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A Chemical Route to High Molecular Weight Vegetable Oil-Based Polyhydroxyalkanoate

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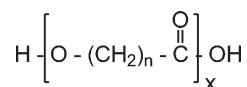
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ABSTRACT: To our knowledge, this is the first description of the material properties of a high molecular weight linear polyester prepared from the methyl ester of 9-hydroxynonanoic acid (HNME). The HNME of high purity was prepared by ozonolysis of castor oil, followed by methanolysis of triglycerides. High molecular weight polyester prepared in bulk by transesterification was a highly crystalline material with limited solubility in chlorinated solvents. The polyester is an analogue of polycaprolactone (PCL), but the longer hydrocarbon chain between ester groups imparted intermediate properties between polyesters and polyethylene, characterized by a higher melting point, higher T_g , better thermal stability, and lower solubility in chlorinated solvents than PCL. Differential scanning calorimetry showed only a single transition-melting at 70 °C with melting enthalpy of 95 J/g. Properties of the material were strongly dependent on the molecular weight. Lower molecular weight material was brittle with low mechanical strength and higher crystallinity and melting point while the high molecular weight polymer was spinnable into fibers of high toughness, strength, and elongation. Dynamic mechanical analysis at 10 Hz revealed a glass transition at −38 °C, and dielectric analysis revealed behavior similar to PCL. The polymer was stable up to about 250 °C as observed by thermogravimetric analysis.

Introduction

In a constant drive to develop new monomers and polymers from renewable resources, polyhydroxyalkanoates of bacterial or plant origin have a special place.^{1–3} However, most of the work is being concentrated on polyhydroxybutyrate/valerate polyesters with side chains.⁴ Polyhydroxyalkanoates with no side chains are also interesting. The chemical structure of this type of polyesters is very simple; it consists of ester and (CH₂) groups, with terminal hydroxyl and carboxyl groups:



Polyesters with $n = 1$ (poly(glycolic acid)), $n = 2$ (poly(hydroxypropionic acid)), $n = 3$ (poly(1,4-hydroxybutyrate)), and $n = 5$ (polycaprolactone) can be made from hydroxy acids or corresponding lactones. Generally, due to a very regular structure, these polyesters are highly crystalline. Polymers with short methylene chains between esters groups have high melting points and glass transition, which decrease with the increasing n up to $n = 3$ –4 and then start increasing slowly with longer methylene chains. One of the issues with polyhydroxyalkanoates is their low thermal stability indicated by significant drop in molecular weight (MW) upon heating at 170–200 °C.⁵ By increasing the length of methylene chain, it is hoped that thermal stability of polyesters would approach that of polyethylene. Poly(9-hydroxynonanoates) of relatively low molecular weights were prepared from dilactones by ring-opening polymerization on a relatively small scale, and some properties were described.⁶ Preparation of the methyl ester of 9-hydroxynonanoic acid ($n = 8$) and some

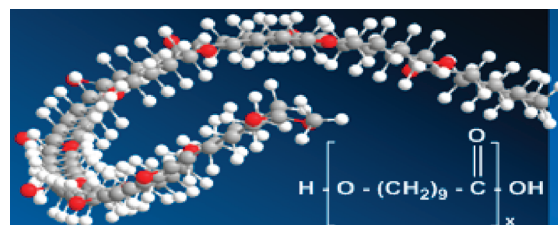
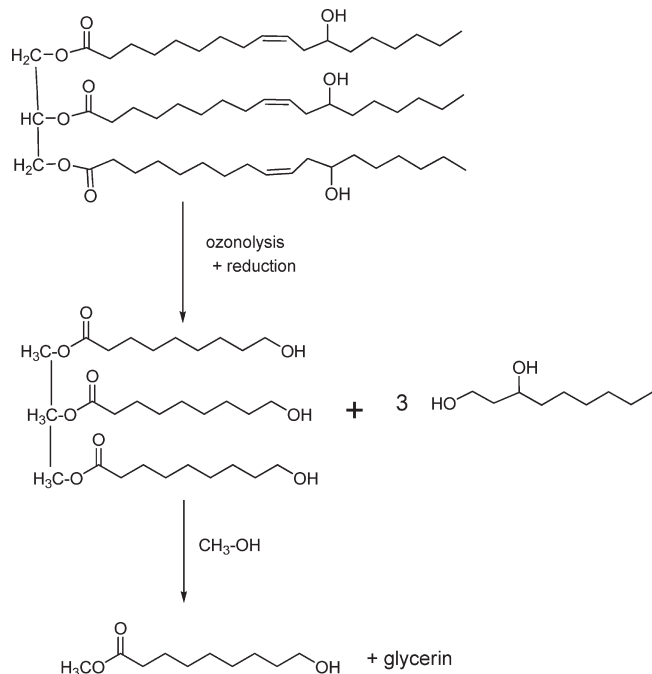


Figure 1. Tridimensional structure of poly(9-hydroxynonanoate).

cursory information on the polymer was published recently.⁷ In this paper we discuss the preparation of high molecular weight polyhydroxynonanoate and its bulk properties. Tridimensional structure of poly(9-hydroxynonanoate) is displayed in Figure 1. This material is potentially biodegradable and may find applications in the biomedical field. Characterization of the polymer structure in solution was difficult because of limited solubility, even at higher temperatures.

