

Thermal and Rheological Properties of Commercial-Grade Poly(Lactic Acid)s

John R. Dorgan,¹ Hans Lehermeier,¹ and Michael Mang²

Poly(lactic acid) is the subject of considerable commercial development by a variety of organizations around the world. In this work, the thermal and rheological properties of two commercial-grade poly(lactic acid)s (PLAs) are investigated. A comparison of the commercial samples to a series of well-defined linear and star architecture PLAs provides considerable insight into their flow properties. Such insights are valuable in deciding processing strategies for these newly emerging, commercially significant, biodegradable plastics. Both a branched and linear grade of PLA are investigated. The crystallization kinetics of the branched polymer are inferred to be faster than the linear analog. Longer relaxation times in the terminal region for the branched material compared to the linear material manifests itself as a higher zero shear rate viscosity. However, the branched material shear thins more strongly, resulting in a lower value of viscosity at high shear rates. Comparison of the linear viscoelastic spectra of the branched material with the spectra for star PLAs suggests that the branched architecture is characterized by a span molecular weight of approximately 63,000 g/mol. The present study conclusively demonstrates that a wide spectrum of flow properties are available through simple architectural modification of PLA, thus allowing the utilization of this important degradable thermoplastic in a variety of processing operations.

KEY WORDS: Poly(lactic acid); polylactide(s); flow; rheology; thermal properties; chain architecture.

INTRODUCTION

As the readers of this journal are aware, there is a need to develop "green" plastic packaging materials that are based on renewable resources, that do not involve the use of toxic or noxious components in their manufacture, and which allow composting to naturally occurring degradation products. Currently, most polymeric packaging materials are based on nonrenewable fossil resources. Incineration of these materials makes a net contribution to atmospheric CO₂ and plastics currently account for in excess of 20% of the nation's landfills. In addition, many widely used materials are made from noxious or toxic monomers.

Such a biodegradable family of polymers made from monomers obtained from *renewable* sources can be produced and will soon be competitive in the marketplace. This material is poly(lactic acid) (PLA). PLA is the polymer of lactic acid made by the bacterial fermentation of carbohydrates (corn is an inexpensive source) using optimized strains of the genus *Lactobacillus*. An independent evaluation of the process economics performed at the Argonne National Laboratory has found that advances in fermentation and separation technologies allow the manufacture of lactic acid for 25 cents per pound and that poly(lactic acid) (PLA) is an economically feasible material [1].

The advantages of PLAs are numerous and include: (1) production of the lactide monomer by fermentation of a renewable agricultural source (corn); (2) fixation of significant quantities of carbon dioxide, the leading greenhouse gas; (3) significant energy savings; (4) the

¹Department of Chemical Engineering, Colorado School of Mines, Golden, Colorado 80401.

²Cargill-Dow Polymers, 15305 Minnetonka Boulevard, Minnetonka, Minnesota 55345.

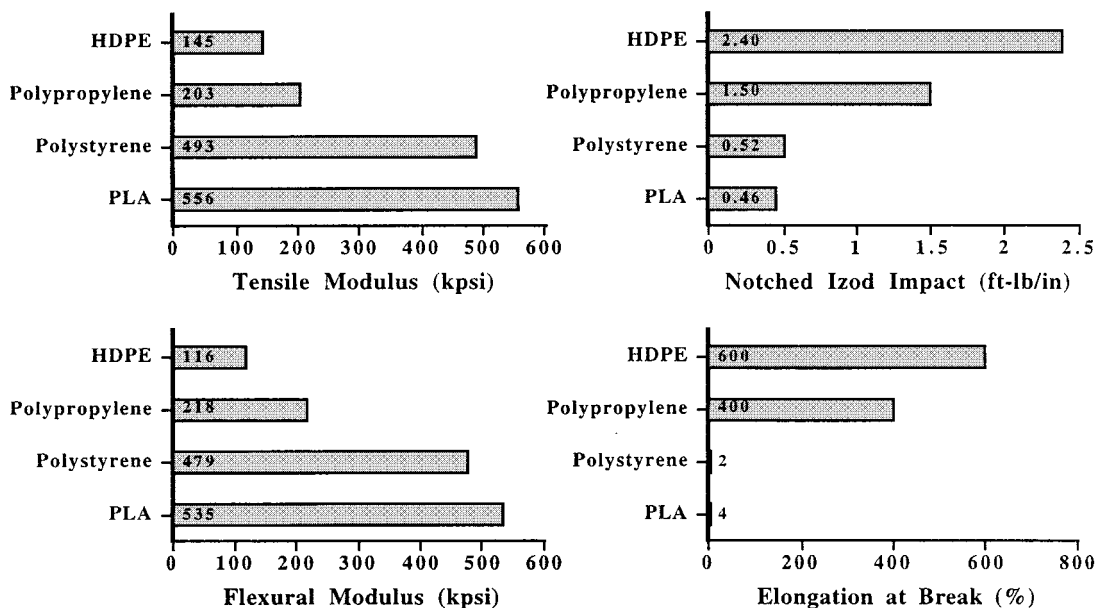


Fig. 1. Comparison of the mechanical properties of PLA with some common plastic packaging materials. Note the close resemblance of PLA to polystyrene in terms of mechanical properties.

ability to recycle back to lactic acid (a nontoxic, naturally occurring metabolite) by hydrolysis or alcoholysis; (5) the capability of producing hybrid paper-plastic consumer packaging that is compostable; (6) reduction of landfill volumes; (7) improvement of America's farm economy; and (8) the all-important ability to tailor physical properties through material modifications.

