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Preparation and Characterization of a Branched Bacterial Polyester

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ABSTRACT: The preparation, rheological behavior, and solution properties of branched poly(3-hydroxy butyrate)-*co*-(3-hydroxy valerate), PHBV, are described. Branching is produced by the use of dicumyl peroxide (DCP) during the reactive extrusion of PHBV. The shear viscosities of reactively extruded PHBV and the straight-chain polymer of similar molecular weight are nearly identical, but the reactively extruded PHBV's elongational viscosity is considerably higher. High elongational viscosity of these polymers results from a branched structure produced when extrusion is carried out in the presence of small amounts of DCP (0.025−0.3 wt %). Strain hardening is observed in the elongational response of the branched PHBV at all deformation rates and increases with increasing concentrations of DCP. Study of the solution properties of the linear and branched PHBV indicates larger hydrodynamic volume compared to that of polystyrene of comparable molecular weight. Mark−Houwink plots, observed for PHBV, exhibited increasing nonlinearity with increasing DCP content. Trifunctional branching frequencies computed on the basis of intrinsic viscosity ratios indicated explosive growth in branching, possibly due to the generation of microgel, when branching reactions are initiated with a DCP level exceeding 0.2 wt %.

Introduction

Poly(3-hydroxy alkanoates) (PHA's) are thermoplastic polyesters made from bacterial fermentation. The polymers are produced as internal carbon and energy storage materials during bacterial growth. Since their discovery in the beginning of this century,[1] PHA's have become one of the most studied biodegradable polymers, made from renewable sources.[2−10] The materials are generally aliphatic, 100% stereospecific, and produced in vivo at high molecular weights (up to several million).

The biodegradability of PHA's makes them desirable materials for a variety of commercial applications. However, thermal processing of the most common and widely studied PHA, poly(β-hydroxy butyrate), PHB, is limited by thermal degradation resulting from the need to process the polymer at or above 190 °C due to its melting temperature of approximately 178 °C. This shortcoming can be overcome by copolymerization of PHB with hydroxyvaleric acid. The resulting copolymer, PHBV, has the lower melting point and lower processing temperatures required to minimize thermal degradation.[2] Since the discovery of PHBV (commercialized under the trade name Biopol), PHA's with a variety of copolymer compositions have been produced by changing the feedstocks and altering the microorganisms.[3−10] These modifications include the introduction of functional groups in the side chains or variation of the number of methylene groups in the polymer's main chain and/or its side chains. By altering the copolymer composition, different polyesters can be formed with properties ranging from highly crystalline, rigid plastics to rubbery elastomers. A feature common to all PHA's produced by microbial synthesis is a highly stereoregular linear polymer chain. Thermal processing of PHA's into useful articles, at least in some cases, requires long-chain branching. Branching and cross-linking in PHA's using peroxides have previously been described.[11−13] In this paper the preparation of branched PHBV polymers via reactive extrusion with peroxides and the characterization of the resulting polymers are reported.

Experimental Section

Sample Preparation. Dicumyl peroxide (DCP) was used as the free radical initiator to produce branching in microbially produced linear chain PHBV with HV content of approximately 5 mol %. DCP was purchased from the Aldrich Chemical Co. and had a purity of greater than 98%. The PHBV was used in pellet form without additional processing.

A homogeneous branched material was obtained by extrusion of PHBV pellets sprayed with DCP dissolved in a volatile solvent (acetone or methanol) and sufficiently mixed to completely coat the DCP onto the pellets. The solvent was allowed to evaporate before the coated pellets were fed into the extruder.

The extruder used was a Leistritz micro 18 in. twin-screw extruder equipped with corotating screws. The L/D ratio was equal to 30/1. During the reaction some volatile byproducts such as acetophenone and α-methylstyrene were formed. Atmospheric devolatilization was used to remove these compounds. The set temperatures used in the subsequent zones of the extruder were 50, 100, 150, 160, 160, and 165 °C.

Polymer Characterization: Rheological Properties. The rheological properties of the branched materials were measured on a Rheometrics elongational flow rheometer (RME) and on a capillary rheometer Rosand, type RH7-2. Measurements of the samples were carried out at a temperature of 175 °C, which is well above the melting point of the material. Transient shear experiments at lower shear rates were carried out on a Rheometrics RDA-2 instrument, using a parallel-plate geometry at 175 °C.

