Micromechanical Behavior Related to the Nanostructure of Biodegradable Polyesters

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ABSTRACT: The microhardness of a series of biodegradable polyesters was determined. The nanostructural features of these materials were studied by wide-angle X-ray scattering (WAXS), small-angle X-ray scattering (SAXS), and differential scanning calorimetry. Analysis of the SAXS and WAXS patterns allowed direct derivation of the degree of crystallinity and crystal thickness values, and correlations of the micromechanical properties are presented. The differ-

ences in the thermal and mechanical properties exhibited by the studied systems and the ones found in other aromatic polyesters are explained as due to the different chemical natures of the monomeric units. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 117: 2591–2596, 2010

Key words: calorimetry; hardness; microstructure; polyesters; SAXS

INTRODUCTION

Aliphatic polyesters have received much attention in the past 2 decades because these materials are, in many cases, biodegradable by hydrolytic degradation. The reason for this behavior is the electrophilic character shown by the aliphatic ester group. Thus, some aliphatic polyesters, such as poly(ϵ -caprolactone), poly(ethylene adipate), and poly(butylene succinate), have been commercialized as biodegradable materials. The number of pharmaceutical and biomedical applications for these polymers is continuously increasing.^{1–3} One of the ways to obtain polyesters with a wide range of applications is through the modification of the chemical structure of the

polymers, for instance, by the introduction of new functional groups in the monomer. The presence of a double or a triple bond in the glycol or dialcohol of the monomeric unit allows further modification of the polyester by means of chemical reactions, such as the addition of bromine, epoxidation, or crosslinking.

A series of aliphatic polyesters (samples 1–6) were synthesized in recent years by Kricheldorf and co-workers.^{4–6} The chemical formulas are given in Figure 1. As shown, samples 1 and 2 are saturated polyesters based on 1,4-butane diol. Samples 3 and 4 are unsaturated polyesters based on *cis*-1,4-butene diol (cBeD), a glycol unit with a *cis* double bond. Finally, samples 5 and 6 are also unsaturated polyesters that contain a triple bond in the glycol unit, 1,4-butyne diol (ByD). As shown in Figure 1, the two polyesters of each pair differ only in the number of methylene groups of the diacid unit, which is 4 or 8, respectively. Samples 1 and 2 are the better known polyesters and have been investigated for a long time.^{4,7–17} There have also been some studies performed on samples 3^{18,19} and 4.^{18,20} In addition, Kricheldorf et al.⁵ recently published an article devoted to samples 3 and 4. However, to our knowledge, there have only been a few studies dealing with samples 5¹⁹ and 6²¹ before the study just reported by Kricheldorf et al.⁶ In this publication,⁶ three methods developed for the synthesis of samples 5 and 6 with high molecular weights were presented and discussed. Method A consisted of the thermal transesterification of ByD with the dimethyl ester of a sebacic acid in bulk catalyzed by Ti(OBu)₄.

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Sample 1: $n = 4$. Sample 2: $n = 8$

(Cis-form)

Sample 3: $n = 4$. Sample 4: $n = 8$

Sample 5: $n = 4$. Sample 6: $n = 8$

Sample 1: Poly(butanediol adipate)

Sample 2: Poly(butanediol sebacate)

Sample 3: Poly(butenediol adipate)

Sample 4: Poly(butenediol sebacate)

Sample 5: Poly(butynediol adipate)

Sample 6: Poly(butynediol sebacate)

Figure 1 Chemical formulas of the studied aliphatic polyesters.

In method B, the direct polycondensation of ByD with sebacic acid was essayed with *p*-toluene sulfonic acid as a catalyst. Finally, method C dealt with the polycondensation of ByD with diacid dichlorides (adipoyl and sebacoyl dichlorides, in our case) in the presence of pyridine as a catalyst. The last method, method C, was the preferred one for obtaining polyesters with satisfactory molecular weights and a smaller fraction of secondary reaction products.