PLA possesses the required mechanical properties needed for many applications. Figure 1 shows a comparison of the mechanical properties of PLA to those of other common commodity plastics [2]. It is evident from the figure that PLA most closely resembles polystyrene, being characterized by a high modulus and low elongation to break. That is to say, PLA is a relatively brittle plastic but possesses good strength. Clearly, from an applications perspective, PLA should be able to compete with polystyrene.

However, for wide-spread acceptance, PLA must be competitive on a cost-performance basis. One of the essential features of cost effectiveness is the ability to run plastic-processing operations at high rates. Various operations require different material properties (for example, in film blowing, extensional strain hardening is highly desirable) and so commodity plastics are engineered to possess properties appropriate for the intended processing operation. A widespread method of imparting different melt flow properties into plastics is to alter the

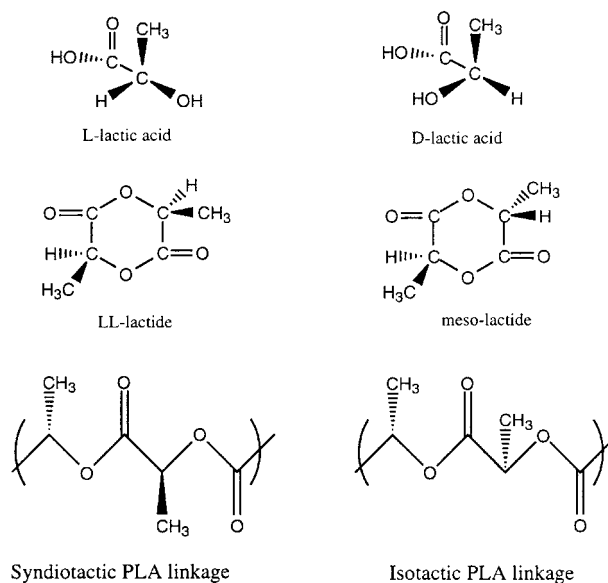


Fig. 2. Stereochemical features of PLAs. Mixed LL and *meso*-lactide content provides a means of controlling crystallinity and other chain properties.

chain architecture through the introduction of branching. This study investigates the effects of branching on the melt rheological and thermal properties of PLA.

MATERIALS AND METHODS

Due to the chiral nature of lactic acid, the stereochemistry of PLA is complex. Figure 2 shows the L and D enantiomers of lactic acid along with its possible dimer rings. These lactide rings are used as the monomer in producing the PLAs of this study. Control of the ratio of L to D monomer content is an important molecular feature of PLAs. Polymerization of the pure LL-lactide or the DD-lactide produces completely syndiotactic polymers (which are the mirror images of each other). Polymerization of the *meso* monomer produces an isotactic chain when the reaction proceeds with D-to-L stereocenter addition and a syndiotactic chain when the addition is D-to-D and L-to-L. Mixing of the monomers produces a polymer in which the strict stereoregularity is disrupted. Because the L-lactic acid is available from fermentation, high L-content polymers are of the greatest commercial interest. The notation here is to specify the L content first, such that a polymer containing 96% L stereocenters is denoted as PLA(96:04).

Polymers were synthesized in the melt using stannous octoate as a catalyst. For the custom synthesized

materials, the lactide monomers were charged at a fixed LL:DD ratio into a Haake Rheodyne 5000 mixing bowl and polymerizations were conducted at 180°C. Linear PLAs were initiated with 1,4-butanediol, four arm by 2,2-hydroxymethyl 1,3-propanediol, and six arm by 1,2,3,4,5,6-hexahydroxyhexane. Acetic anhydride was added in slight excess to convert the alcohol groups on the chain ends to nonreactive species. The PLAs were dissolved in dichloromethane to make a 10 wt.% solution that was subsequently added to a 50:50 by weight mixture of dichloromethane and methanol. Precipitation was aided by adding additional methanol, as needed, until the polymer could be filtered off as a white fibrous material.

Commercial grades of PLA were supplied by Cargill-Dow Polymers (CDP). These polymers have a 96:04 L:D content and are also produced by melt polymerization using stannous octoate as a catalyst. The commercial-grade branched material is produced through peroxide-initiated crosslinking of the linear material by reactive extrusion [3]. The reader is referred to a review of PLA polymerization chemistries for fur-