Polymer Characterization: Molecular Weight and Solution Properties Analysis. The molecular weight of the starting polymers and branched materials was determined using size-exclusion chromatography (SEC) methods. Relative molecular weight distribution averages were determined by polystyrene calibration. SEC separation was accomplished with three mixed bed styragel-type SEC columns (Polymer Laboratories Inc.). A set of 15 nearly monodisperse polystyrene calibrants (Toya Soda Co.) ranging in molecular weight from 1 600 000 to 580 were used to generate the calibration curve.

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Table 1. Molecular Weight Distribution Averages, Intrinsic Viscosities, and Branching Parameters for PHBV Polymers

polymer	DCP (wt %)	M_n(G)[c] (g/mol)	M_w(G) (g/mol)	M_z(G) (g/mol)	M_n(V)[d] (g/mol)	M_w(V) (g/mol)	M_z(V) (g/mol)	IV (dL/g)	g_v	B_n[e]
PHBV1[a]	0	157 950	472 700	905 500	111 050	303 650	562 100	2.20	1.0	0
PHBV2[b]	0	129 750	380 900	747 150	93 850	248 700	466 650	1.88	1.0	0
PHBV3	0.025	125 650	380 400	749 150	87 850	243 200	463 000	1.90	1.0	0
PHBV4	0.05	129 350	403 050	833 800	90 150	261 400	524 900	1.95	0.977	0.34
PHBV5	0.1	135 150	417 900	928 550	89 100	272 050	549 800	1.93	0.963	0.57
PHBV6	0.2	127 900	465 150	1 289 500	87 400	312 150	844 700	1.98	0.934	1.10
PHBV7	0.3	109 100	561 400	3 012 500	72 900	437 150	2 520 000	1.84	0.786	5.69

[a] Unprocessed PHBV. [b] Extruded PHBV. [c] Molecular weight based on polystyrene calibration. [d] Molecular weight based on viscosity. [e] Branches/molecules.

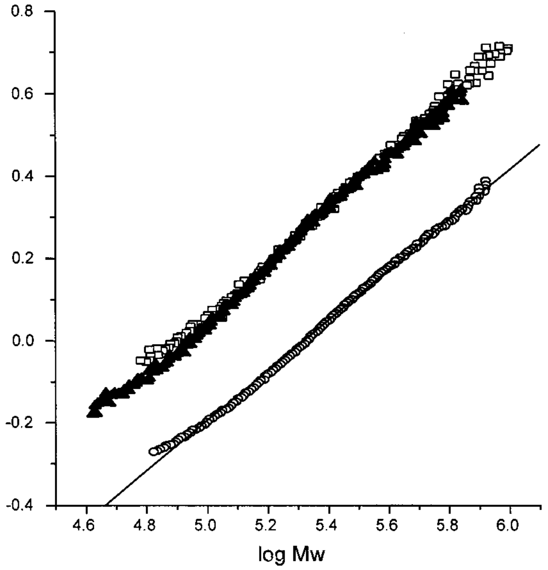

Figure 1. Mark−Houwink plots for polystyrene (circles), PHBV (squares), and processed PHVB (triangles).

The chromatographic mobile phase and polymer solvent was chloroform (Burdick and Jackson Co.). A gravimetrically determined flow rate of 0.89 mL/min was used. An injection volume of 400 μL was employed, and the concentration of injected polymer solutions was 0.2% (w/v).

Absolute molecular weight distribution averages and Mark−Houwink constants were obtained using a dual-detector model 150 CV chromatograph (Waters Chromatography Inc.). This SEC system detected eluting polymer with an in-line viscometric (VISC) detector and a differential refractive index (DRI) detector. The determination of molecular weight distribution averages followed the general procedures previously described.[14] Mark−Houwink constants were determined using the general methodology recently described.[15]

Results and Discussion

Molecular Weight Analysis of PHBV. Molecular weight distribution averages and weight-average intrinsic viscosities for extruded PHBV polymers prepared with DCP levels ranging from 0 to 0.3 wt % are summarized in Table 1. Molecular weights were determined by two size-exclusion chromatography (SEC) methods: SEC/viscometry (SEC/VISC) and polystyrene-based SEC (conventional SEC).

