+x}{1-x} \\ \frac{\bar{M}_{\mathrm{w}}}{M_{\mathrm{n}}} &= 1+x \end{aligned} \tag{1}$$

where N_i^{p} is the number of polymer molecules of i monomers, x is the conversion of lactic acid or the probability of addition of a monomer, N_0 is the number of monomers, and m is the molecular weight of the unit (the notation will be N_i^{p} for the polycondensated chains before transesterification and N_i^{t} after that). Under these assumptions, the polymerization degree, $\bar{\mathrm{D}}$Pn, $\bar{X}_0$, and the total number of polymer chains are

$$\bar{X}_0 = \frac{1}{1-x} \tag{2}$$

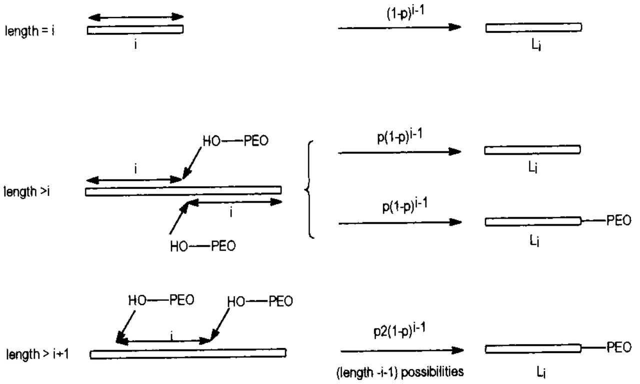
$$N_{\mathrm{PLLA\ chains}} = \sum N_i^{\mathrm{p}} = N_0(1-x) \tag{3}$$

Transesterification. According to the proposed synthetic scheme, and considering an equal reactivity of all the OH end groups of PEG, every transesterification randomly breaks the PLLA blocks or chains (linked already to a PEG chain or free). In this way, a PEG attack on a free PLLA leads to a free residual PLLA plus a linked PEG−PLLA, while the attack on a PLLA block in a copolymer leads to two new PLLA blocks linked to PEG chains (see Scheme 1). According to this, one original PLLA chain, after undergoing n transesterifications, would lead to one free PLLA chain plus n PLLA blocks in the copolymers.

The average number of OH end groups which are going to attack every original polycondensated PLLA chain will be called A_{OH}. From this, it is clear that

$$\bar{X}_{\mathrm{E}} = \frac{\bar{X}_0}{A_{\mathrm{OH}}+1} \tag{4}$$

Scheme 2



where $\bar{X}_0$ and $\bar{X}_{\mathrm{E}}$ are the $\bar{\mathrm{D}}$Pn of the original PLLA chains and the $\bar{\mathrm{D}}$Pn of the final (linked or free) PLLA blocks or chains, respectively ($\bar{X}_{\mathrm{E}} \le \bar{X}_0$).

Probabilistic Treatment. In a transesterification reaction of a difunctional PEG or an aliphatic diol on PLLA chains, the probability that an ester group undergoes a transesterification during the reaction is (with $N_{\mathrm{OH}} = 2N_{\mathrm{PEG}}$)

$$p = c\frac{N_{\mathrm{OH}}}{N_{\mathrm{es}}} = c\frac{2N_{\mathrm{PEG}}}{N_0 x} = 2\frac{cR}{x} \tag{5}$$

where N_{OH} is the number of total hydroxyl end groups of PEG, N_{es} is the total number of esters, c is the conversion of the OH-PEG end groups, and R is the molar feed ratio in terms of (moles of diol)/(moles of LLA units), and

$$N_{\mathrm{es}} = \sum_{i=1}^{\infty} [(i-1)N_i^{\mathrm{p}}] = (\text{using (1)})\ N_0 x$$

Scheme 2 shows the different ways to obtain PLLA blocks or chains of length i from the polycondensated PLLA chains. The first possibility to consider is an original chain with i units which does not undergo any transesterification. As the number of esters is $i - 1$, the probability of this process is $(1 - p)$ to the power of $i - 1$. The second case to analyze is a polycondensated PLLA with more than i units, that undergoes a transesterification on the i position, leading to a chain or block with i units. The probability of this process taking place is equal to the probability of the attack on this ester, multiplied by the probability that $i - 1$ esters do not undergo transesterification. Depending on the orientation of the ester group, this possibility will lead to a free chain or to a block. This is represented by the arrows in Scheme 2. Finally, if the original PLLA chain is longer than $i + 1$, then the possible i block is also included in the structure, and two simultaneous or consecutive attacks on the correct positions will lead, in this case, only to a block with i units. The probability of this process occurring is the probability of attack on the two esters groups, multiplied by the probability that $i - 1$ esters do not undergo any attack. The number of times that this length will be included in the structure is the length $(-i - 1)$.