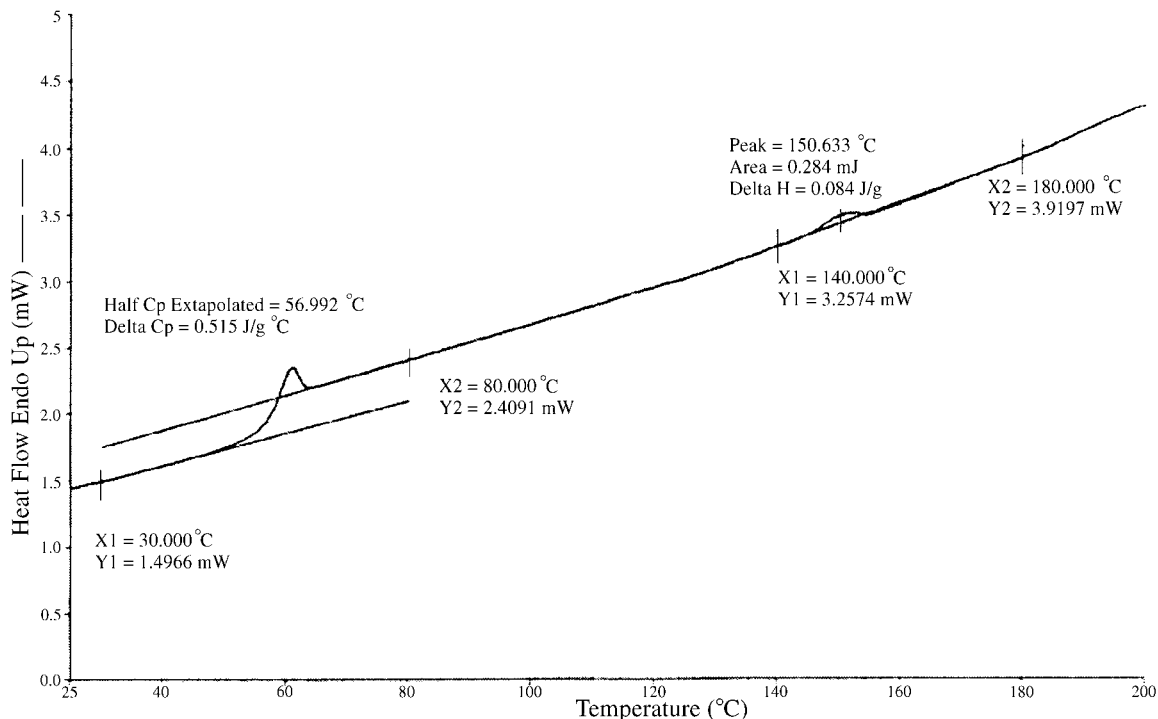


Fig. 3. DSC trace for a linear PLA; data, collected as samples, are heated from 25 to 200°C at 10°C/min. Pretreatment of the sample consists of heating to 200°C at 10°C/min, holding at 200°C for 5 min, and cooling to 25°C at 5°C/min.

ther details [4]. The linear material has a weight average molecular weight of $M_w = 111$ kg/mol and a polydispersity of 2.1; the branched PLA has a weight average molecular weight $M_w = 149$ kg/mol and a polydispersity of 2.9.

Materials were dried overnight in a vacuum oven at 40°C and 10 in. of water vacuum prior to testing. For dynamic testing, disks were compression molded at 180°C and redried at 40°C overnight in a vacuum oven.

RESULTS

The thermal properties of the two samples are manifested in the representative DSC traces shown in Figs. 3 and 4. Figure 3 is a characteristic result for the linear PLA sample. Five such linear samples were tested, leading to a measured glass transition temperature of $T_g = 58.4^\circ\text{C}$ and a standard deviation of $\pm 0.3^\circ\text{C}$. The corre-

sponding melting temperature for the linear material is $T_m = 151.7 \pm 0.6^\circ\text{C}$. Figure 4 is a characteristic result for the branched PLA sample. Testing of five samples gave a measured glass transition temperature of $T_g = 57.9 \pm 0.3^\circ\text{C}$ and a melting temperature of $T_m = 152.6 \pm 0.3^\circ\text{C}$. Accordingly, it is deduced that the transition temperatures are not influenced by changing the chain architecture through peroxide-initiated crosslinking.

However, it does appear that the rate of crystallization is affected. While both the linear and branched PLA samples received the same pretreatment, it is clearly evident from a comparison between Figs. 3 and 4 that the branched material undergoes significantly more recrystallization during the second heating. The interpretation of the broad exothermic trough as recrystallization was confirmed by annealing a branched sample at 100°C, rapidly cooling to 25°C, and reheating to 200°C at 10°C/min. Using this annealing procedure, the trough can be made to disappear and the degree of crys-