9-Hydroxynonanoic acid is very expensive, mainly due to a very limited production. However, we have demonstrated an efficient method for generation of the acid by ozonolysis of oils.⁷ Most standard vegetable oils consist of five major fatty acids (FA), two saturated (palmitic, stearic), and three unsaturated (oleic, linoleic, and linolenic). All three unsaturated acids have one double bond between the 9th and 10th carbons. When ozonolysis is carried out on these fatty acids, at least one component will have nine carbon atoms. However, saturated fatty acids are not affected by ozonolysis, and they have to be separated from the mixture. Castor oil has about 90% ricinoleic acid, with a double bond between the 9th and 10th carbons, and about 5% of unsaturated fatty acids and a low content of saturates, less than 5%. Thus, castor oil may be a preferable source for preparations of 9-hydroxynonanoic acid and its methyl ester. Ozonolysis of

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Scheme 1. Preparation of Methyl 9-Hydroxynonanoate (9-HNME) from Castor Oil

oils followed by reduction leads to a triglyceride of hydroxynonanoic acid (ozo-polyol) and a number of byproducts of lower molecular weights, which can be removed by distillation or extraction with solvents. The polyol is then treated with methanol to obtain a monomer, methyl 9-hydroxynonanoate. Monomer synthesis is illustrated in Scheme 1. Monomer purity was crucial for a high degree of polymerization. A sufficient quantity of polymer was prepared for the characterization and testing of mechanical and dielectric properties.

Experimental Section

Materials. Castor oil, having iodine value 83 and hydroxyl number 168 mg KOH/g, was purchased from Alfa Aesar. Methanol, HPLC grade methylene chloride, 1,2-dichloroethane, and anhydrous sodium sulfate were purchased from Fisher Scientific (Pittsburgh, PA). Sodium borohydride (98%) and Amberlite IR-120H ion-exchange resin were obtained from Aldrich (Milwaukee, WI). Titanium(IV) isopropoxide (>98%) was purchased from Acros Organics.

Methods. Hydroxyl numbers were determined using the phthalic anhydride method according to ASTM D 1957-86. A GPC/LS system consisting of a Waters 515 pump (Waters Corp., Milford, MA), a ThermoSphere HPLC chiller/heater with a set of five Phenogel columns from Phenomenex (Torrance, CA) covering a MW range of 100 to 5×10^5 , a Dawn EOS, multiangle laser-light scattering detector, a ViscoStar viscometer, and an Optilab rEX differential refractometer (all three detectors from Wyatt Technology Corp., Santa Barbara, CA) were used for assessing molecular weight and MW distribution. Hot chloroform (48 °C) was used as eluent at the flow rate of 1.0 mL/min.

FTIR spectra were recorded on a Perkin-Elmer, Waltham, MA Spectrum-1000 Fourier transform infrared spectrometer, scanning from 500 to 4000 cm^{-1} . Proton nuclear magnetic resonance and NMR experiments were performed on a Bruker Advance DPX-300 spectrometer at 300 MHz with a 5 mm broadband probe. Deuterated chloroform was used as solvent.

A Shimadzu GC/MS gas chromatograph with a QP5000 mass spectrometer detector was used to investigate purity of the monomer. Experiments were carried out with methylene

chloride as solvent and with the flow rate of 0.089 MPa (13 psi) and split flow of 72.4 mL/min. Column ZB-5 (30 m, $d = 0.32$, polarity 8) with phases consisting of 5% phenol and 95% of dimethylpolysiloxane was used to identify the monomer. The temperature of the column was 210 °C.

A differential scanning calorimeter (DSC) model Q100, from TA Instruments, New Castle, DE, was used for studying melting and glass transition of monomers and polymers. Measurement was performed at a heating rate of 10 °C/min from −80 to 160 °C. Thermogravimetric analyzer (TGA) model Q50 (TA Instruments) was used for examining thermal stability of polyesters. All experiments were carried out under the nitrogen with the heating rate of 10 °C/min from room temperature up to 700 °C.