Significant differences between molecular weight averages calculated by the two methods are apparent in Table 1. Molecular weights determined by conventional calibration were nearly twice the values measured by SEC/VISC. The source of this discrepancy was traced to differences between the solution properties of PHBV and polystyrene. As shown in Figure 1, the intrinsic viscosity (IV) of PHBV was approximately twice the IV of polystyrene at constant molecular weight. These differences result from the larger hydrodynamic volume for PHBV compared to that of polystyrene of equivalent molecular weight. Consequently, calibration based on polystyrene calibration overestimates PHBV molecular weights. For example, M_w(G) for unextruded PHBV, based on polystyrene calibration determinations, was approximately 56% larger than the viscosity-based value, M_w(V) (see Table 1).

Dependence of Molecular Weight on Extrusion. Extrusion of PHBV without DCP decreased the weight-average molecular weight of the polymer from 303 650 to 248 700 g/mol (see Table 1). Observed molecular weight results were consistent with degradative chain scission upon extrusion. Corresponding solution properties for PHBV and extruded PHBV depicted in Figure 1 exhibited the expected linear Mark−Houwink plot[16] of a flexible linear chain. The near-perfect overlap of the data indicated no measurable changes in chain conformation accompanied the chain degradation.

Rheological Properties of Branched PHA Polymers. The products of reactive extrusion of PHBV in the presence of dicumyl peroxide (DCP) were first analyzed by a variety of rheological techniques. Polymers produced using different levels of DCP were characterized for their degree of branching using both a Rheometrics elongational flow rheometer (RME) and a capillary rheometer. Although the RME gives exact elongational viscosity values in a uniform uniaxial flow field, the experimental method is quite cumbersome whereas the use of a capillary rheometer is much more straightforward.

The molecular weight dependence of the zero shear viscosity for both the linear and the branched polymers using different levels of DCP is represented in Figure 2. The molecular weight data used in the figure were based on polystyrene calibration. The experimental value of the slope of the viscosity−MW dependence for the linear PHBV's is equal to 3.35. This is close to the theoretical value of 3.4 for linear polymers of narrow molecular weight distributions at molecular weights above the critical molecular weight for entanglement. As can be noticed, the zero shear viscosities of the branched materials produced at DCP levels lower than 0.3 wt % coincide well with the curve for the linear polymers. At the highest DCP concentration, the zero shear viscosity becomes smaller than the corresponding value for the linear polymer. This is characteristic for a highly branched material showing a considerable decrease in the radius of gyration compared to the corresponding linear polymer.[17]

Shear viscosity as a function of shear rate for polymers having different degrees of branching were measured on a capillary rheometer at a temperature of 175 °C. Shear rates lower that 10 s^{-1} could not be obtained due to the long equilibration time required and the

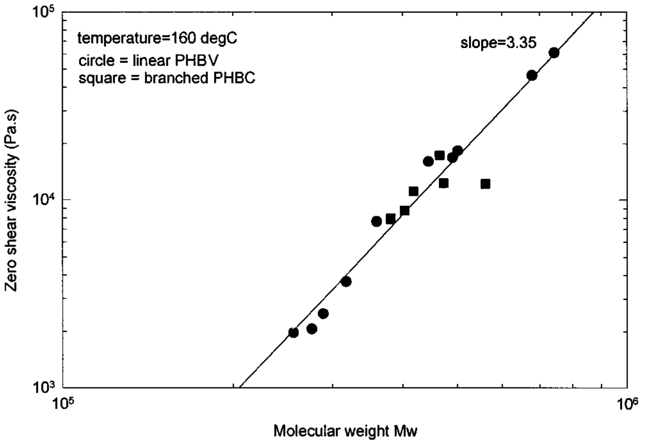

Figure 2. Dependence of the zero shear viscosity of linear and branched PHBV on the molecular weight of the polymer. Molecular weights are based on polystyrene calibration.

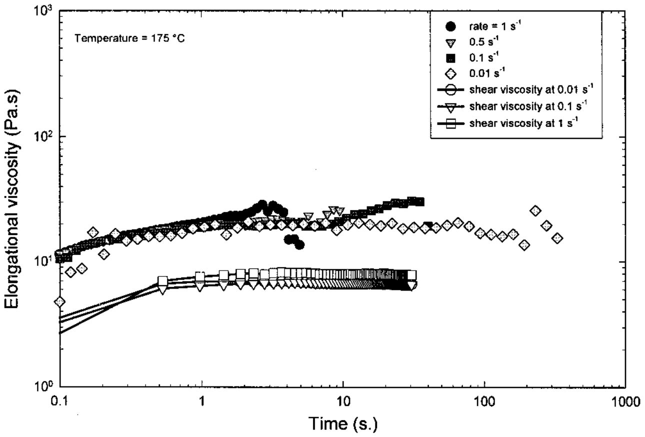

Figure 3. Start-up experiments in the shear flow and in elongational flow for linear PHBV (Rheometrics RME).