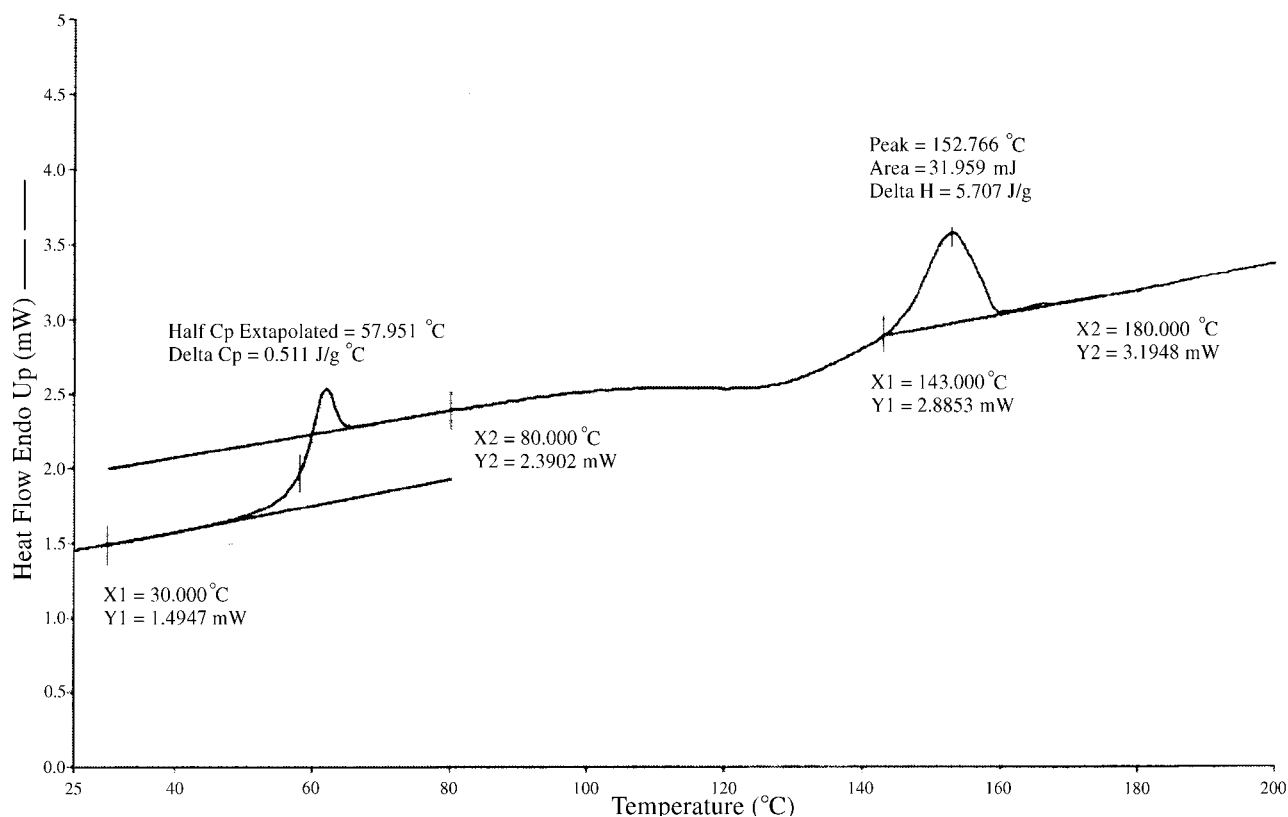


Fig. 4. DSC trace for a branched PLA; data in the same manner as for the linear sample. Note the broad recrystallization upon heating and the fact that the degree of crystallization is higher than in the linear material.

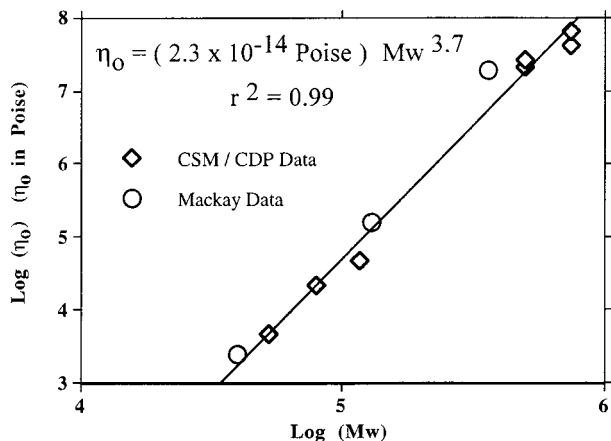


Fig. 5. Scaling of the zero shear viscosity with molecular weight for PLA(100:0) at 180°C.

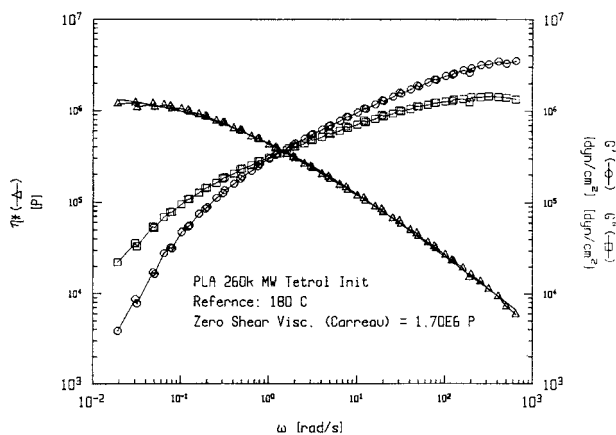


Fig. 6. Viscoelastic spectra for a tetrol-initiated (TI) four-arm PLA star, having a molecular weight of 260 kg/mol and a polydispersity of $p = 1.7$.

tallinity (as measured by the heat of fusion) is increased. Thus, it is inferred that the crystallization kinetics of the branched material are faster than the corresponding linear material.