According to this, the number of PLLA blocks (linked) or chains (free) with a length i will be

$$N_i{}^{\mathrm{t}}{}_{\text{free PLLA}} = N_i{}^{\mathrm{p}}(1-p)^{i-1} + \sum_{j=i+1}^{\infty} N_j{}^{\mathrm{p}} p(1-p)^{i-1}$$

$$= (\text{using (1)})\ N_0(1-x)^2 b^{i-1} + N_0(1-x)^2 p(1-p)^{i-1} \sum_{j=i+1}^{\infty} x^{i-1}$$

$$= N_0(1-x)(1-b)b^{i-1} \qquad \text{with } b = x(1-p) \quad (6)$$

$$N_i{}^{\mathrm{t}}{}_{\text{linked PLLA}} = \sum_{j=i+1}^{\infty} N_j{}^{\mathrm{p}} p(1-p)^{i-1} + \sum_{j=i+2}^{\infty} (j-i-1) N_j{}^{\mathrm{p}} p^2 (1-p)^{i-1}$$

$$= (\text{using (1), (5)})\ N_0(1-x)^2(1-p)^{i-1} p \sum_{j=i+1}^{\infty} x^{j-1} + N_0(1-x)^2 p^2 (1-p)^{i-1} \sum_{j=i+2}^{\infty} (j-i-1)x^{j-1}$$

$$= 2N_0 cR(1-b)b^{i-1} \qquad (7)$$

From (6) and (7),

$$N_{\text{free PLLA chains}} = \sum_{i=1}^{\infty} N_i{}^{\mathrm{t}}{}_{\text{free PLLA}} = N_0(1-x)(1-b)\sum_{i=1}^{\infty} b^{i-1} = N_0(1-x)$$

This is what we expected: the N(original PLLA chains, (3)), because the transesterification reactions do not change the number of free PLLA chains.

$$N_{\text{PLLA blocks}} = \sum_{i=1}^{\infty} N_i{}^{\mathrm{t}}{}_{\text{linked PLLA}} = N_0 px(1-b)\sum_{i=1}^{\infty} b^{i-1} = (\text{using (5)})\ 2N_0 cR \qquad (8)$$

This result is also to be expected: the number of reacted OH-PEG, cN_{OH} (from (5)).

Now, we can statistically calculate the already defined $\bar{X}_{\mathrm{E}}$ ((4)) and the $\overline{\mathrm{D}}$Pn of the final PLLA blocks and chains. From (6) and (7),

$$\bar{X}_{\mathrm{E}} = \frac{\sum N_i{}^{\mathrm{t}} i}{\sum N i^{\mathrm{t}}} = \frac{\sum_{i=1}^{\infty} [N_0(1-x)(1-b)b^{i-1} + N_0 px(1-b)b^{i-1}]i}{\sum_{i=1}^{\infty} [N_0(1-x)(1-b)b^{i-1} + N_0 px(1-b)b^{i-1}]} = \frac{N_0}{N_0(1-b)} = \frac{1}{1-b} \qquad (9)$$

But this is the same expression obtained from a nonstatistical treatment ((4)):

$$\bar{X}_{\mathrm{E}} = \frac{\bar{X}_0}{A_{\mathrm{OH}}+1} = \frac{1/(1-x)}{cN_{\mathrm{OH}}/N_{\mathrm{PLLA}}+1} = \frac{1/(1-x)}{cN_{\mathrm{OH}}/[N_{\mathrm{es}}/(\bar{X}_0-1)]+1} = \frac{1}{1-x+xp} = \frac{1}{1-b}$$

using (2) and with $A_{\mathrm{OH}} = cN_{\mathrm{OH}}/N_{\mathrm{PLLA}}$. This fact confirms the probabilistic treatment.