In the preceding studies, the correlation between the nanostructure and the micromechanical properties of the polymers was well characterized.^{22–26}

The aim of this study was to investigate the nanostructure and micromechanical properties of these three different types of polyesters, that is, saturated, unsaturated with a cis double bond, and unsaturated with a triple bond in the monomeric unit.

EXPERIMENTAL

Materials

Samples 1 and 2 were synthesized according to a method previously developed in our laboratory.⁴ In this method, we essentially used the cyclic initiator 2,2-dibutyl-2-stanna-1,3-dioxepane (DSDOP) to react with a dicarboxylic acid dichloride, thus obtaining the corresponding polyester based on 1,4-butane diol. After repeated washing and purification, the final products were dried *in vacuo* at 40°C.

Samples 3 and 4 were prepared by the polycondensation of *cis*-1,4-butenediol with dicarboxylic acid dichlorides in the presence of pyridine as a catalyst.⁵

After precipitation and filtration, the polyesters were dried *in vacuo* at 20°C.

Samples 5 and 6 were obtained by the polycondensation of butyne-1,4-diol (ByD) with dicarboxylic acid dichlorides with pyridine as a catalyst.⁶ After precipitation and filtration, the final products were dried *in vacuo* at 20°C overnight.

The samples were compression-molded in a press at $22 \pm 1^\circ\text{C}$ before their characterization by different methods.

Techniques

The samples were characterized by wide-angle X-ray scattering (WAXS) and small-angle X-ray scattering (SAXS), differential scanning calorimetry (DSC), and microhardness (*H*) measurements.

For the WAXS study, a Seifert diffractometer (reflection mode) was used. The working conditions were as follows: voltage = 40 kV, intensity = 35 mA, angular range = $5\text{--}35^\circ$ (2θ), scan rate = 0.05, and slits = 0.3 and 0.1.

SAXS patterns were obtained with a synchrotron radiation source at the A2 beamline in Hamburger Synchrotronstrahlungslabor, Deutsches Elektronen Synchrotron, Hamburg. Scattering patterns were recorded with a one-dimensional detector. A wavelength (λ) of 0.15 nm was used. The sample-to-detector distance was 200 cm. The data were corrected for the detector response and beam intensity. Application of Bragg's law to the scattering maxima was used to calculate the long period (*L*).

DSC measurements were performed in a Perkin-Elmer DSC-7 (Shelton, CT) differential scanning calorimeter in an inert N_2 atmosphere. The temperature range covered was 30–130°C. The heating rate was 10°C/min. Typical sample weights were about 5 mg. Table I summarizes the melting temperature (T_m) and the melting enthalpy (ΔH_m) values of the samples.

Microhardness *H* was measured at room temperature with a Leitz tester (Wetzlar, Germany) equipped with a Vickers diamond pyramid. *H* values were derived from the optical measurement of the residual impression left behind upon load release, according to $H = 1.854P/d^2$, where *d* is the length of the indentation diagonal in *m* and *P* is the applied load in *N*. A loading cycle of 6 s was used to minimize the sample creep under the indenter. Loads of 98 and 147 mN were used to correct for the instant elastic recovery. For each load, at least eight measurements were averaged.

RESULTS

Crystallinity derived from WAXS and nanostructure

Figure 2 shows the WAXS patterns for all of the samples studied. It is important to note that,

TABLE I
Values of L from SAXS, T_m , ΔH_m , H , α_{WAXS} , l_c (Derived as $l_c \approx L\alpha_{\text{WAXS}}$), and H_c
of the Aliphatic Polyesters

Sample	L (nm)	T_m (°C)	ΔH_m (J/g)	H (MPa)	α_{WAXS}	l_c (nm)	H_c (MPa)
1	11.5	56.2	106.6	42 ± 3	0.70	8.0	60
2	10.0	62.3	119.7	33 ± 3	0.55	5.5	60
3	*11.4	60.1	80.1	29 ± 2	0.58	*6.7	50
4	10.4	52.8	93.7	25 ± 2	0.51	5.3	49
5	11.4	43.0	51.8	27 ± 2	0.54	6.1	50
6	10.1	60.0	74.2	28 ± 3	0.50	5.0	57