Dielectric properties were investigated on a dielectric analyzer (DEA) model 2970 from TA Instruments, at six frequencies of 1, 10, 100, 1000, 10 000, and 100 000 Hz. The heating rate was 2 °C/min, in the temperature range −100 to 50 °C.

Dynamic mechanical tests were carried out on DMA 2980 from TA Instruments, at 10 Hz, and at a heating rate of 2 °C/min in a temperature interval from −120 to 50 °C.

Stress-strain behavior was studied on a Q-Test 2 tensile tester from MTS, Eden Prairie, MN. Sample dimensions for the measurement were $7 \times 0.35 \times 50$ mm (gauge length was 50 mm). The extension rate was 50 mm/min (100%/min).

Intrinsic viscosity was determined using chloroform as solvent at 40 °C and an Ubbelohde viscometer. The concentrations were 0.318, 0.606, 0.733, and 0.911 g/dL. Flow times varied from 153 s for the solvent to 331 s for the highest concentration.

X-ray analysis was done on the XRD-6000 (Shimadzu, Japan) in 2θ range from 2° to 50°.

Preparation of Polyhydroxynonanoate. Pure methyl 9-hydroxynonanoate having molecular weight of 188.26 and OH number of 298 mg KOH/g was made in several steps involving ozonolysis of oil, reduction, and preparation of methyl esters.⁷ Briefly, ozonolysis of castor oil was carried out in a three-neck round-bottom flask at 0 °C by passing oxygen with 7% ozone through the 10% solution in methanol/methylene chloride (45/55) until an ozone detector after the reactor indicated an excess of ozone. The ozonides formed were reduced with NaBH_4 to obtain a triglyceride polyol and byproducts. Methyl esters of HNA were obtained by methanolysis of the triglyceride polyol in the presence of CH_3OK .

Purification of Methyl Esters. Amberlite, an ion-exchange resin having capacity 4.4 meq/g, was added to the mixture containing methyl esters of 9-hydroxynonanoic acid, palmitic and stearic acid, glycerol, and methanol to neutralize the catalyst. Methanol was removed on a rotary evaporator at 80 °C under the medium and high vacuum. The mixture of 9-hydroxynonanoic methyl ester, glycerol, and methyl esters of palmitic and stearic acids were transferred into a separatory funnel. Glycerol settled at the bottom of the funnel was drained from the mixture. Residual glycerol was washed with a small amount of distilled water. The methyl esters were mixed with 5-fold excess of hexane, shaken vigorously, and cooled at −20 °C in a refrigerator. After several hours, the upper layer (hexane with methyl esters of saturated fatty acids) was decanted, and the lower layer containing pure 9-hydroxynonanoate was left to warm to room temperature. The residual hexane was removed on a rotary evaporator. The procedure was repeated until at least 95% purity of the monomer was achieved, the other components being nonan-1,3-diol, possibly traces of lactone of hydroxynonanoic acid and methyl palmitate and stearate. Purity of 9-hydroxynonanoate was confirmed by GC/MS, OH number measurement and also by using GPC and NMR methods.

Polymerization of Methyl 9-Hydroxynonanoate. Transesterification was carried out in a three-neck round-bottom flask equipped with a stirrer, nitrogen inlet, and thermometer. The reaction was run at 160 °C in bulk at normal pressure for the first

3 h, bubbling dry nitrogen through the mixture. The catalyst was Ti(IV) isopropoxide (0.5 wt %). The reaction was characterized by a fast initial rate of methanol removal from the mixture. The temperature and pressure profile was 3 h at 160 °C at normal pressure, followed by 2 h at 180 °C and 1 h at 200 °C, then temperature was raised to 220 °C, and high vacuum was applied for 3 h. Total reaction time was 9 h.

PHNA was purified by precipitation in methanol from solution. The polymer was filtered and dried in the oven at 65 °C to a constant mass.