resulting thermal degradation occurring within this time period. Again, almost no differences in shear behavior could be observed between materials prepared using different levels of DCP.[18]

Figure 3 compares the transient response in both a shear and an elongational flow field for a linear PHA, at low rates of deformation. The experiments were carried out on a Rheometrics elongational flow rheometer. The results are shown at four different strain rates ranging from 0.01 to 1 s^{-1}. For these rates of deformation both the shear and the elongational response are situated within the linear viscoelastic region, with a ratio between the elongational and the shear viscosity of 3. This is equal to the theoretical Trouton ratio for the linear viscoelastic region. The mechanical response almost instantaneously attains equilibrium, indicating the near absence of elasticity in the polymer melt.

Figure 4 shows the elongational flow properties of the material produced from the straight-chain PHBV shown in Figure 3 after reaction with 0.2 wt % DCP. The shear viscosity shows a nonlinearity, especially at the higher deformation rates. Moreover, the time required to reach equilibrium increases considerably compared to that of the linear polymer. This can be attributed to the presence of higher relaxation times in the relaxation spectrum of the reacted polymer. However, the branched structure becomes much more evident from the elongational viscosity for which a clear strain hardening is observed at all deformation rates. Rupture of the sample occurred before a steady-state value of the elongational viscosity could be attained. As the mean value for M_w of the branched material is comparable to the respective value of the linear polymer, it can be concluded that the stiffening effect is caused by the presence of long-chain branching in the DCP-modified polymer rather than by the presence of a certain amount of high molecular weight polymer chains which can lead to a similar effect.[19] This effect of long-chain branching on the elongational viscosity has previously been reported for other polymers.[20-22]

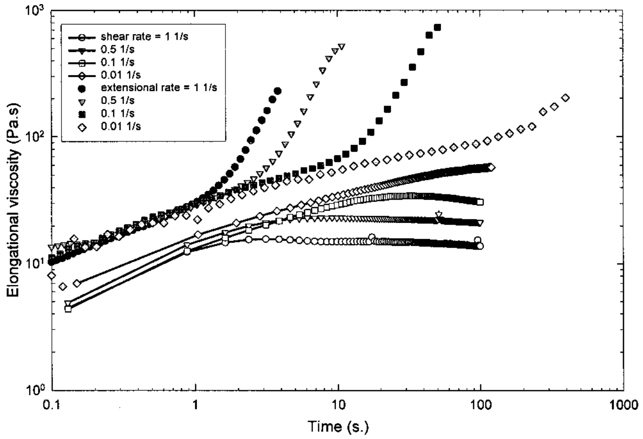

Figure 4. Start-up experiments in the shear and elongational viscosity for a branched PHBV produced using 0.2% DCP (Rheometrics RME).

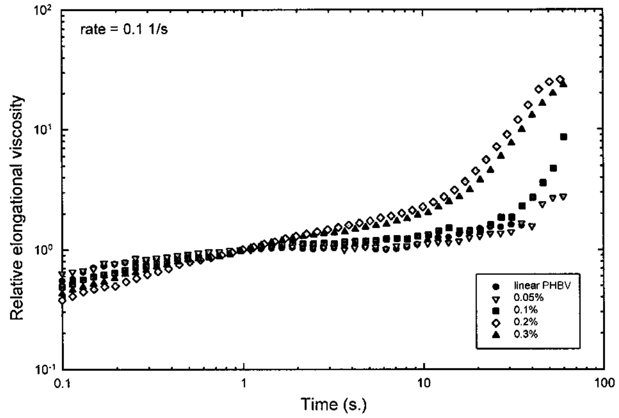

Figure 5. Effect of the concentration of DCP on the start-up of the elongational flow.

Figure 5 shows the increase in elongational viscosity at a strain rate of 0.1 s^{-1} for the PHBV polymers produced using different concentrations of DCP. To scale for small differences in molecular weight, hence small shifts in the steady-state viscosity values, the different curves have been divided by the respective viscosity at a strain of 0.1. This explains why all curves coincide at that particular strain value. From the figure it is clear that the extent of the strain hardening increases with an increasing concentration of DCP. An increasing concentration of free radical initiator will increase the number of radicals formed. Increasing the DCP concentration will increase the frequency of the branches rather than their length. Even at a concentration of 0.05 wt % a minor degree of strain hardening can be observed, indicating some degree of branching. Interestingly, no differences in the strain hardening were observed between 0.2 and 0.3 wt % DCP, at least not at the time scales or the strains probed here (Figure 5).