Scaling of viscosity with molecular weight is one of the long-standing issues in polymer rheology. In this study, the complex viscosity versus shear rate is fit to the Carreau model using the Rheometrics Rhecalc software package in order to determine complex zero shear viscosities. Figure 5 shows the relationship between the zero shear viscosities and the weight averaged molecular for PLA(100:0) at 180°C. Included in this figure, is data from a recent study of the rheological properties of

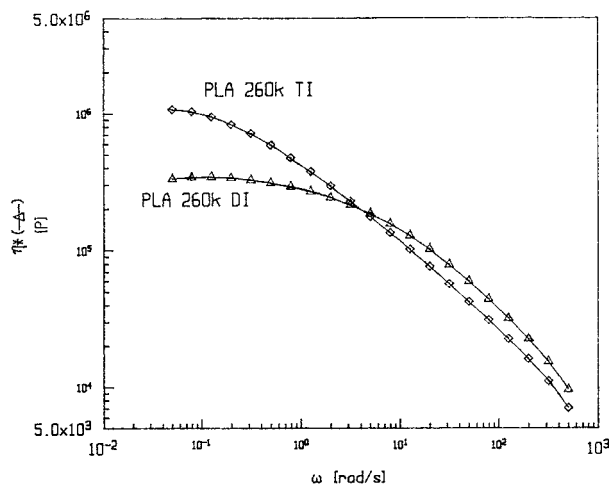


Fig. 7. Comparative flow curves for a tetrol-initiated (TI) four-arm PLA star and a diol-initiated (DI) linear PLA both having nominal molecular weights of 260 kg/mol. The star is characterized by a higher zero shear viscosity and stronger shear thinning. The test weight average molecular weight of the star is 230 kg/mol and the polydispersity is $p = 1.7$; the linear chain has a weight average molecular weight of 250 kg/mol and a polydispersity of $p = 1.6$.

linear PLAs by Mackay and co-workers [5]. A scaling exponent of 3.7 is found, rather than the usual 3.4 power normally associated with linear polymers. This observation is consistent with the high C_∞ values measured by Pennings and is in qualitative agreement with other recent results on PLAs [6]. However, the strong scaling exponent must be viewed with considerable skepticism given the usual uncertainty in molecular weight measurements and the fact that all of the data fall roughly within one order of magnitude in MW. Witzke and co-workers report the normal 3.4 power for amorphous PLAs having an L content less than 85% [2].

Figure 6 shows the dynamic viscoelastic spectrum of a tetrol initiated four-arm PLA star. One distinction between the linear and the star architecture is that the linear material exhibits a maxima in $G''(\omega)$ shortly after passing through the cross-over point [i.e., the frequency ω where $G'(\omega) = G''(\omega)$]. In contrast, $G''(\omega)$ continues to increase after the cross-over point for star polymers. This behavior is predicted by the Pearson–Helfand and subsequent theories [7–9]. Additional discussion of the dynamics of PLA star polymer dynamics can be found in Ref. [10]. This reference also discusses the comparative flow properties of star and linear architectures, an example of which is shown in Fig. 7. In this figure, the complex viscosity of the four-arm tetrol-initiated star is