Results and Discussion

Methyl 9-hydroxynonanoate of 95% purity was used for the preparation of the polyester. GC-MS analysis showed that main impurities were an unknown compound, assumed to be lactone or dilactone of 9-hydroxynonanoate (2.5%), 1,3-nonanediol (1.2%), and traces of methyl palmitate, methyl stearate, and a small quantity of dehydrated 9-oxynonanoate. The measured OH number of 299.5 mg KOH/g (theoretical 298) suggests somewhat higher purity than obtained by GC. The GPC chromatogram in THF of the sample after purification shows a single peak. The transesterification reaction of 9-hydroxynonanoate was monitored by GPC with THF as a solvent (while the polymer was still soluble in THF). After 3 h of reaction at 160 °C around 94% of monomers reacted. After running the reaction at 180 °C for 2 and 1 h at 200 °C, the number-average molecular weight was 5400 (relative to polystyrene), and polydispersity was 1.7. After running the reaction at high vacuum at 220 °C for 3 h, the process was stopped when mechanical stirring became very difficult. This polymer of high molecular weight was no longer soluble in THF but was partially soluble in chloroform above 30 °C. Molecular weight was estimated from intrinsic viscosity and GPC/light scattering measurements. The NMR spectrum of the polymer (Figure 2) shows the disappearance of peaks that were present in the monomer spectrum at 3.50–3.70 ppm corresponding to protons from the end methyl group, protons on the carbon attached to the alcohol group, and the hydrogen from the alcohol group. A new peak appears at 4.10 ppm, which was assigned to the protons from the methylene group attached to the ester $-\text{OC}(=\text{O})-\text{C}-$. The FTIR spectrum of the monomer (Figure 3) shows a very strong OH peak at 3385 cm^{-1} and the ester carbonyl peak at 1726 cm^{-1} . The absence of the OH peak from the polymer spectrum indicated high molecular weight of the polymer.

A summary of all spectral data for the 9-hydroxynonanoate follows. GC-MS: EI- MS (70 eV) m/z 74.05 (M^+). FTIR: 3379, 2930, 2857, 1738, 1439, 1364, 1244–1172, and 1103–1053 cm^{-1} . ^1H NMR (CDCl_3 300 MHz) δ (ppm): 1.30–1.60 (m, 12H, methylene $-\text{C}-$), 2.30 (t, 2H, methylene $-\text{C}(=\text{O})\text{O}-\text{C}-$), 3.50–3.70 (2H, methylene $-\text{O}$ and 3H, methyl $-\text{OC}(=\text{O})-\text{C}-$).

The polymer of high molecular weight was virtually insoluble in chlorinated solvents, THF, DMAc, ethyl acetate, or DMF at room temperature. The solutions had a gel-like appearance. The polymer displays a limited solubility in chloroform even at elevated temperatures. Intrinsic viscosity measured in chloroform at 40 °C was 0.96 dL/g, indicating a high molecular weight. The Huggins coefficient, k' , from the Huggins equation ($\eta_{\text{sp}}/c = [\eta] + k'[\eta]^2c$) was found to be $k' = 0.3592$, while intrinsic viscosity and the constant, k'' , from the Kraemer equation ($\ln(\eta_r)/c = [\eta] + k''[\eta]^2c$) were $[\eta] = 0.962\text{ cm}^3/\text{g}$, $k'' = -0.1452$, and $k' - k'' = 0.50$.

GPC/light scattering studies of molecular weight distribution of chloroform solutions at 50 °C were difficult due to limited solubility and some adsorption of the polymer on column material as well as low dn/dc value. Figure 4 displays GPC/molar mass curves vs elution time. The resulting weight-average molecular weight was 62 200 g/mol, and measured dn/dc was 0.057 mL/g.

Density of the undrawn poly(9-hydroxynonanoate), calculated from the weight and volume of a square sample sheet,

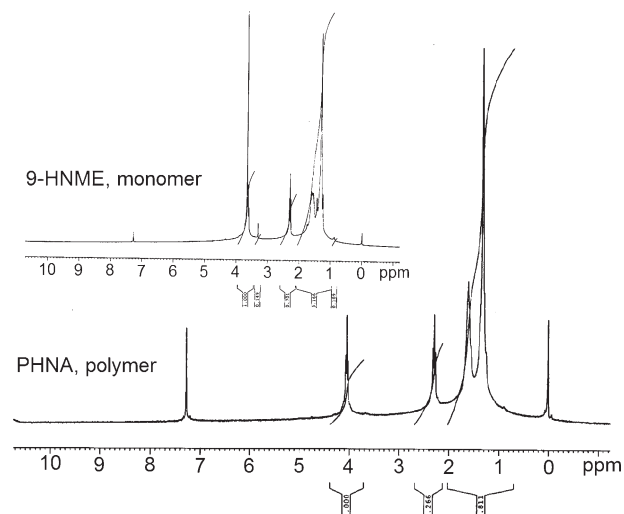


Figure 2. NMR spectra of 9-hydroxynonanoate and polyhydroxynonanoate.