The L and l_c values for sample 3 are indicated with an asterisk (see the text for an explanation).

whereas samples 1 and 2 were well characterized from the crystallographic point of view,^{8,13–17} there was a lack of crystallographic information about samples 3, 4, and 6. The existing data were very scarce and poor.^{18,20} In addition, to our knowledge, the diffractogram corresponding to poly(butynediol adipate), sample 5, has never been reported before. All of the diffractograms showed a diffraction maximum at $21.3\text{--}21.6^\circ$ (2θ ; where θ is the scattering angle). The α_{WAXS} value of every sample was calculated as the ratio of the area corresponding to the crystalline peaks to the total area of the diffractogram. The α_{WAXS} values ranged between 0.5 and 0.7 (see Table I).

Figure 3 shows the SAXS patterns of all of the samples, that is, the scattering intensity as a function of the reciprocal vector s (nm^{-1} ; $s = 2 \sin \theta / \lambda$, and $\lambda = 0.15 \text{ nm}$). From the maxima position, the long spacing L corresponding to each sample could be derived ($L = 1/s$).

The values for L derived from the SAXS maxima, α_{WAXS} , and crystal thickness ($l_c \approx L\alpha_{\text{WAXS}}$) obtained from these polyesters are listed in Table I. As we did not have information about the L value for sample 3, we assumed that, similarly to samples 1 and 5, $L \approx 11.4 \text{ nm}$ for this sample, and consequently, $l_c \approx 11.4 \times 0.58 = 6.7 \text{ nm}$. The L and l_c values for sample 3 are indicated with an asterisk in Table I.

Most of the crystallographic data of these polyesters that appear in the literature corresponded to sample 1, poly(butanediol adipate).^{8,13–16} It is known that this polyester can crystallize in two crystalline forms, α (monoclinic) and β (orthorhombic),^{11,13,14,16} with the α form being the most stable from the structural point of view.¹¹ In this study, we dealt with the α form of sample 1 (see Fig. 2). Assuming, in a first approximation, that $l_c \approx L\alpha_{\text{WAXS}}$, we found, for sample 1, a value of $l_c \approx 11.5 \times 0.7 = 8.0 \text{ nm}$. Interestingly, in refs. 11 and 12, slightly different values of L and l_c are listed for sample 1. Thus, taking into account the information given in ref. 11, L and l_c were about 14.3 and 7.4 nm for the β form and 15.7 and 9.0 nm for the α form. From ref. 12, the l_c values corresponding to the α and β form were 8.5 and 7.0 nm, respectively.

Figure 2 WAXS diagrams of the studied aliphatic polyesters (for sample identification, see Fig. 1).

Figure 3 SAXS patterns of the investigated materials (for sample identification, see Fig. 1).

For sample 2, poly(butanediol sebacate), it has been shown that this polyester crystallizes in the orthorhombic system, with the main crystallographic constants having been determined by Almontassir et al.¹⁷

Thermal behavior

The DSC curves are shown in Figure 4. As shown in Table I, all of the samples presented low T_m 's. In these experiments, the heating runs could not start at temperatures lower than room temperature. For this reason, we concluded that, at least in case of sample 5, the obtained ΔH_m value could have been lower than the real one.

Among the different values of the melting enthalpy of a 100% crystalline material (ΔH_m^0),^{7–9} and the equilibrium melting temperature (T_m^0)^{9–12} found in the literature for the α form of poly(butanediol adipate), we selected values of $\Delta H_m^0 = 123.9$ J/g⁷ and $T_m^0 = 63^\circ\text{C}$.¹⁰ The crystalline density (ρ_c) of sample 1 was 1.23 g/cm³.^{9,15} According to the Thomson–Gibbs equation

$$T_m = T_m^0 [1 - (2\sigma_e / \Delta H_m^0 \rho_c l_c)] \quad (1)$$

Substituting T_m , T_m^0 , ΔH_m^0 , ρ_c , and l_c with their corresponding values, we derived the free surface energy (σ_e) for sample 1 as $\sigma_e = 12.3$ erg/cm². This value was notably lower than the ones derived for the poly(ethylene) (PE) samples ($\sigma_e = 79$ – 91 erg/cm²)²⁷ or for the poly(ethylene oxide) samples ($\sigma_e = 41$ – 66 erg/m²).²⁸