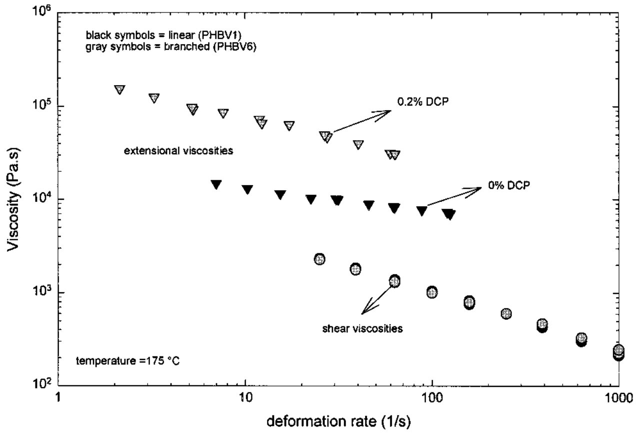

Figure 6. Effect of branching on the shear viscosity (circles) and the elongational viscosity (triangles), as measured in a capillary rheometer. The elongational viscosity was determined from the entrance pressure drop using Cogswell's analysis (capillary data).

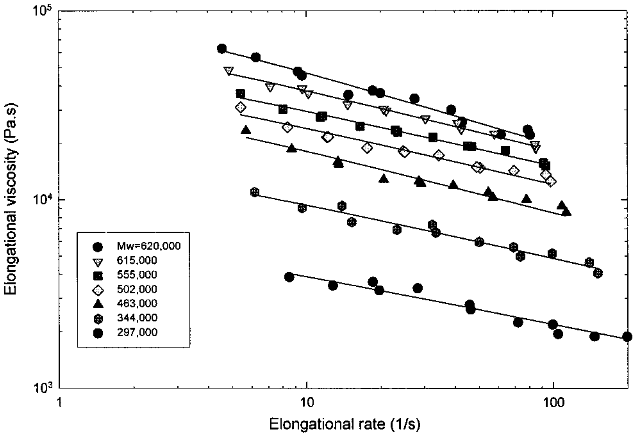

Figure 7. Effect of molecular weight on the elongational viscosity of linear PHBV (capillary data).

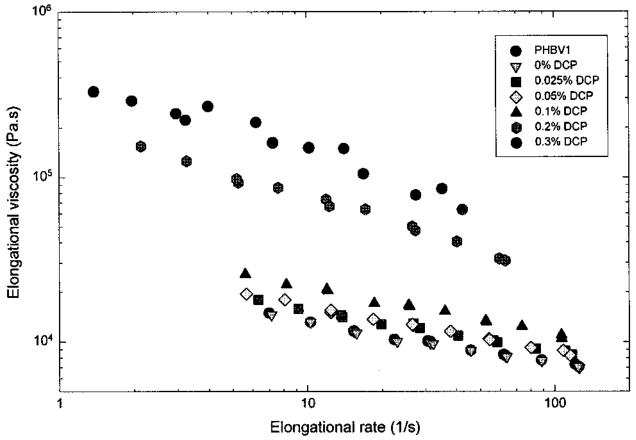

Figure 8. Effect of branching on the elongational viscosity for branched PHBV as determined from entrance pressure drop.

This may be due to rupture of the sample before a steady state in the elongational viscosity could be attained. An increase in the initial slope of the transient of the elongational response was also observed. This trend reflects the increasing elasticity of the polymer with increasing branching level. Similar conclusions could be drawn from normal force measurements where an increase in the first normal force difference N1 was observed with increased level of branching (data not included).

Next to the RME rheometer other more approximate methods have been proposed in the literature to measure the elongational flow properties of molten polymers. One of these methods is the use of convergent flow as can be carried out in a capillary rheometer. In the latter the elongational viscosity can be calculated from the entrance pressure drop (Bagley correction) using Cogswell's analysis.[23] The usefulness of this approach has been demonstrated recently by Laun and by Padmanabhan et al.[24,25] These researchers showed that the elongational viscosity calculated using this approach was comparable to the value obtained from the transient response at a strain level of about 3 irrespective of the rate of deformation. Figure 6 shows both the shear and the elongational viscosity of a linear and a branched PHBV prepared using 0.2 wt % DCP as measured in a capillary rheometer. The data illustrate that the shear viscosities of both linear and branched polymers are almost equal, as these are mainly determined by the molecular weight of the polymer. Elongational viscosity is much larger for the branched material than for the linear polymer due to the existence of strain hardening in the elongational response of the branched product.