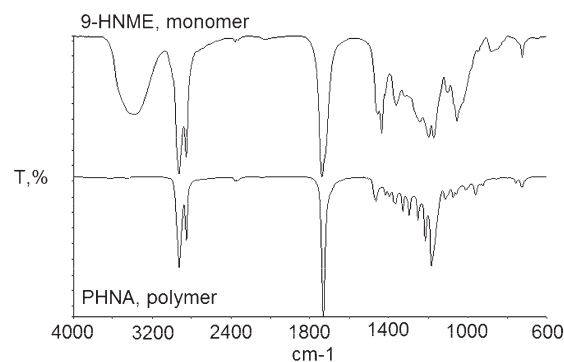


Figure 3. FTIR spectra of the monomer and polymer.

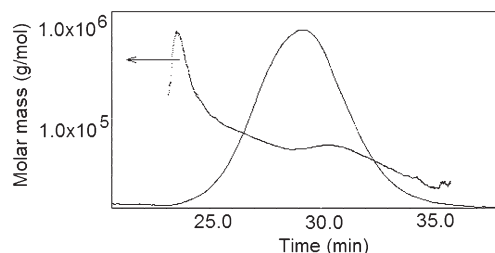


Figure 4. GPC/light scattering and molar mass curves for the PHNA in chloroform at 50 °C.

was found to be 1.06 g/cm^3 . This is in line with other polyhydroxyalkanoates where longer methylene chains give lower density: polyglycolide, $\rho = 1.50\text{ g/cm}^3$; poly(3-hydroxypropionic acid), $\rho = 1.42\text{--}1.44$ (crystalline) g/cm^3 ; poly(4-hydroxybutyrate), $\rho = 1.21$ (amorphous)– 1.28 (crystal) g/cm^3 ; PCL, $\rho = 1.11\text{ g/cm}^3$.

PHNA, like other polyalkanoates, is a crystalline material displaying sharp peaks in the X-ray diffractogram and sharp melting and crystallization peaks in DSC. X-ray diffraction (XRD) of the PHNA crystallized from the melt (Figure 5) shows a number of sharp peaks indicating high degree of crystallinity. The instrument software estimated the degree of crystallinity of 58%, based on the somewhat arbitrary separation of areas of amorphous halo under crystalline peaks. It has been found that crystallinity in polycaprolactones decreases with increasing molar mass,¹¹ and that is also true for PHNA. The peaks correspond to d -spacings of 0.36–0.18 nm. The crystalline structure of the

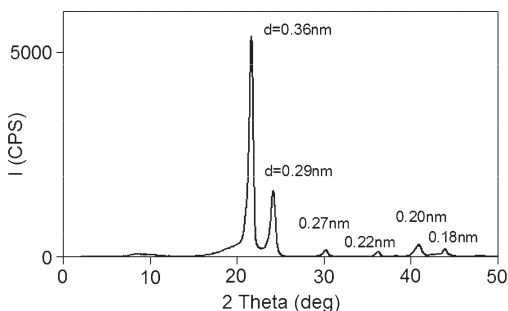


Figure 5. X-ray diffractogram of PHNA.

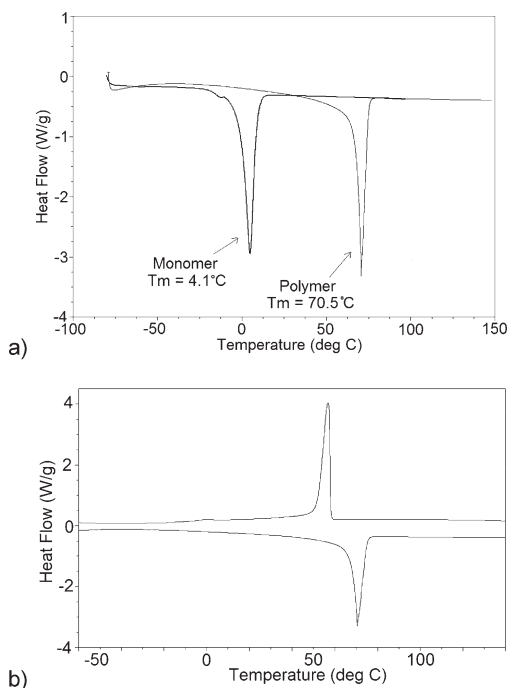


Figure 6. DSC thermogram of (a) polyhydroxynonanoate and the monomer and (b) heating-cooling cycle for PHNA.

polymer is being investigated and will be the topic of another paper.

DSC curves for the PHNA shown in Figure 6, display a melting peak temperature, T_m , at 70.5 °C and crystallization peak temperature, T_c , at 56.8 °C. In a sample with a lower molecular weight DSC melting was at 74 °C, somewhat lower than in polyhydroxydecanoate ($T_m = 77\text{--}78$ °C) studied by Carothers.¹² A very sharp crystallization peak in the cooling cycle, close to the melting endotherm, indicated high crystallization rate. Enthalpies of melting and crystallization are 94.3 and 101.6 J/g, respectively. No glass transition can be observed by DSC even after quenching in liquid nitrogen because of the low content of the amorphous phase. It should be emphasized that the degree of crystallinity as well as properties are strongly dependent on thermal history of the sample.

