Synthesis and Structure of a New Polyalcohol

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ABSTRACT: A new polyalcohol is prepared by reduction of the perfectly alternating ethylene−carbon monoxide copolymer. The low melting temperature of this atactic material (137 °C) is attributed to the 1,4-arrangement of the hydroxyl side groups. The different orientations of these slightly bulky groups with respect to the molecular plane give rise to less efficient packing of the chains in the crystal lattice. The reflections in the X-ray diffraction pattern are indexed on the basis of an orthorhombic lattice. The derived unit cell dimension are $a = 8.78$ Å, $b = 5.47$ Å, and $c = 7.47$ Å, and the crystalline density (1.08 g/cm^3) is significantly less than the crystalline density of atactic poly(vinyl alcohol) (1.35 g/cm^3), which has a 1,3-arrangement of the hydroxyl substituents. Solution cast polyalcohol films could be drawn at 110 °C to a ratio of about 10; a tensile strength of 0.5−0.6 GPa and a (maximum) tensile modulus of 11 GPa are attained.

Introduction

Organometallic catalyst systems enable the production of perfectly alternating ethylene−carbon monoxide copolymers (polyketones),[1,2] and a regular 1,4-arrangement of the dipolar carbonyl functionality is obtained. In comparison to polyethylene, the polyketone shows a much higher melting temperature (260−280 °C), due to the more polar nature of the polymer.[3]

In Table 1 the members of two groups of polymers are arranged in the order of the degree of oxidation. Commercially available atactic poly(vinyl alcohol) grades are prepared by polymerization of vinyl acetate followed by hydrolysis.[4] Polyketene can be synthesized from ketene using a BF$_3$/benzonitrile catalyst.[5] An amorphous low-molecular-weight material is obtained presumably due to mainly chemical defects and perhaps the steric hindrance and significant repulsion forces between the carbonyl groups. Poly(glycolic acid) is commonly prepared by ring-opening polymerization of glycolide.[6]

From imperfectly alternating ethylene−carbon monoxide copolymers two new polymers have been synthesized, viz. a polyalcohol[8] and a polyester.[9] The latter polymer was produced via oxidation with hydrogen peroxide or organic peracids. A random terpolymer, containing ethylene glycol/succinic acid and hydracrylic acid units, is obtained, but this synthesis route is unlikely to yield complete conversion. A more convenient route to such a polyester is the synthesis of poly(hydracrylic acid) from β-propiolactone by ring-opening polymerization.[10] Two crystalline structures have been reported for this homopolymer, i.e., the α-form and the β-form.[11,12] The melting temperature is rather low and its thermal stability is poor, because the polymer easily decomposes, forming acrylic acid.

In the present work, we have prepared a polyalcohol (PAl) from the perfectly alternating ethylene−carbon monoxide copolymer by reduction with sodium borohydride. Oriented solution cast film samples are characterized by means of thermal, IR, and NMR analysis and X-ray diffraction techniques. The differences in melting temperature and crystal packing between this regular, though atactic, 1,4-polyalcohol and poly(vinyl alcohol) (i.e., a 1,3-polyalcohol) are studied.

Experimental Section

Materials. Commercial laboratory grade starting materials were used as received. Alternating polyketones were prepared according to the description given in refs 1 and 3. The molecular weights of these polyketone samples were derived from the intrinsic viscosity in *m*-cresol (25 °C) using the following Mark−Houwink equation.[13]

$$[\eta]_{m\text{-cresol},25\,°\mathrm{C}} = 1.01 \times 10^{-4}\overline{M_{\mathrm{w}}}^{0.85} \qquad (1)$$