One of the difficulties in the interpretation of the viscosity data as derived from a capillary rheometer, and how they are linked to the structure of the polymer, is that branching as well as an increase in molecular weight of linear PHBV will have a similar effect on the absolute values of the elongational viscosity. Figure 7 shows the elongational viscosity for linear PHBV with increasing molecular weights. It is clear that an increase in molecular weight leads to an increase of the absolute values of the elongational viscosity but also to an increase of the shear viscosity as can be observed in Figure 2. An increase of the elongational viscosity can also be expected from an increase of the level of branching as shown in Figure 8. At higher deformation rates a clear distinction can be made between the branched materials produced using 0.2 and 0.3 wt % DCP both in normal force measurements and in the uniaxial elongational flow measurements. As discussed previously, the influence of an increasing degree of branching on the shear viscosity, at a constant molecular weight, is negligible (Figure 3).

It can be concluded that both an increasing degree of branching and an increase of molecular weight have a similar effect on the value of the elongational viscosity as measured in a capillary rheometer but a different effect on the shear viscosity. Branching can only be characterized using a capillary rheometer by considering the ratio of the elongational to the shear viscosity at a particular rate of deformation but corrected for differences in molecular weight. The effect of M_w can be taken into account by dividing the ratio of the elongational to the shear viscosity for the branched material by the same parameter for the linear polymer, considered at the same rate and at the same value for the shear viscosity. Using viscosity ratios assumes that a similar shear viscosity for the branched and the linear PHBV corresponds to an identical molecular weight of both materials.

In Figure 9 the effect of DCP concentration on the ratio of elongational to shear viscosity, corrected for differences in molecular weight, is plotted at a rate of

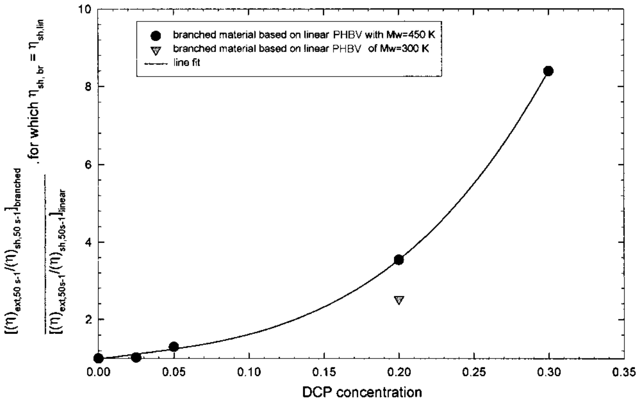

Figure 9. Influence of DCP concentration on the degree of strain hardening as determined in a capillary rheometer. Branched PHBV produced from linear PHBV with M_w of 450 000 g/m (circles) and 3 000 000 g/m (triangle). Fitted line shown for 450 000 g/mol data.

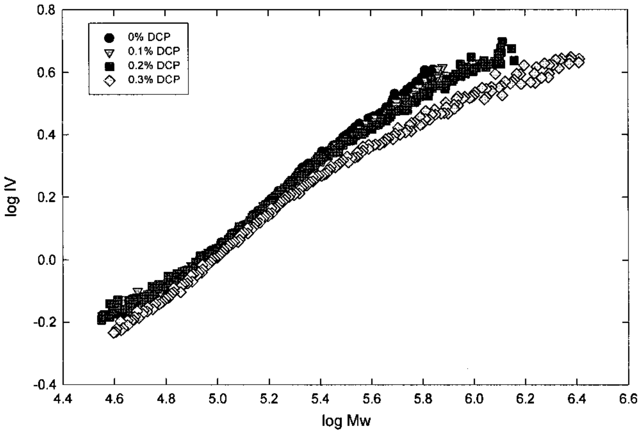

Figure 10. Mark−Houwink behavior of PHBV as a function of wt % DCP.

deformation of 50 s^{-1}. It is clear that an increasing concentration of DCP results in an increase of the degree of branching, hence an increase of the strain hardening. Adding 0.025 wt % DCP does not lead to any noticeable degree of strain hardening. At 0.05 wt % a clear effect can already be noticed. Note that at a concentration of 0 wt % DCP the relative number is equal to 1, indicating a rheological behavior identical as for the nonreacted material, i.e., a linear polymer showing no strain hardening.