The partial molecular weight distribution of the PLLA blocks and chains is, omitting the effect of the end groups in the molecular weight,

$$\bar{M}_{\mathrm{w}}/\bar{M}_{\mathrm{n}} = \frac{\sum N_i{}^{\mathrm{t}}(im)^2/\sum N_i{}^{\mathrm{t}}(im)}{\sum N_i{}^{\mathrm{t}}(im)/\sum N_i{}^{\mathrm{t}}} = \frac{m(1+b)/(1-b)}{m/(1-b)} = 1+b = 1+x-xp = (\bar{M}_{\mathrm{w}}/\bar{M}_{\mathrm{n}})_{\mathrm{polycon}} - xp$$

Global Molecular Weight Distribution. Transesterification by a Difunctional PEG. The PEG chains will be as unreacted PEG, diblocks, or triblocks. The following equations assume that PEG is monodisperse.

The number of unreacted PEG, from (4) and knowing that $N_{\mathrm{PEG}} = N_{\mathrm{OH}}/2$, will be (from (5))

$$N_{\text{unreacted PEG}} = N_{\mathrm{PEG}}(1-c)^2 = N_0 R(1-c)^2 \qquad (10)$$

and the number of diblocks L$_i$-PEG-OH, from (7)

$$N_i{}^{\mathrm{t}}{}_{\text{diblocks}} = N_i{}^{\mathrm{t}}{}_{\text{linked PLLA}}(1-c) = 2N_0 cR(1-b)(1-c)b^{i-1} \qquad (11)$$

The number of triblocks L$_j$-PEG-L$_k$, where $j+k=i$ [(L$_i$)-PEG], is, for $i > 1$ and from (7) and (8),

$$N_i{}^{\mathrm{t}}{}_{\text{triblocks}} = \frac{1}{2}\sum_{j=1}^{i\text{-}1}\left[N_j{}^{\mathrm{t}}{}_{\text{linked}}\, c\left(\frac{N_k{}^{\mathrm{t}}{}_{\text{linked}}}{N_{\text{PLLA blocks}}}\right)\right] = \frac{1}{2}\frac{c}{N_0 px}\sum_{j=1}^{i\text{-}1}[N_0 px(1-b)b^{j-1}][N_0 px(1-b)b^{k-1}] = N_0 c^2 R(1-b)^2(i-1)b^{i-2} \qquad (12)$$

Finally, and omitting the effect of the end groups in the molecular weight, the following expressions are obtained:

free PLLA chains, L$_i$, (6)

$$N_{i\ \text{free PLLA}}^{\,\text{t}} = N_0(1-x)(1-b)b^{i-1}$$
$$\text{with } M_i = mi$$

diblocks, L$_i$-PEG-OH, (11)

$$N_{i\ \text{diblocks}}^{\,\text{t}} = 2N_0cR(1-b)(1-c)b^{i-1}$$
$$\text{with } M_i = mi + M_{\text{PEG}}$$

triblocks, L_i-PEG, $i > 1$, (12)

$$N_{i\ \text{triblocks}}^{\,\text{t}} = N_0c^2R(1-b)^2(i-1)b^{i-2}$$
$$\text{with } M_i = m_i + M_{\text{PEG}}$$

unreacted PEG, (10)

$$N_{\text{unreacted PEG}} = N_0R(1-c)^2$$
$$\text{with } M_i = M_{\text{PEG}}$$

Let's call $M_{\text{PEG}}/m = a$, and using (6), (10), (11), and (12):

$$\begin{aligned}\sum_{i=1}^{\infty} N_i^{\,\text{t}} &= \sum_{i=1}^{\infty} N_{i\ \text{free PLLA}}^{\,\text{t}} + \sum_{i=1}^{\infty} N_{i\ \text{diblocks}}^{\,\text{t}} + \sum_{i=2}^{\infty} N_{i\ \text{triblocks}}^{\,\text{t}} + N_{\text{unr PEG}}\\ &= (\text{using } (5))\ N_0(1-x)(1-b)\sum_{i=1}^{\infty} b^{i-1} + 2N_0cR(1-b)(1-c)\sum_{i=1}^{\infty} b^{i-1} + N_0c^2R(1-b)^2\sum_{i=2}^{\infty}(i-1)b^{i-2} + N_0R(1-c)^2\\ &= N_0[1-x+R] \end{aligned} \tag{13}$$

$$\begin{aligned}\sum_{i=1}^{\infty} N_i^{\,\text{t}}M_i &= \sum_{i=1}^{\infty}[N_{i\ \text{free PLLA}}^{\,\text{t}}(im)] + \sum_{i=1}^{\infty}[N_{i\ \text{diblocks}}^{\,\text{t}}(im+am)] + \sum_{i=2}^{\infty}[N_{i\ \text{triblocks}}^{\,\text{t}}(im+am)] + N_{\text{unr PEG}}(am)\\ &= (\text{using } (5))\ N_0m(1-x)(1-b)\sum_{i=1}^{\infty} ib^{i-1} + 2N_0mcR(1-b)(1-c)\sum_{i=1}^{\infty}(i+a)b^{i-1} + N_0mc^2R(1-b)^2\sum_{i=2}^{\infty}(i-1)(i+a)b^{i-2} + N_0maR(1-c)^2\\ &= N_0m[1+aR] \end{aligned} \tag{14}$$