Polyalcohol Synthesis and Sample Preparation. Polyalcohol was synthesized by reduction of polyketone using sodium borohydride. Various polyketone samples were used with weight-average molecular weights of 45 000, 175 000, 310 000, and 450 000 kg/kmol. The polyketone powder (4 g) was dispersed in 160 mL of a 1:1 (v/v) mixture of ethanol and water. After heating to 78 °C, 4.7 g of NaBH$_4$ was slowly added. After 24 h of stirring at that temperature, all solids had disappeared. Upon cooling the lower layer of salt- and water-rich liquid was discarded; the upper layer was neutralized with 10% HCl and concentrated in a rotary evaporator to about 20% of its original volume, inducing precipitation of the polyalcohol. After cooling, the product was filtered off, redissolved in 1:1 aqueous ethanol, and reprecipitated three times by evaporative concentration. Transparent films were cast from viscous solutions in *N*-methylpyrrolidinone; the solvent was subsequently removed under vacuum. The thin films (60−200 μm) were cut into small strands (2−3 mm width) and drawn batchwise at 110 °C (initial rate of deformation 100%/min).

Analysis. IR spectra were recorded on a BioRad FTS40 FT-IR spectrometer. ^{1}H NMR spectra in dimethyl-d_6 sulfoxide (DMSO) were obtained using a Bruker AC 300 (300 MHz) spectrometer. To shift the absorption of moisture, trifluoroacetic-d_1 acid was added in some cases. Thermograms of the materials were recorded using a Perkin Elmer DSC 7 thermal analyzer at a scanning speed of 20 °C/min. The peak temperatures were taken as melting points, and the heats of fusion were calculated from the area of the melting peaks. X-ray diffraction patterns were recorded using a Statton camera equipped with a graphite monochromator with a sample to film distance of 33.7 mm. Tensile testing of drawn films and fibers were performed at room temperature (21 °C) and 65% relative humidity, using an Instron tensile tester, operating at a crosshead speed of 10 mm/min for a sample gauge length of 100 mm.

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Table 1. Melting Temperature (T_m) and Crystalline Density (ρ_c) of Various Flexible Chain Polymers Arranged in the Order of the Degree of Oxidation[a]

	formula	ρ_c [g/cm^3]	T_m [°C]		formula	ρ_c [g/cm^3]	T_m [°C]
PE	$(-CH_2-CH_2-)_n$	1.00	141				
PVAl	$(-CH_2-CH(OH)-)_n$	1.35	267	PAl	$(-CH_2-CH_2-CH(OH)-)_n$		
PK[b]	$(-CH_2-C(O)-)_n$			POK−C$_2$	$(-CH_2-CH_2-C\ (O)-)_n$	1.38[c]	278[d]
PG	$(-CH_2-C(O)-O-)_n$	1.70	233	PHA	$(-CH_2-CH_2-C(O)-O-)_n$	1.44[e]	122

[a] PE = polyethylene (ref 7); PVAl = poly(vinyl alcohol) (ref 7); PK = polyketene (ref 5); PG = poly(glycolic acid) (ref 7); PAl = polyalcohol (this work); POK-C$_2$ = polyolefin ketone (ref 5); PHA = poly(hydracrylic acid) (ref 7). [b] Amorphous polymer. [c] Crystalline density of the POK-α structure. [d] Melting temperature of highly oriented polyketone-C$_2$ (POK-β → melt). [e] Crystalline density of the β-form.

Infrared spectrum (transmission, film on silicon wafer, from aqueous methanol solution): 3301 (strong), 2937, 2920, 2858, 1668 (very weak), 1572 (very weak), 1446, 1338, 1188 (weak), 1102, 1038, 761 (weak), 639 cm^{-1}.

^{1}H nuclear magnetic resonance (NMR) spectrum (DMSO-d_6): $\delta = 1.25$ ppm, triplet-like broadened band assigned to the syndiotactic; $\delta = 1.36$ ppm, band assigned heterotactic; and $\delta = 1.48$ ppm, doublet-like broadened resonance assigned to isotactic, about 1:2:1 intensities, CH$_2$; $\delta = 3.34$ ppm, a broadened absorption attributed to CH; and $\delta = 4.32$ ppm, a multiplet for OH. All absorptions were referenced to tetramethylsilane (TMS).

^{13}C NMR spectrum (DMSO-d_6): $\delta = 33.5$, 33.7 ppm assigned to CH$_2$; $\delta = 70.1$, 70.5, 70.9 ppm attributed to CH with different tacticities. All absorptions were referenced to TMS, and no carbonyl absorption was visible in the 200−220 ppm region.