Solution Properties Analysis of Branching in PHBV. The rheological properties of PHBV polymer correlate with changes in polymer structure which are consistent with chain branching. Additional insight into the nature of PHBV branching was obtained from solution properties analysis.

Mark−Houwink plots for PHBV of varying DCP content displayed changes in polymer solution properties consistent with the formation of branches.[16] As shown in Figure 10, Mark−Houwink plots exhibited increasing nonlinearity with increasing DCP content. The curvature in the plots was particularly apparent for the polymer of greatest DCP content, 0.3 wt %. The trend in the Mark−Houwink exponent, alpha, as a function of DCP content also tracked polymer chain branching. Alpha decreased with increasing DCP as shown in Figure 11. Variations in molecular weight and intrinsic viscosity with DCP content, depicted in Figure 12, were consistent with the expected increase in molecular weight and corresponding intrinsic viscosity decrease due to branch formation as DCP content increased.

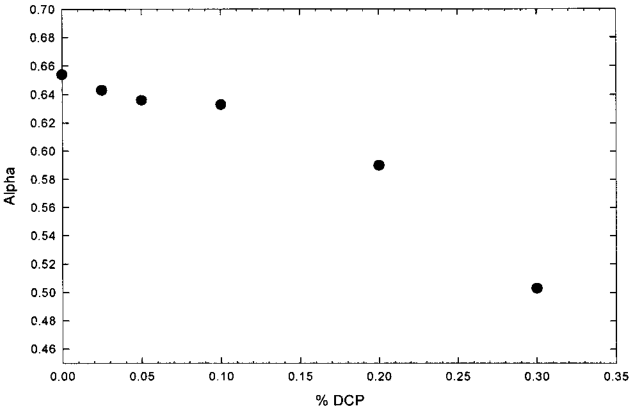

Figure 11. Mark−Houwink exponent (alpha) versus wt % DCP.

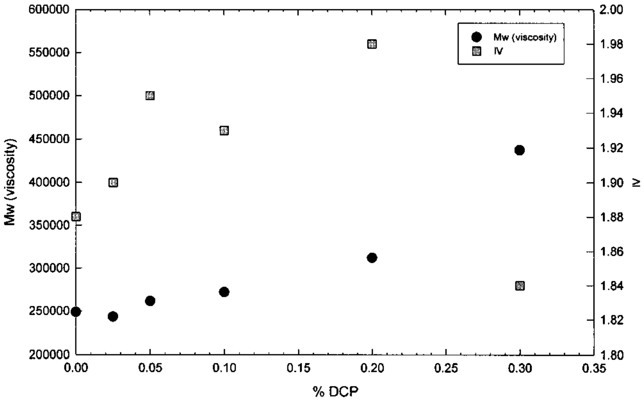

Figure 12. M_w and IV for PHBV as a function of wt % DCP.

Models for DCP Promoted Branching. Insights into the nature of branched PHBV were obtained from *g*-factors calculated from Mark−Houwink plots. The analysis of branching frequency from *g*-factors is well-known[26] for trifunctional long-chain branching:

$$g_M = [(1 + B_n/7)^{1/2} + 4B_n/(9\pi)]^{-1/2} \tag{1}$$

where g_M is the ratio at constant molecular weight of the radius of gyration for branched polymer, $\langle R_g\rangle_b$, to radius of gyration for the linear polymer, $\langle R_g\rangle_l$:

$$g_M = \langle R_g\rangle_b/\langle R_g\rangle_l \tag{2}$$

The *g*-factor based on radii of gyration can be related[25] to the intrinsic viscosity *g*-factor at constant molecular weight, g_v, by

$$g_M = g_v = ([\eta]_b/[\eta]_l)^{1/\epsilon} \tag{3}$$

where $[\eta]_b$ and $[\eta]_l$ are the intrinsic viscosities of the branched and linear polymers, respectively, and ϵ is a constant varying between 0.5 and 1.5 depending on the draining of the polymer.[27]

In the present study PHBV was assumed to be free draining for which ϵ has a value of unity.[27] Intrinsic viscosities for the branched and linear polymers shown in Figure 11 were used to generate plots of g_v versus log molecular weight presented in Figure 13.