From (12) and (13),

$$\begin{aligned}\sum_{i=1}^{\infty} N_i^{\,\text{t}}M_i^{\,2} &= \sum_{i=1}^{\infty}[N_{i\ \text{free PLLA}}^{\,\text{t}}(im)^2] + \sum_{i=1}^{\infty}[N_{i\ \text{diblocks}}^{\,\text{t}}(im+am)^2] + \sum_{i=2}^{\infty}[N_{i\ \text{triblocks}}^{\,\text{t}}(im+am)^2] + N_{\text{unr PEG}}(am)^2\\ &= (\text{using } (5))\ N_0m^2(1-x)(1-b)\sum_{i=1}^{\infty} i^2b^{i-1} + 2N_0m^2cR(1-b)(1-c)\sum_{i=1}^{\infty}(i+a)^2b^{i-1} + N_0m^2c^2R(1-b)^2\sum_{i=2}^{\infty}(i-1)(i+a)^2b^{i-2} + N_0m^2a^2R(1-c)^2\\ &= \frac{N_0m^2}{(1-b)^2}\{(1+b)(1-b) + R[a^2(1-b)^2 + 4ac(1-b) + 2c^2]\} \end{aligned} \tag{15}$$

From (12) and (13),

$$\bar{M}_{\text{n}} = \frac{\sum N_i^{\,\text{t}}M_i}{\sum N_i^{\,\text{t}}} = m\frac{1+aR}{1-x+R} \tag{16}$$

M_{n} is a constant because the transesterification reaction does not change the number of species or chains. This is the same equation deduced from a global balance (nonstatistical). (This confirms again the statistical treatment).

$$\begin{aligned}\bar{M}_{\text{n}} &= \frac{\text{total mass}}{\text{no. of molecules}} = \frac{\text{PLLA mass} + \text{PEG mass}}{\text{free PLLAs} + \text{copolymers}}\\ &= \frac{mN_0 + N_{\text{PEG}}(ma)}{N_0(1-x) + N_{\text{PEG}}} = m\frac{1+aR}{1-x+R}\end{aligned}$$

Finally, from (14) and (15),

$$\bar{M}_{\text{w}} = \frac{\sum N_i^{\,\text{t}}M_i^{\,2}}{\sum N_i^{\,\text{t}}M_i} = \frac{m}{(1-b)^2} \times \frac{(1+b)(1-b) + R[a^2(1-b)^2 + 4ac(1-b) + 2c^2]}{1+aR} \tag{17}$$

$$\frac{\bar{M}_{\text{w}}}{\bar{M}_{\text{n}}} = \frac{[1-x+R)]}{(1-b)^2} \times \frac{\{(1+b)(1-b) + R[a^2(1-b)^2 + 4ac(1-b) + 2c^2]\}}{[1+aR]^2} \tag{18}$$

Figures 3−5 show theoretical curves of the $\bar{X}_{\text{E}}$, $\bar{M}_{\text{w}}$, and polydispersity variation versus conversion for reactions with different feed ratios according to (9), (17), and (18). The experimental $\bar{X}_{\text{E}}$ points obtained by ^{1}H NMR