Comparison of melting points of linear polyhydroxyalkanoates is given in Figure 7. It shows decreasing melting points and glass transitions with increasing hydrocarbon chains up to 3–4 methylene groups. A slow increase of both T_m and T_g follows. Melting points should approach T_m of polyethylene (PE) asymptotically but T_g may have a different trend since PE glass transition is below -80 °C. Bacterial polyhydroxy alkanates such as poly(3-hydroxybutyrate) (P3HB), poly(3-hydroxyvalerate) (P3HV), or higher hydroxy acids and their copolymers display decreasing melting points from about 180 °C ($T_g = 1\text{--}4$ °C) for

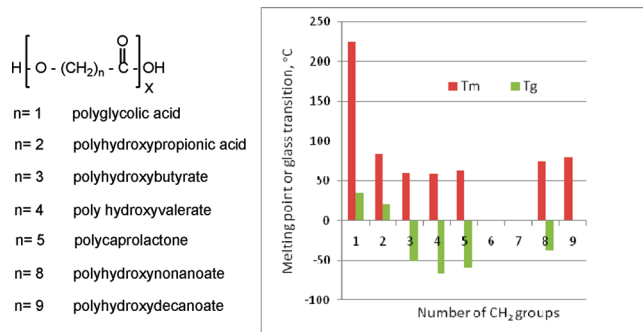


Figure 7. Melting points and glass transitions of linear polyhydroxyalkanoates.

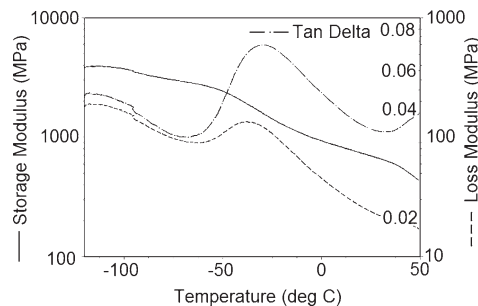


Figure 8. Storage and loss modulus and tan delta vs temperature at 10 Hz from DMA.

P3HB to 112 °C ($T_g = -12$ °C) for P3HV. Poly(lactic acid) (PLA) is an important polyalkanoate with a high melting point of 175 °C and T_g at about 65 °C.⁴

Dynamic Mechanical Analysis. Molecular dynamics was studied by dynamic mechanical and dielectric spectroscopy. DMA curves of PHNA are presented in Figure 8. Chain dynamics should be similar to that of PCL, which was thoroughly studied by DMA.^{11,13,14} DMA of PCL displayed an α -peak associated with cooperative motion of segments, at -50 °C, which shifted to higher temperatures with increasing crystallinity. PHNA displayed two peaks on the loss modulus and tan δ vs temperature curves (at 10 Hz) the higher being α (glass) transition at about -38 °C (loss maximum). The lower (β) transition, observed somewhat above -120 °C, is typical for most hydrocarbon chains and was assigned to the Schatzki mechanism of crankshaft rotation involving 4–6 carbon atoms.¹⁵ Activation energy for the α relaxation was $E_a = 250$ kJ/mol. The apparent activation energy for the α -relaxation in PCL of different degrees of crystallinity, was reported to be in a wide range 230–615 kJ/mol,¹¹ but another reference gave 123 kJ/mol.¹⁴ Evidently, E_a is dependent on many parameters which vary from sample to sample. Storage modulus in a glassy state was around 3000 MPa, dropping in a rubbery state of the non-crystalline part to around 1000 MPa. The relatively small drop at T_g is related to the small mass fraction of the amorphous phase or high degree of crystallinity.

Dielectric Properties of Poly(9-hydroxynonanoate). Dielectric analysis allows much wider frequency range than DMA and is a valuable technique for probing molecular motions in polymers. While dielectric studies of PCL are well covered,^{16,17} there are no data on relaxations in PHNA. As in DMA, dielectric relaxation spectra of PCL display α -, β -, and γ -peaks where the β -peak, occurs at approximately -90 °C at a frequency of 1 Hz, is strongly influenced by the water content and disappears in a dry sample.¹¹ PHNA as well as PCL belongs to the A2 group of polymers due to an

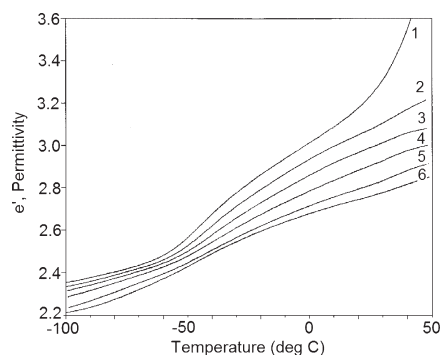


Figure 9. Permittivity of polyhydroxynonanoate vs temperature at six frequencies.