Thermal analysis (20 °C/min): For unoriented material thoroughly dried at 250 °C the observed glass transition temperature ranges from 53 °C for low-molecular-weight polymer to 56 °C for high-molecular-weight polymer. For unoriented low-molecular-weight samples a small melting endotherm is detected between 128 and 132 °C.

Results and Discussion

Polyalcohol Synthesis. Exploratory reduction experiments with NaBH$_4$ using a perfectly alternating low-molecular-weight polyketone were run in *m*-cresol as an effective solvent for the starting material. The reduced product could be isolated by coagulation with water, acetone, methanol, or ethanol as antisolvents. It was discovered serendipitously that a 1:1 (w/w) mixture of ethanol and water redissolved the polyalcohol, even though each of these solvents alone did not. Thus, reduction in aqueous ethanol as a dispersant for polyketone was investigated with a view to eliminate the need for *m*-cresol with its practical drawbacks, viz. toxicity and stench. The latter synthesis route resembles the reduction of an imperfectly alternating low-molecular-weight polyketone in methanol, as described by Morishima et al.[8] or the reduction of alternating norbonene−carbon monoxide copolymer by Liaw et al.[14] Even though polyketone shows a vanishingly small solubility in aqueous ethanol, the reaction could be carried out in this medium, albeit that high-molecular-weight polymer required fine grinding prior to reaction. As a consequence of a heterogeneous reduction reaction, long reaction times were necessary in all cases. Product isolation could be performed by separating the clear polymer-containing solution from the heavier salt-rich lower layer, neutralizing the polymer solution with HCl, evaporating until the polymer precipitated upon removal of most of the ethanol/water mixture and washing or dissolution−concentration−precipitation. Progress of the reaction could be monitored easily by observing the disappearance of solids, followed by verification by IR in an isolated sample that the 1700 cm^{-1} carbonyl absorption had disappeared.

Table 2. Solvents and Nonsolvents at Room Temperature for High-Molecular-Weight Polyalcohol (M_w = 450 000 kg/kmol)

nonsolvents	swelling agents	solvents
2-propanol	acetic acid (25%)	water/ethanol (1:1 w/w)
tetrahydrofuran	acetic acid (99%)	water/methanol (1:1 w/w)
sec-butyl alcohol	trifluoroacetic acid (50%)[a]	acetic acid (50%)
trifluoroacetic acid	dimethyl formate	*N*-methylpyrrolidinone
formic acid (50%)	dimethyl sulfoxide	*m*-cresol
diethyl ether	water	
methyl ethyl ketone	methanol	
dichloromethane	ethanol	
dioxan		
nitrobenzene		
pyridine		
p-xylene		
toluene		

[a] A slight discoloration of the polymer occurred.

Oriented Polyalcohol Films. To process the resulting polyalcohol from solution, a number of solvents have been screened; the results are listed in Table 2. Aqueous ethanol or aqueous methanol cannot be applied to cast a film from solution and to achieve subsequent concentration of the polymer. Water is only a swelling agent, and due to the faster evaporation of the alcoholic solvent, liquid−liquid demixing was observed prior to solidification and a nontransparent brittle film is formed. To avoid these concentration fluctuations during solidification, *N*-methylpyrrolidinone was used, and strong transparent films were cast. The solvent was removed at room temperature by evaporation under vacuum.

Thermograms of oriented films, drawn to a ratio of 9 at 100 °C, are given in Figure 1. Usually, a glass transition temperature is visible at 40−45 °C; for unoriented material thoroughly dried at 220 °C it is found at 53−56 °C.

During thermal analysis the weight loss was monitored, and a pronounced reduction in weight occurred at 100 °C for undried material. Thus, the reduction in glass transition temperature can be ascribed to moisture. Furthermore, in some cases a broad endotherm is observed in the thermograms between 60 and 110 °C, resulting from anorganic remnants of the reduction reaction. The strong endotherm, observed between 130 and 140 °C, is attributed to melting of crystalline polymer.