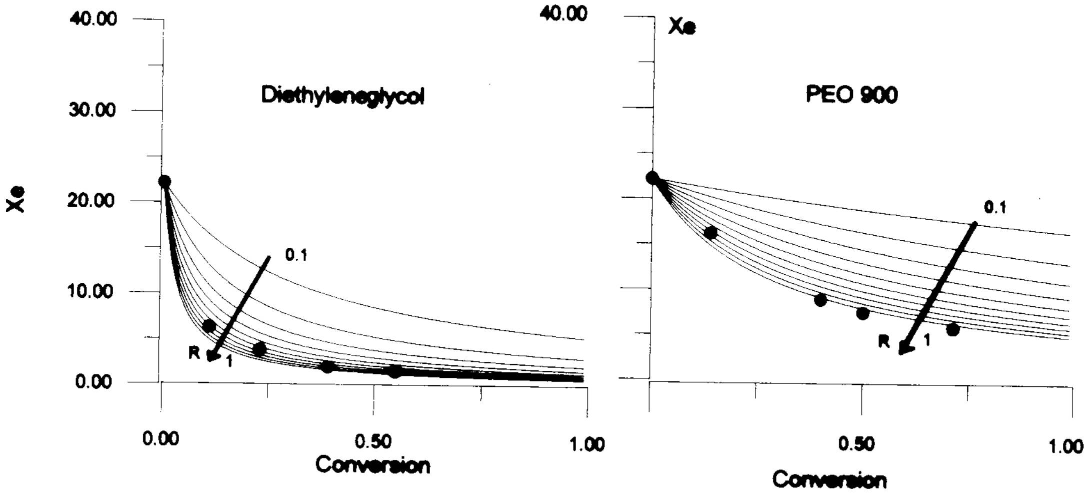


Figure 3. Theoretical (according to (9)) and experimental $\bar{X}_E$ data ($\bar{D}$Pn of the PLLA chains or blocks) in the solution reaction versus conversion.

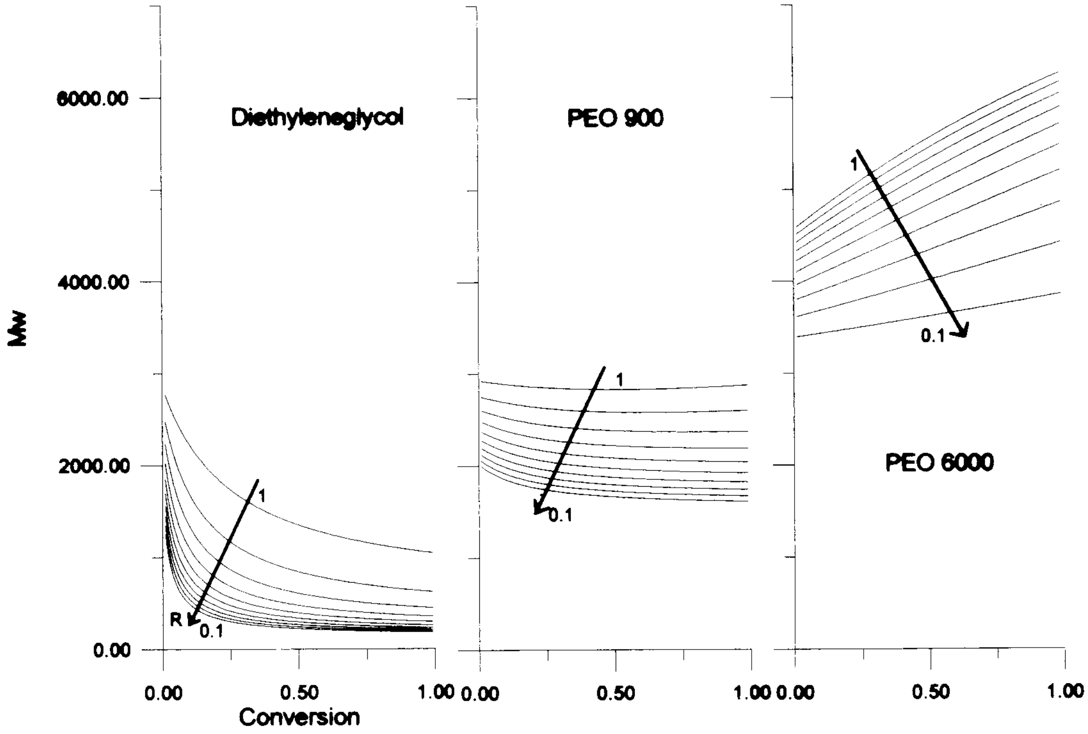


Figure 4. Theoretical curves of $\bar{M}_w$ variation versus conversion for reactions with different feed ratio (*R*) according to (17).

from the spectra of different samples corresponding to the solution reactions are also quoted in Figure 3. A good agreement between experimental and theoretical data is attained, taking into account that the experimental reaction ratio of PLA and PEG is 1 (corresponding to the lower theoretical curve).