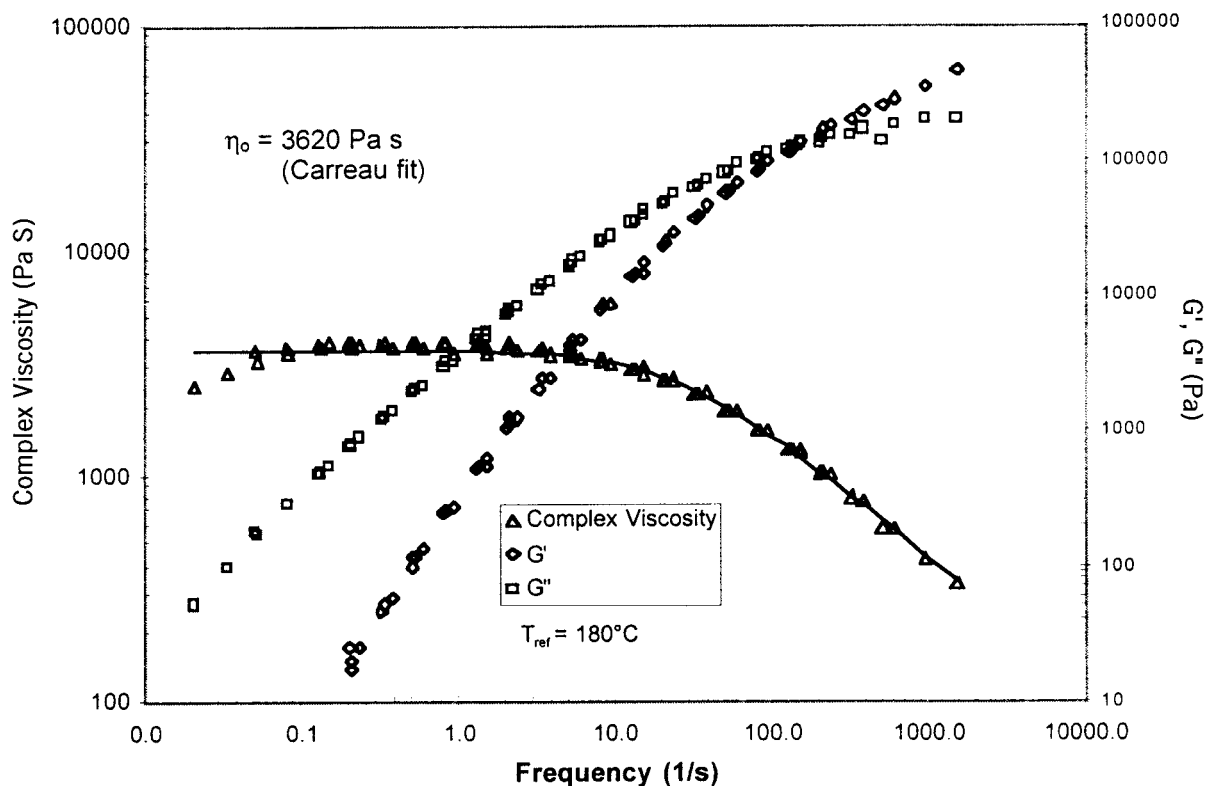


Fig. 8. Viscoelastic spectra for a linear commercial grade PLA(96:04) having a weight average molecular weight of 111 kg/mol and a polydispersity of $p = 2.1$. The measured zero shear viscosity is 3620 Pa s while the correlation of Fig. 3 provides a value of 3780 Pa s.

plotted on the same scale as a linear PLA of the same composition and molecular weight. It is seen that the star material has a higher zero shear viscosity and a lower viscosity at high shear rates. Such findings are typical for branched materials [11].

Attention is now turned to the commercial-grade materials. Figure 8 provides the viscoelastic spectrum for the linear architecture, while Fig. 9 shows the results obtained for the branched material. Some interesting points can be made. First, if the correlation of Fig. 5 is used to predict the zero shear viscosity of the linear commercial material, a value of 3780 Pa s is obtained. This is in good agreement with the measured value of 3620 Pa s (4.4% error). Second, the spectra for the branched commercial material in Fig. 9 shares many features with the star polymer spectra of Fig. 6. This includes a broad curvature over many decades of frequency in the viscoelastic moduli and the lack of an immediate maxima in $G''(\omega)$ after the cross-over point.

The most striking rheological contrast is evidenced in Fig. 10 where the flow curves of the commercial-

grade branched material is compared to the linear material. Again, a strong similarity with the model system of PLA four-arm stars vs. linear PLA is exhibited. These finding, combined with the above results, suggest that the peroxide cross-linked PLA is starlike in many of its rheological features.

DISCUSSION

For star polymers and other highly branched systems, the span molecular weight (M_s) is an important concept. The span molecular weight is simply defined as the longest linear chain span found in the polymer molecule, starting at one chain end and ending at another. For example, in a star polymer, the longest span begins at the end of one of the star arms and ends at another. Accordingly, the span molecular weight is equal to twice the arm molecular weight for star polymers. Theory predicts and experiment confirms that the zero shear viscosity of well-defined monodisperse star polymers depends only on the span molecular weight.