Microindentation hardness

According to the two-phase model, the hardness of a semicrystalline polymer is given by the following equation:²⁹

$$H = H_c \alpha + H_a (1 - \alpha) \quad (2)$$

Figure 4 DSC diagrams of (a) saturated polyesters based on 1,4-butanediol (samples 1 and 2), (b) unsaturated polyesters based on 1,4-*cis*-butanediol (samples 3 and 4), and (c) unsaturated polyesters based on 1,4-butanediol (samples 5 and 6). T is temperature in $^\circ\text{C}$.

Figure 5 Dependence of H on α of the studied polyesters (for sample identification, see Fig. 1). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

where H_c and H_a are the crystalline and amorphous hardnesses values, respectively, and α is the degree of crystallinity. From preceding publications,^{5,6,7-9} we knew that all of the samples under study present T_g values well below 0°C . Because in all cases, $H_a \approx 0$, eq. (2) can be written as

$$H \approx H_c \alpha \quad (3)$$

Thus, from eq. (3), we derived H_c for all of the samples as $H_c \approx H/\alpha_{\text{WAXS}}$. The H_c values are also collected in Table I.

Figure 5 illustrates the dependence of the hardness with α for the investigated polyesters. For the three sets of samples, H increased with α_{WAXS} . All of the hardness data were located in an area in which l_c varied between 5 and 8 nm and H_c varied between 50 and 60 MPa. Although samples 1 and 2, on one side, and samples 3, 4, and 5, on the other side, showed similar H_c values, that is, 60 and 50 MPa, respectively, sample 6 presented an intermediate H_c value of about 57 MPa.

DISCUSSION

The hardness dependence upon α for the polyesters under study was similar to the one shown by polyolefins such as linear polyethylene (see Fig. 10 in ref. 30). However, the values exhibited by linear PE for H (67–76 MPa) and H_c (86–93 MPa) were notably higher.²⁷

Figure 6 shows the relationship between H_c and the reciprocal of l_c ($1/l_c$) for all of the samples under study. By extrapolation of the regression line, a hardness value for infinitely long crystals (H_c^∞) of 64

MPa was obtained. This value was also much lower than 170 MPa, which is the ideal hardness of an infinitely thick PE crystal.²⁵ From $H_c^\infty = 64$ MPa, and with the following expression taken into account²⁹

$$H_c = H_c^\infty / (1 + b/l_c) \quad (4)$$

one obtains for the b parameter (a measure of the hardness depression from H_c^∞) a value of 1.1 nm. This value was very close to the one derived for the α form of the aromatic polyester poly(butylene terephthalate) (PBT). For PBT, $b = 1.5$ nm.²³ This was an indication that the degree of disorder at the crystal surface was similar for both kinds of polymers, that is, PBT and the aliphatic polyesters included in this study. However, PBT exhibited much higher H , H_c , and H_c^∞ values (153, 287, and 370 MPa, respectively).^{23,24} These large differences may have originated with the presence in PBT of the terephthalic acid aromatic units, which conferred a much higher rigidity on the polymeric chains. The aromatic units are also responsible for the high hardness values exhibited by other aromatic polyesters, such as poly(ethylene terephthalate) ($H = 220$ MPa, $H_c = 287$ MPa, $H_c^\infty = 380$ MPa, and $b = 1.9$ nm)³¹ and poly(ethylene naphthalene-2,6-dicarboxylate) ($H = 300$ MPa, $H_c = 341$ MPa,³¹ $H_c^\infty = 550$ MPa, and $b = 1.8$ nm).³² For the same reason, the T_m 's of these aromatic polyesters were 221°C for PBT,³³ 260 – 270°C for poly(ethylene terephthalate),³⁴ and 270°C for poly(ethylene naphthalene-2,6-dicarboxylate),³⁵ these

Figure 6 Relationship between H_c and $1/l_c$ of the studied polyesters (for sample identification, see Fig. 1). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

were much higher than those values exhibited by the aliphatic polyesters included in this study, which ranged between 43 and 62.3°C (see Table I).