The different melt reactions are summarized in Figure 6, where $\bar{X}_E$ is represented versus *p* (defined in (5) and related to the feed ratio). Points are the experimental values, and the dark area corresponds to the theoretical range of the experimental data, taking into consideration that all the reactions reach the same conversion, 90%. Again, the agreement between experimental and theoretical data is excellent.

This model could be easily adapted to the transesterification of a monofunctional reactive, or the degradation of polyesters by random scission, or the transesterification process concomitant with the polycondensation, or even to the study of transesterifications reactions between different polymer chains.

The good agreement between the experimental results obtained for treatments in melt and in solution and the theoretical considerations demonstrates that, in the range of temperatures used in this work, the behavior of the PLLA–PEG system is explained satisfactorily by taking into consideration transesterification reactions, better that pure thermodegradative scissions of the PLLA ester linkages. This is supported by the results

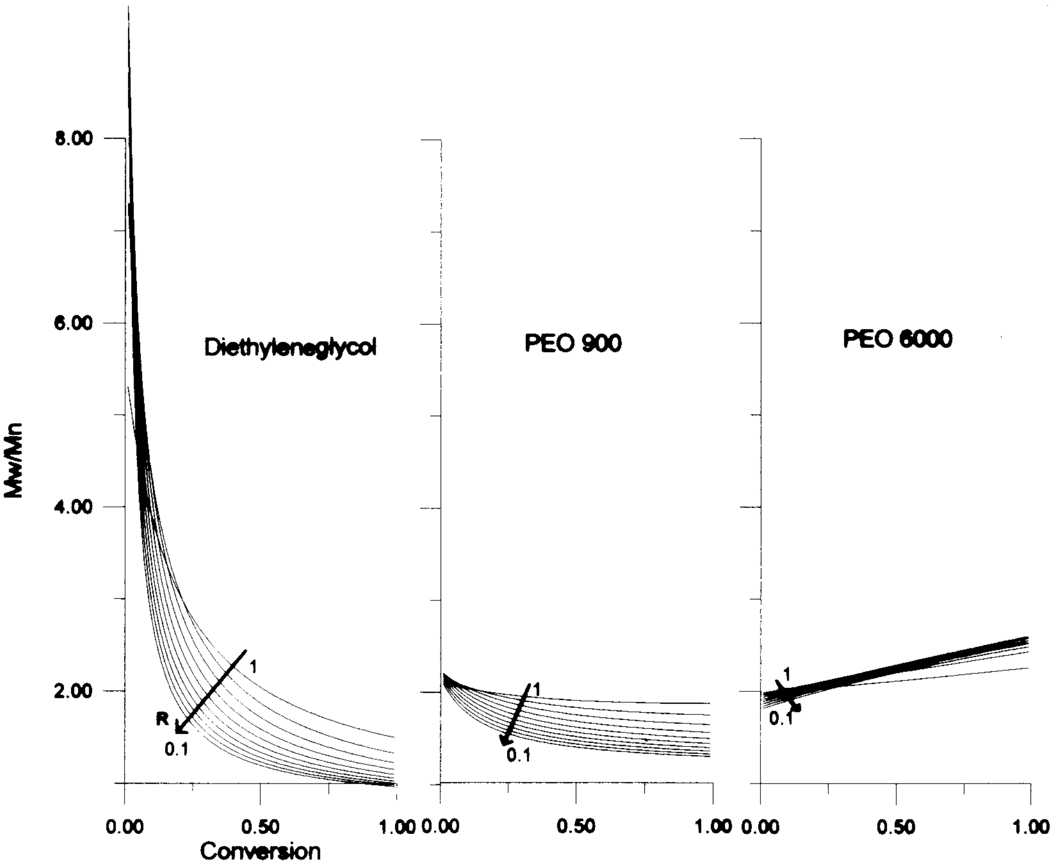


Figure 5. Theoretical curves of polydispersity variation versus conversion for reactions with different feed ratio (*R*) according to (18).