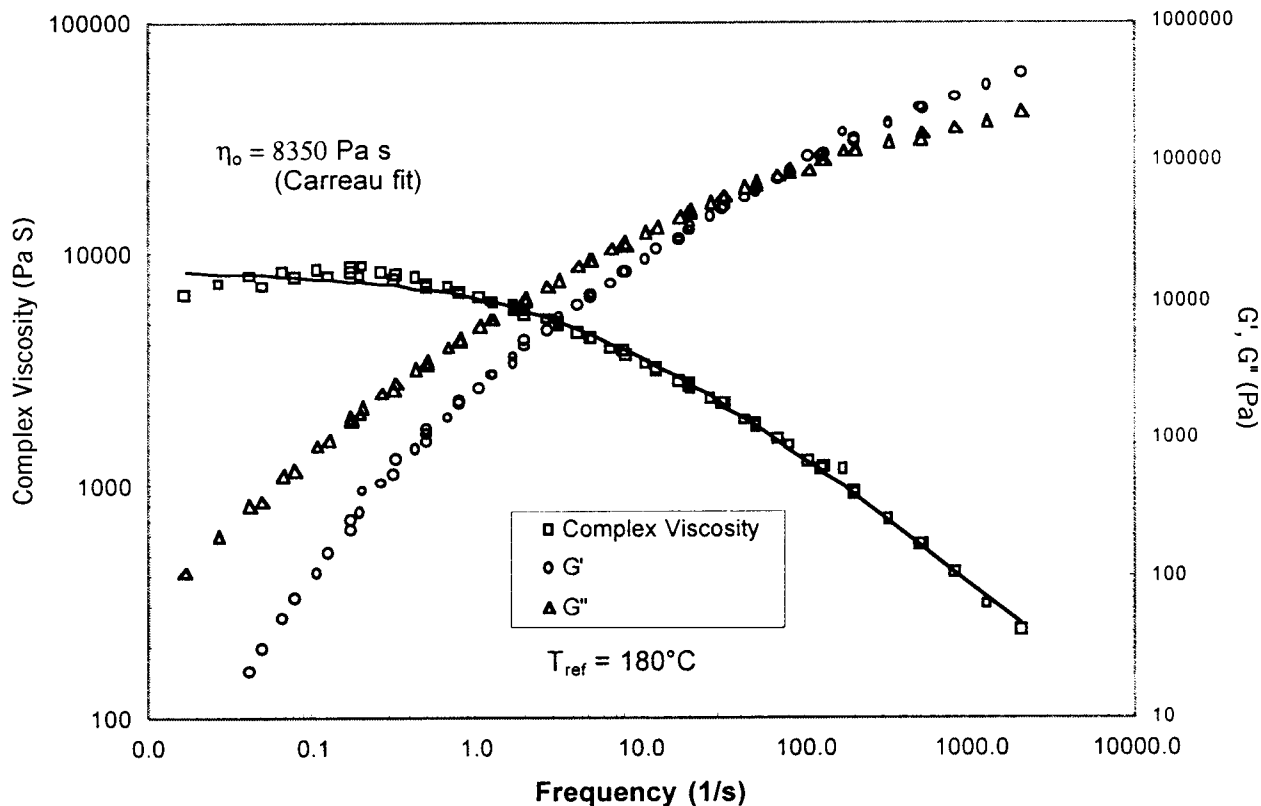


Fig. 9. Viscoelastic spectra for a branched commercial-grade PLA(96:04) having a weight average molecular weight of 149 kg/mol and a polydispersity of $p = 2.9$. Note the similarity of these spectra to those of the four-arm star shown in Fig. 4.

Figure 11 presents an engineering correlation between the measured zero shear viscosity and the span molecular weight. This correlation is derived from earlier results on six different PLA star polymers [10]. The spread in the data is probably due to polydispersity effects. Despite these limitations, the data can be usefully employed in order to infer something about the structure of the peroxide-branched commercial-grade PLA.

If the measured zero shear viscosity of the branched PLA is inserted into the correlation of Fig. 11, a span molecular weight may be calculated. This calculation results in a value of around 65,000 g/mol (63,300 g/mol). If instead, the molecular weight of the branched material is divided by two, then a value of about 75,000 g/mol is arrived at (74,500 g/mol). This agreement is reasonable, given the scatter in the data of Fig. 11, along with the usual uncertainty in molecular weight determination. The peroxide crosslinking must produce a material with less than two crosslinks per chain, otherwise a gel would be produced. Ideally, the reaction could be controlled such

that, on average, there is only one crosslink per chain. The resulting branched material then looks like a four-arm star with significant polydispersity in the arms (an asymmetric four-arm star). The value obtained for the span molecular weight for the measured sample is lower than the idealized four-arm star, but is within the range of error associated with the correlation. However, it could also be due to the presence of linear chains in the branched material. The GPC traces for the branched material are continuous, so resolving the linear and branched content is a difficult undertaking. The present approach, based on zero shear viscosity, provides a simpler, and more direct, method for gathering insight into the molecular structure of the branched commercial sample.

CONCLUSIONS

The present study examines several features of two commercial grade PLA samples; one linear and one