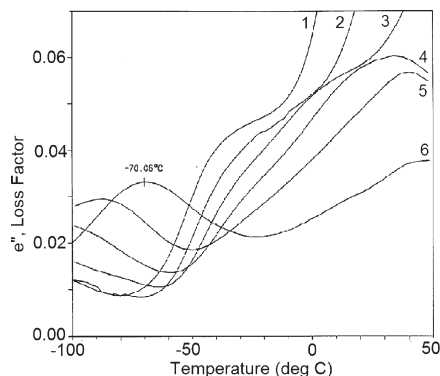


Figure 10. Change of loss factor with temperature and frequency for polyhydroxynonanoate (1, 1 Hz; 2, 10 Hz; 3, 100 Hz; 4, 1000 Hz; 5, 10 000 Hz; 6, 100 000 Hz).

electric dipole normal to the main chain together with a component of the monomeric dipole parallel to the backbone.^{18,19} Permittivity of the PHNA polyester was measured in the temperature range from -100 to 50 °C, at 6 decades of frequencies (Figure 9). Low permittivity values below -50 °C are characteristic for the glassy semicrystalline solid. Only group dipoles respond to the alternating electrical field. Permittivity jump starts at about -50 °C and ends up at -30 °C at 1 Hz, but the shift to higher temperatures occurs with increasing frequency. This jump is a consequence of the orientation of segment dipoles in the direction of the field; i.e., it is related to the glass transition. Continuously increasing permittivity above 20 °C is the consequence of increasing ionic conductivity as the sample approaches the melting point.

Absolute values of dielectric losses of PHNA, particularly that of lower molecular weight, were very low. These were comparable to those in polyethylene, which is expected in polyesters with long methylene chains between ester groups. The dielectric loss curve at 1 Hz displays the α peak at -34 °C, which shifts to higher temperatures at higher frequencies (Figure 10). This glass transition temperature is close to that obtained by dynamic mechanical measurements. The apparent activation energy for the α transition was calculated from the temperature shift of the maxima with frequency:

$$\log f = f_0 - (E_a/RT) \log e$$

where E_a is apparent activation energy, f the frequency, R the gas constant, and T the absolute temperature. E_a for the low-frequency region (1–100 Hz) was 57.9 kJ/mol. This value is considerably lower than apparent activation energy of 278 kJ/mol for the α -transition that we measured in a commercial PCL, suggesting higher mobility of segments in PHNA. This is

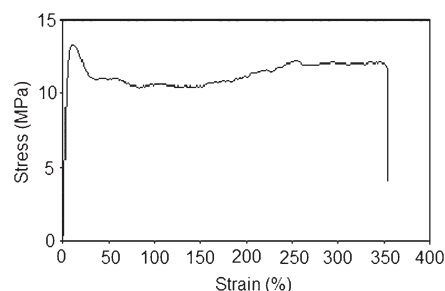


Figure 11. Stress–strain curve for polyhydroxynonanoate.

unexpected since about 15 deg lower T_g in PCL would suggest the opposite, and lower activation energy in PHNA may be due to lower crystallinity. β -peaks are observed on curves with 100 000 and 10 000 Hz (-71 and -87 °C, respectively), while those at lower frequencies are below the range of measurements. The β -peaks correspond to γ relaxation in PCL; i.e., they are characteristic for the Schatzki type of rotations. This polymer is less susceptible to water absorption than PCL because of a longer methylene chain. High losses at low frequencies (100 Hz and less) above glass transition are due to increased ionic conductivity. Apparent activation energy measured on a lower molecular weight PHNA sample ($M_n \sim 20$ 000) gave an activation energy for the β -transition, $E_{a\beta} = 36$ kJ/mol.

Tensile Properties of Poly(9-hydroxynonanoate). Tensile tests were carried out at 50 mm gauge length, 0.35 mm thick samples at the extension rate 50 mm/min (100%/min). The stress strain curve of a PHNA specimen displayed in Figure 11 is typical for a highly crystalline material. It displays a yield point at about 13 MPa and 10% elongation, followed by drawing and sample orientation until the break, observed between 100 and 350% elongation. Young modulus obtained from the initial linear part of the curve was about 200 MPa, indicating that the polymer is rather soft. Properties of industrial polyester films and fibers are usually improved by drawing and orientation. The average break stress was 9.1 MPa (coefficient of variation-COV = 17%), elongation at break 221% (COV = 47%), yield stress 13.9 MPa (COV = 11%), yield elongation 9.7% (COV = 11%), and Young modulus 172 MPa (COV = 20%). Preparation of samples for mechanical tests was difficult, and some defects like bubbles may have affected the final results and caused a relatively large scattering of values.