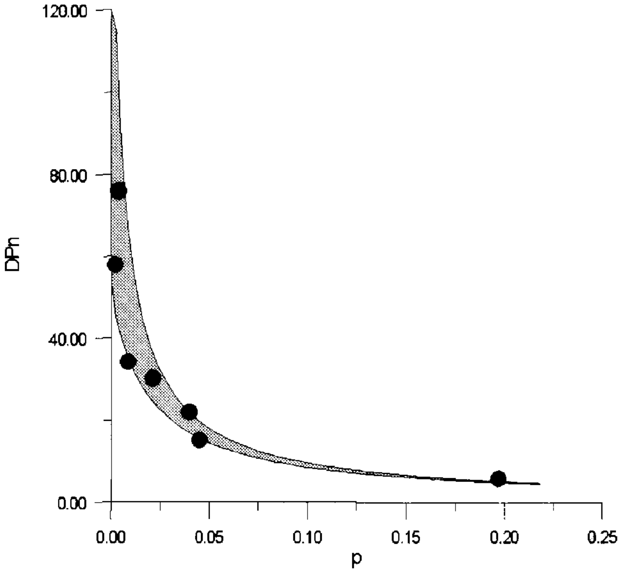


Figure 6. Theoretical range (dark area) and experimental points of $\bar{X}_E$ versus *p*.

obtained in solution, which correspond to a reaction temperature where the thermal degradation can be rejected.

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Appendix

The solutions to the different summations that appear in the treatment are

$$\sum_{i=1}^{\infty} r^{i-1} = \frac{1}{1-r}$$

$$\sum_{i=1}^{\infty} i r^{i-1} = \frac{1}{(1-r)^2}$$

$$\sum_{i=1}^{\infty} i^2 r^{i-1} = \frac{1+r}{(1-r)^3}$$

$$\sum_{i=s+1}^{\infty} r^{i-1} = r^s \frac{1}{1-r}$$

$$\sum_{i=s+2}^{\infty} (i-s-1) r^{i-1} = r^{s+1} \frac{1}{(1-r)^2}$$

$$\sum_{i=1}^{\infty} i^3 r^{i-1} = \frac{1+4r+r^2}{(1-r)^4}$$

$$\sum_{i=1}^{\infty}(i+s)r^{i-1}=\frac{1+s(1-r)}{(1-r)^2}$$

$$\sum_{i=2}^{\infty}(i-1)(i+s)r^{i-1}=\frac{1+r+(s+1)(1-r)}{(1-r)^3}$$

$$\sum_{\mathrm{i}=1}^{\infty}(i+s)^2r^{i-1}=\frac{1+r+2s(1-r)+s^2(1-r)^2}{(1-r)^3}$$

$$\sum_{i=2}^{\infty}(i-1)(i+s)^2r^{i-1}$$

$$=\frac{1+4r+r^2+2(s+1)(1+r)(1-r)+(s+1)^2(1-r)^2}{(1-\mathrm{r})4}$$

$$=\frac{s^2(1-r)^2+4s(1-r)+2(1+r)+2}{(1-r)^4}$$

$$\sum_{i=2}^{\infty}(i-1)r^{i-2}=\sum_{i=1}^{\infty}ir^{i-1}=\frac{1}{(1-r)^2}$$

Nomenclature

N_i^{p} = number of i species before the transesterification reaction
N_i^{t} = number of i species after the transesterification reaction
N_0 = number of initial LLA monomers
m = molecular mass of the LLA unit (=72 g/mol) [constant]
x = molar conversion of LLA in the previous polycondensation
$\bar{X}_0$ = number polymerization degree of the original PLLA chains
$N_{\mathrm{PLLA\ chains}}$ = number of original PLLA chains
$\bar{X}_{\mathrm{E}}$ = number polymerization degree of the final PLLA blocks and chains
A_{OH} = average number of OH-PEG groups which react with every original PLLA chain
$N_{\mathrm{OH}} = 2N_{\mathrm{PEG}}$ (number of initial OH-PEG groups)
N_{PEG} = number of PEG molecules
$p = cN_{\mathrm{OH}}/N_{\mathrm{es}} = 2cR/x$ (5) (probability that an ester group undergoes a trasesterification reaction in the whole reaction course)
c = conversion of OH-PEG
N_{es} = number of ester bonds of the original PLLA chains
$R = N_{\mathrm{PEG}}/N_0$ (feed molar ratio in terms of moles of PEG/moles of LLA) [constant]
$b = x(1-p)$
$N_{\mathrm{free\ PLLA\ chains}}$ = number of free PLLA chains
$N_{\mathrm{PLLA\ blocks}}$ = number of PLLA blocks (linked to PEG chains)
$N_{\mathrm{unreacted\ PEG}}$ = number of unreacted PEG molecules
M_{PEG} = molecular mass of PEG [constant]
M_i = molecular mass of the i species
$a = M_{\mathrm{PEG}}/m$ [constant]

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