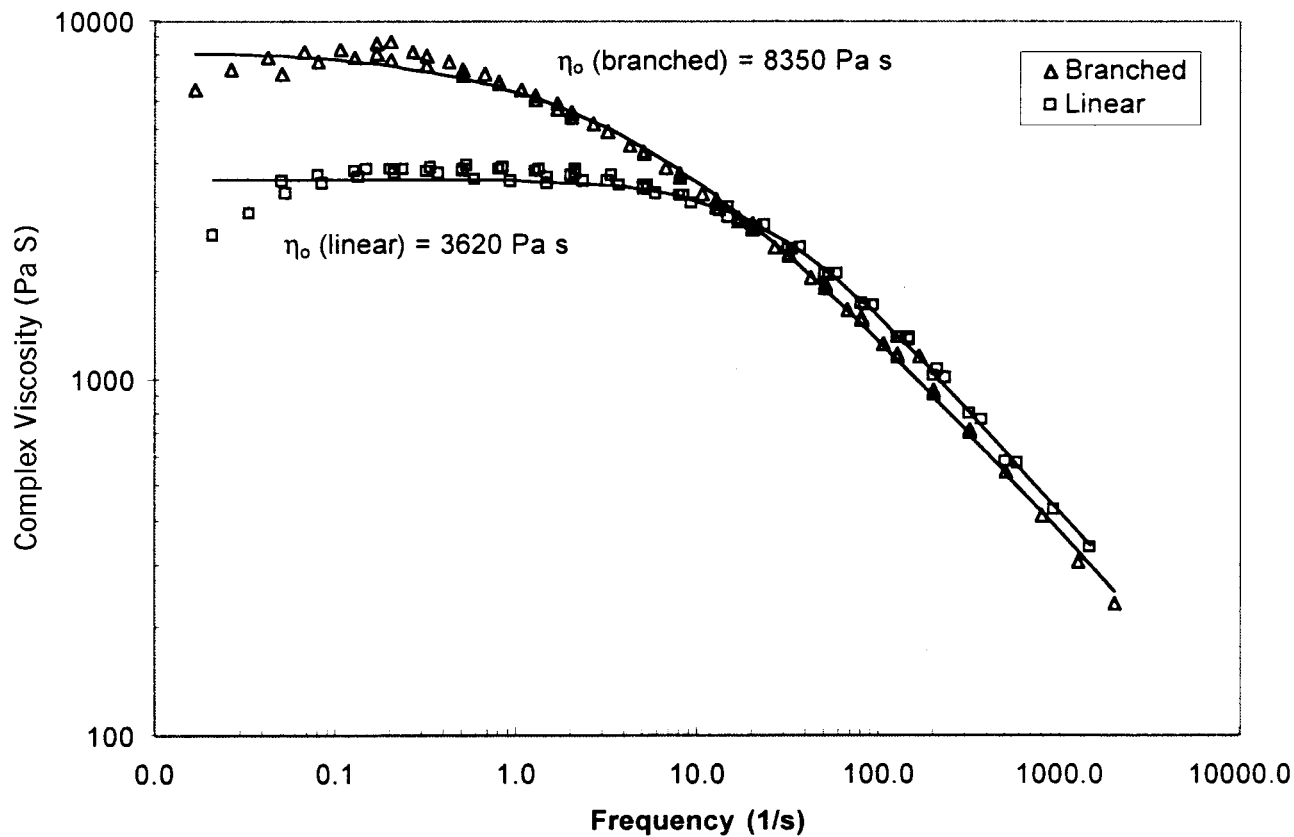


Fig. 10. Comparative flow curves for the commercial-grade branched and linear materials. Branching provides a higher zero shear viscosity and stronger shear thinning. These results closely resemble those of Fig. 5.

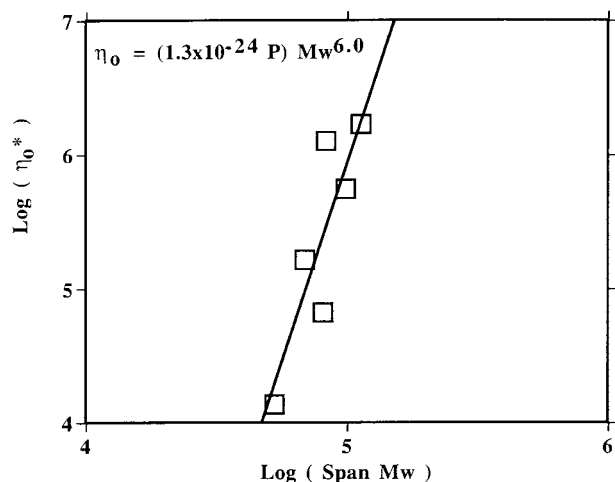


Fig. 11. Engineering correlation between the zero shear viscosity and the span molecular weight, as determined using a series of four- and six-arm PLA stars.

branched. Differential scanning calorimetry measurements demonstrate that the glass transition and melting temperatures of the different architectures are indistinguishable. However, the branched material crystallizes more quickly than does its linear counterpart.

Through a comparison with very well-defined linear and star PLA samples, significant insight into the commercial samples can be gained. Longer relaxation times in the terminal region for the branched material, compared to the linear material, manifests itself as a higher zero shear rate viscosity. However, the branched material shear thins more strongly, resulting in a lower value of viscosity at high shear rates. Comparison of the linear viscoelastic spectra of the branched material with the spectra for star PLAs suggests that the branched architecture is characterized by a span molecular weight of approximately 63,000 g/mol. The present study conclusively demonstrates that a wide spectrum of flow properties are available through simple architectural modifica-

tion of PLA thus allowing the utilization of this important degradable thermoplastic in a variety of processing operations.

REFERENCES

1. R. Datta, S. Tsai, P. Bonsignore, S. Moon, and J. R. Frank (1995) *FEMS Microbiol. Rev.* **16**, 221–231.
2. D. R. Witzke (1997) *Introduction to Properties, Engineering, and Prospects of Polylactide Polymers*, Michigan State University, Ann Arbor, MI, p. 389.
3. P. R. Gruber, M. H. Hartmann, J. J. Kolstad, D. R. Witzke, and A. L. Brosch (1996) *Method of Crosslinking PLA*, USA, PCT 94/08 508.
4. M. H. Hartman (1998) *High Molecular Weight Polylactic Acid Polymers* D. H. Kaplan (Ed.), Springer Verlag: Berlin, pp. 367–411.
5. J. J. Cooper-White and M. M. Mackay (1999) *J. Polym. Sci. Part B: Polym. Phys.* **37**, 1803–1812.
6. J. Wang, R. Kean, J. Randall, and D. Giles (1997) *Society of Rheology Annual Meeting Poster PO24: Melt Rheology of Polylactide*, Columbus, OH.
7. D. S. Pearson and E. Helfand (1984) *Macromolecules* **17**, 888–895.
8. R. C. Ball and T. C. B. McLeish (1989) *Macromolecules* **22**, 1911–1913.
9. S. T. Milner and T. C. B. McLeish (1997) *Macromolecules* **30**, 2159–2166.
10. J. R. Dorgan and J. S. J. Williams (1999) *Rheology* **43**, 1141–1155.
11. W. W. Graessley (1977) *Accnts. Chem. Res.* **10**, 332–339.