As shown in Table I, the T_m and the ΔH_m values for sample 1 were lower than for sample 2. However, H for the former was higher than for the latter. This was probably due to the fact that the α and l_c values for sample 1 were larger than for sample 2. When compared the features of samples 1 and 2 with those of the well-known polyester poly(ϵ -caprolactone), we determined that some characteristics of the latter were similar to those exhibited by poly(butanediol adipate) and poly(butanediol sebacate). Thus, poly(ϵ -caprolactone) had a T_m of about 56°C,³⁶ in addition, according to ref. ³⁷, $T_m^0 = 69.2^\circ\text{C}$ and $\Delta H_m^0 = 157 \text{ J/g}$. Taking into account the crystallographic data published in ref. ³⁸, we determined the ρ_c of poly(ϵ -caprolactone) to be about 1.18 g/cm^3 . We had no data concerning H of poly(ϵ -caprolactone). However, from Tabor's relation, $H/\sigma_y \approx 3$,³⁹ with the yield stress value listed in ref. ⁴⁰ for this polymer, that is, $\sigma_y = 4.91 \text{ MPa}$, H should have been about 15 MPa; this value was notably lower than the values found for samples 1 and 2 (see Table I). From the foregoing, it seems clear that poly(butanediol adipate) and poly(butanediol sebacate) exhibited better mechanical properties than poly(ϵ -caprolactone).

CONCLUSIONS

The analysis of the data offers a correlation between the nanostructure and the micromechanical properties of these biodegradable systems. It turns out that poly(butanediol adipate), sample 1, with the highest α_{WAXS} , exhibits the largest hardness values.

The aliphatic polyesters included in this study show a H - α_{WAXS} relationship similar to that found in linear PE. However, H_c and the calculated hardness values for infinitely thick crystals are much lower than those of linear PE.

Although the value derived for the b mechanical parameter of the aliphatic polyesters is similar to that of PBT, the latter shows notably higher thermal and mechanical properties because of the presence of aromatic cycles in the monomeric units.

The saturated polyesters poly(butanediol adipate) and poly(butanediol sebacate) exhibit slightly higher H values than poly(ϵ -caprolactone), also a biodegradable polyester that has found a wide variety of applications in recent years.