At increasing molecular weight a broadening of the melting endotherm is observed, which is accompanied by a slight reduction in the melting temperature (from 137° to 132 °C) and in the area of the melting peak (from 38 to 29 J/g). This result implies that the crystallinity is less developed in the higher molecular weight materials.

We were expecting a melting temperature for the polyalcohol in the temperature region of 180−220 °C.

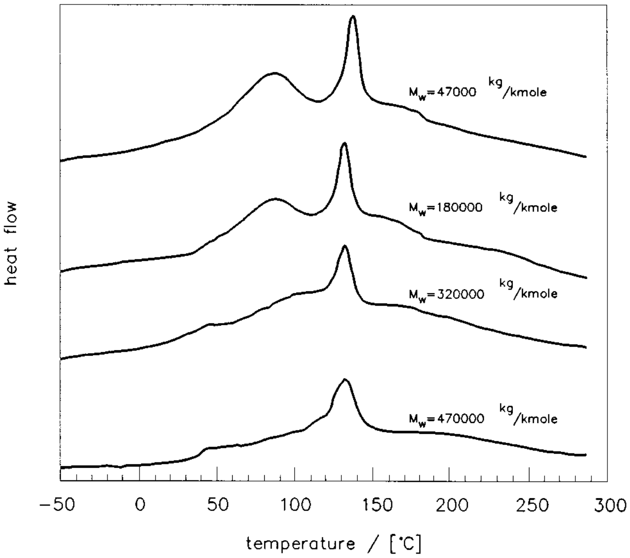

Figure 1. Thermograms of oriented polyalcohol films drawn to a ratio of 9 at 100 °C (scanning speed 20 °C/min).

Because of the increased intermolecular interactions (hydrogen bonds), the melting temperature was envisioned to be significantly higher than for polyethylene. Like poly(vinyl alcohol), the polyalcohol is basically an atactic material, but we anticipated that the nonstereoregular defects can easily be incorporated into the crystal lattice.[15] Moreover, it has been argued that ethylene−vinyl alcohol copolymers (EVAl) are cocrystallizable over the whole composition range.[16] For example, for a random (atactic) EVAl copolymer with about the same molar ratio of methylene (CH_2) to hydroxy methine ($CH(OH)$) units as the polyalcohol, a melting temperature of 182 °C is reported,[16,17] and the crystalline density is about 1.2×10^3 kg/m^3. The incorporation of ethylene units into the poly(vinyl alcohol) crystal lattice predominantly affects the packing of the chains in the direction of the intermolecular hydrogen bonds (i.e., along the *a*-axis in the crystal unit cell).

The polyalcohol produced via reduction of polyketone can be regarded as an atactic homopolymer, and in NMR and IR analysis chain defects in the form of unreduced carbonyl groups were below the detection limit. These particular features are generally favorable for a high melting temperature. Notwithstanding the good purity of the polymer, the melting temperature is even 4−10 °C lower than that for polyethylene. This effect can be explained by the different orientations of neighboring hydroxyl groups compared to those of poly(vinyl alcohol) or ethylene−vinyl alcohol copolymers. Polyalcohol consists of 1,4-glycol units, whereas poly(vinyl alcohol) consists of 1,3-glycol units (see Figure 2). It can be expected that intramolecular hydrogen bonding in poly(vinyl alcohol) via a six-membered ring facilitates the incorporation of the nonstereoregular defects into the crystal lattice, featuring an extended chain zigzag conformation of the atactic poly(vinyl alcohol). The formation of an intramolecular hydrogen bond in polyalcohol is less favorable, because of the required seven-membered ring formation, which is less stable and additionally distorts the conformation characteristics of an extended chain.