Mechanical tests show the highest elongation of 354% and tensile strength (yield) 16.1 MPa. These results are strongly influenced by the molecular weight of the sample and degree of crystallinity (thermal history). At lower molecular weights and higher crystallinity, the samples are quite brittle, unsuitable for mechanical testing. Comparison of mechanical properties of polyhydroxyalkanoates reported in the literature is not straightforward since they are often obtained under different experimental conditions but also at different molecular weights, crystallinity, and orientation of particular samples. In the family of linear PHA's, poly(glycolic acid) (PGA) is the strongest material with tensile strength of 70 MPa but the lowest elongation of only few percents.^{2,4} All higher linear polyalkanoates have tensile strengths in the unoriented state between 15 and 40 MPa and elongations at break ranging from 150 to 1000% (tensile strength and elongation at break for a commercial polyethylene, PE, are 35 MPa and 10–1000%, respectively). Tensile strength of P3HB and PLLA are in the same range, but elongations at break are below 10%. Modulus of elasticity for PGA is 6900 MPa,⁴ poly(hydroxypropionic acid) above 1300 MPa,²⁰

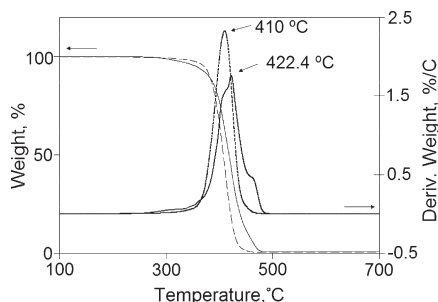


Figure 12. TGA curves for PHNA (—) and PCL (---) in nitrogen.

PCL 400 MPa, and P(4HB) 70 MPa (tensile modulus of PE is 800–1100 MPa).

Thermal Stability of PHNA. The thermal stability of PHNA was estimated from the weight loss with temperature and compared with that of polycaprolactone (PCL). Thermogravimetric curves of PHNA and PCL are shown in Figure 12. Onset of degradation was found at about 250 °C both in PHNA and in PCL, but initial loss, up to 10%, in PHNA was higher than in PCL; however, at higher temperatures PHNA displayed lower loss than PCL. Higher initial loss in PHNA was attributed to low molecular impurities such as dimers and cyclics. On the other hand, PCL was of very high purity, possibly heat stabilized. Since the melting point of the PHNA is below 100 °C, it seems that processing could be carried out considerably above the melting without fear of degradation. Temperatures at which PHNA had 10% and 50% weight loss were 354 and 417 °C, respectively (PCL: $T_{10\%} = 382$ °C and $T_{50\%} = 407$ °C). The maximum rate of degradation of 1.8%/°C takes place at 422 °C (PCL: 2.3%/deg at 410 °C). At a heating rate of 10 °C/min polyhydroxynonanoate degraded completely up to 480 °C. Several shoulders on the derivative curve point to a complex mechanism of degradation. Studies of thermal degradation of poly(3-hydroxybutyrate) occurring at 170–200 °C indicated random scission at ester groups, resulting predominantly in dimers, trimers, and tetramers.^{5,21–24} Degradation at higher temperatures gave a number of unsaturated compounds such as propene, 2-butenic acid, propenyl-2-butenate, etc.²⁵ Degradation in our case is more similar to that of poly(ϵ -caprolactone), starting at ester bonds, accompanied by fragmentation and formation of low molecular components at higher temperatures.⁶ The first step generates water, CO₂, and carboxylic acid as evolved products.²⁶ Although we compared degradation of PHNA with a commercial PCL which may contain heat stabilizers, our sample displayed overall better thermal stability.

Polyhydroxynonanoate fibers were made by extrusion at 140 °C from the melt flow index instrument. Thus, processing of the polymer into fibers or films without degradation is feasible.

Conclusions

A completely bio-based, high molecular weight polyester was successfully prepared by self-transesterification of methyl

9-hydroxynonanoate. The polyester has higher melting point (70 °C) and glass transition (−31 °C) than polycaprolactone. The new polymer is potentially biodegradable but more thermally and hydrolytically stable than polyalcanoates with shorter methylene chains between ester groups and may have some interesting applications in industry and medicine as a replacement for PCL.

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