References

1. Vert, M. *Biomacromolecules* 2005, 6, 538.
2. Edlund, U.; Albertsson, A.-C. *Adv Drug Delivery Rev* 2003, 55, 585.
3. Bastioli, C. *Macromol Symp* 1998, 135, 193.
4. Kricheldorf, H. R.; Langanke, D.; Spickermann, J.; Schmidt, M. *Macromolecules* 1999, 32, 3559.
5. Chatti, S.; Behnken, G.; Langanke, D.; Kricheldorf, H. R. *Macromol Chem Phys* 2006, 207, 1474.
6. Kricheldorf, H. R.; Gao, Q.; Buzin, P.; Schwartz, G. *Macromol Chem Phys* 2008, 209, 385.
7. Rabinovitch, B.; Nistratov, V. P.; Babinkov, A. G.; Shvetsova, K. G.; Larina, V. N. *Polym Sci USSR* 1984, 26, 826.
8. Nikolic, M. S.; Djonlagic, J. *Polym Degrad Stab* 2001, 74, 263.
9. Penning, J. P.; St. John Manley, R. *Macromolecules* 1996, 29, 77.
10. Righetti, M. C.; Pizzoli, M.; Lotti, N.; Munari, A. *Macromol Chem Phys* 1998, 199, 2063.
11. Gan, Z.; Kuwabara, K.; Abe, H.; Iwata, T.; Doi, Y. *Biomacromolecules* 2004, 5, 371.
12. Gan, Z.; Kuwabara, K.; Abe, H.; Iwata, T.; Doi, Y. *Polym Degrad Stab* 2005, 87, 191.
13. Pouget, E.; Almontassir, A.; Casas, M. T.; Puiggali, J. *Macromolecules* 2003, 36, 698.
14. Gan, Z.; Abe, H.; Doi, Y. *Macromol Chem Phys* 2002, 203, 2369.
15. Noguchi, K.; Kondo, H.; Ichikawa, Y.; Okuyama, K.; Washiyama, J. *Polymer* 2005, 46, 10823.
16. Zhao, L.; Wang, X.; Li, L.; Gan, Z. *Polymer* 2007, 48, 6152.
17. Almontassir, A.; Gestí, S.; Franco, L.; Puiggali, J. *Macromolecules* 2004, 37, 5300.
18. Pourjavadi, A.; Zohourian, M. J. *J Polym Mater* 1993, 10, 233.
19. Vlad, S.; Oprea, S.; Stanciu, A.; Ciobanu, C.; Bulacovschi, V. *Eur Polym J* 2000, 36, 1495.
20. Marvel, C. S.; Young, C. H. *J Am Chem Soc* 1951, 73, 1066.
21. Marvel, C. S.; Young, C. H. *J Am Chem Soc* 1950, 72, 1674.
22. Baltá Calleja, F. J.; Salazar, J. M.; Asano, T. *J Mater Sci Lett* 1988, 7, 165.
23. Giri, L.; Roslaniec, Z.; Ezquerra, T. A.; Baltá Calleja, F. J. *J Macromol Sci Phys* 1997, 36, 335.
24. Fakirov, S.; Boneva, D.; Baltá Calleja, F. J.; Krumova, M.; Apostolov, A. A. *J Mater Sci Lett* 1998, 17, 453.
25. Flores, A.; Baltá Calleja, F. J.; Bassett, D. C. *J Polym Sci Part B: Polym Phys* 1999, 37, 3151.
26. Cagiao, M. E.; Ania, F.; Baltá Calleja, F. J.; Hiram, M.; Shimomura, T. *J Appl Polym Sci* 2000, 77, 636.
27. Baltá Calleja, F. J.; Santa Cruz, C.; Bayer, R. K.; Kilian, H. G. *Colloid Polym Sci* 1990, 268, 440.
28. Baltá Calleja, F. J.; Santa Cruz, C. *Acta Polym* 1996, 47, 303.
29. Baltá Calleja, F. J.; Fakirov, S. *Microhardness of Polymers; Solid State Science Series*; Cambridge University Press: Cambridge, England, 2000; p 11.
30. Flores, A.; Ania, F.; Baltá Calleja, F. J. *Polymer* 2009, 50, 729.
31. Santa Cruz, C.; Baltá Calleja, F. J.; Zachmann, H. G.; Chen, D. *J Mater Sci* 1992, 27, 2161.
32. Rueda, D. R.; Viksne, A.; Malers, L.; Baltá Calleja, F. J. *Macromol Chem Phys* 1994, 195, 3869.
33. Di Lorenzo, M. L.; La Pietra, P.; Errico, M. E.; Righetti, M. C.; Angiuli, M. *Polym Eng Sci* 2007, 47, 323.
34. Köncke, U.; Zachmann, H. G.; Baltá Calleja, F. J. *Macromolecules* 1996, 29, 6019.
35. Buchner, S.; Wiswe, D.; Zachmann, H. G. *Polymer* 1989, 30, 480.
36. Rosa, D. S.; Neto, I. C.; Calil, M. R.; Pedrosa, A. G.; Fonseca, C. P.; Neves, S. J. *J Appl Polym Sci* 2004, 91, 3909.
37. The Advanced Thermal Analysis System. <http://athas.prz.rzeszow.pl> (accessed September 2008)
38. Hu, H.; Dorset, D. L. *Macromolecules* 1990, 23, 4604.
39. Tabor, D. *Hardness of Metals*; Oxford University Press: London, 2000.
40. Gorrasi, G.; Tortora, M.; Vittoria, V.; Galli, G.; Chiellini, E. *J Polym Sci Part B: Polym Phys* 2002, 40, 1118.