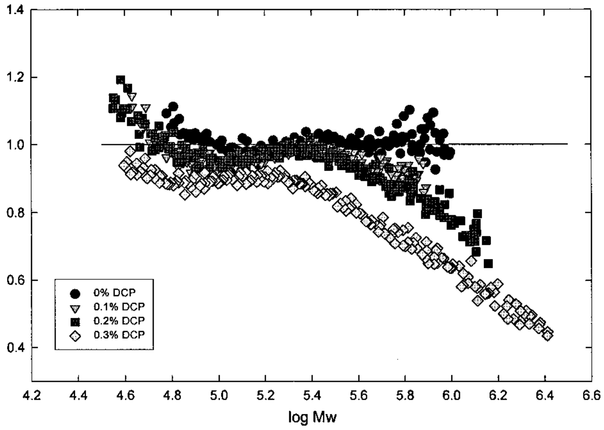

Figure 13. Dependence of g_v on polymer molecular weight as a function of wt % DCP.

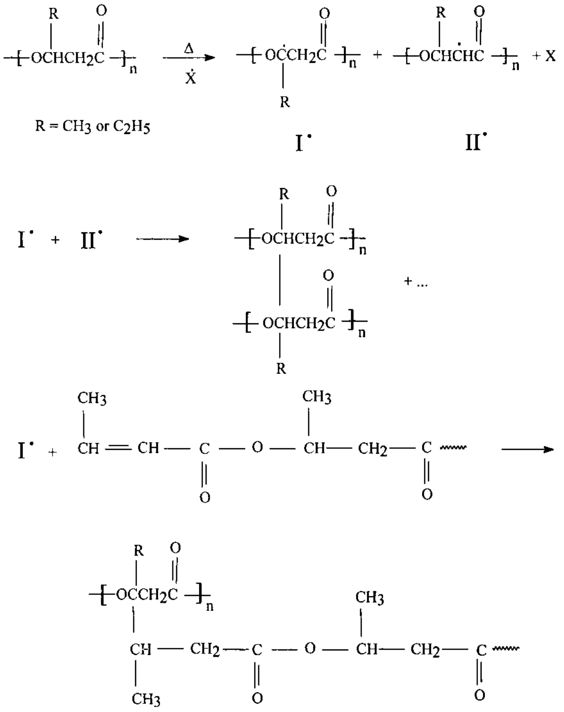

Figure 14. Structure of branched polymer obtained after a free radical reaction.

The g_v for PHBV extruded without DCP present varied within experimental error about the predicted g_v value of 1 (horizontal line in Figure 13) for a linear flexible chain. Addition of 0.1 wt % DCP produced a detectable reduction of g_v above log $M_w = 5.5$ (M_w = 316 228 g/mol). DCP levels of 0.2 and 0.3 wt % further reduced g_v at higher molecular weight and produced an onset of g_v lowering at lower molecular weight.

Application of eq 1 to calculate B_n from average g_v for the polymers is summarized in Table 1. Branching was detected for polymer prepared in the presence of as little as 0.05 wt % DCP. However, the relatively slow increase in B_n until the 0.2 wt % DCP level suggests that network formation has probably not occurred. Above a DCP level of 0.2 wt % the number of branches grows explosively, suggesting the possible formation of highly swollen microgel. Possible structures consistent with the formation of branched PHBV are shown in Figure 14.

Conclusions

Reactive processing of PHBV with a free radical initiator, such as DCP, leads to a branching of the polymeric structure of the material. The consequence of this architectural change can clearly be observed in the solution properties and rheological response of the material. The shear viscosities of the branched polymers hardly differ from the behavior of the linear polymers. However, an increase of the frequency of the branches leads to an increased elasticity of the product. Even more sensitive becomes the response of the material in an elongational flow field. Branching of the polymers leads to the occurrence of strain hardening in a way that directly depends on the concentration of free radical initiator used. It has been shown that this rheological method becomes very sensitive to the degree of branching as even small levels can be detected. The difference in elongational behavior can be detected from uniaxial elongational flow measurements as well as from entrance pressure drops in a capillary rheometer. Solution properties analysis provides additional insight into structure of branched PHBV branching. Trifunctional branching frequencies computed on the basis of intrinsic viscosity ratios indicate explosive growth in branching, possibly due to the generation of microgel, when branching reactions are initiated with a dicumyl peroxide level exceeding 0.2 wt %.

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