In the case of an all-trans conformation of the polyalcohol backbone, the different orientations of the slightly bulky hydroxyl side groups with respect to the molecular plane can contribute to a less efficient lateral packing of the chains in the crystal lattice than for poly(vinyl alcohol). To gain insight into the crystal packing density, drawn film samples were studied using X-ray diffraction techniques. Flat-plate and precession X-ray diffraction photographs were recorded; a flat plate photograph is displayed in Figure 3. From the discrete reflections on the equator it can be concluded that the polymer chains are periodically packed in the lateral direction with respect to the fiber axis. The low degree of arcing of the reflections implies that the molecular chains are effectively oriented during the drawing process. Moreover, the clearly visible layer lines point to periodicity of the polymer chains along the fiber axis. However, despite the good molecular alignment, some streaking is observed especially on the second layer line. This observation points to a distortion of the side-by-side packing of the chains in the direction of the fiber axis. The distortion is most likely caused by the different orientations of the hydroxyl groups with respect to the molecular plane. In other words, due to the different tacticities of the hydroxyl side groups, the chains cannot pack in a perfectly regular fashion in the fiber axis direction.

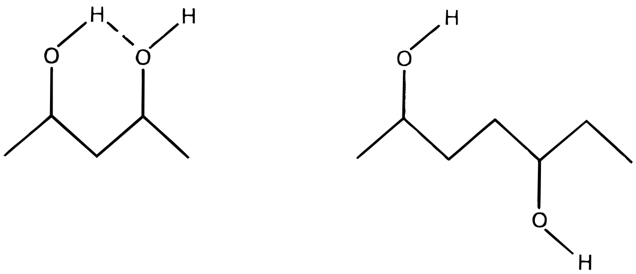

Figure 2. Repeating units in poly(vinyl alcohol) (1,3-glycol units) and polyalcohol (1,4-glycol units), demonstrating the capability of poly(vinyl alcohol) to form intramolecular hydrogen bonds.

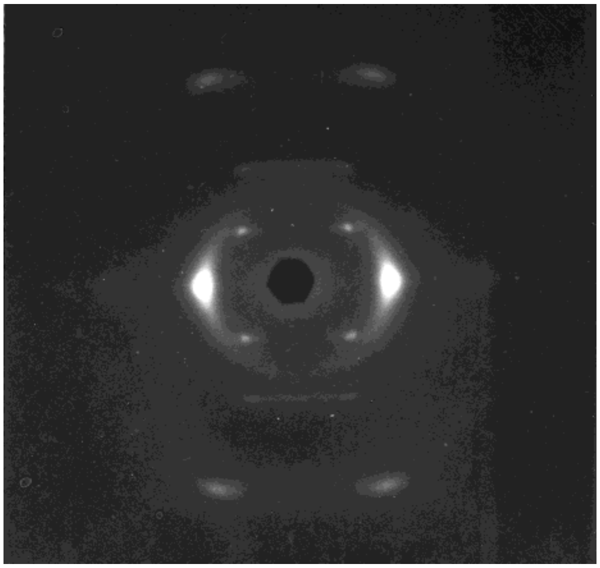

Figure 3. Flat-plate X-ray diffraction photograph of an oriented polyalcohol film drawn to a ratio of 9 at 110 °C (fiber axis is vertical).

The reflections were indexed on the basis of an orthorhombic lattice. From five reflections the dimensions of the crystal unit cell were derived using a least-squares procedure (see Table 3). The intensity of the

Table 3. Unit Cell Dimensions of Various Flexible Chain Polymers with an All-Carbon Backbone[a]

	a [Å]	*b* [Å]	*c* [Å]	ρ_c [g/cm^3]	structure
PAl	8.78	5.47	7.47^b	1.08	
POK-α	6.91	5.12	7.60^b	1.38	orthorhombic
POK-β	7.97	4.76	7.57^b	1.30	orthorhombic
PVAl	7.81	2.52^b	5.51	1.35	monoclinic ($\beta = 91.7°$)
PE	7.40	4.93	2.54^b	1.00	orthorhombic

[a] PAl, this work; POK-α, ref 3; POK-β, refs 18 and 19; PVAl, ref 14; PE, refs 20 and 21. [b] Direction of the fiber axis.

Table 4. Indexing for Polyalcohol and the Intensity, Calculated and Observed 2*θ* Values for Different Reflections

hkl	I^{obs}	$2\theta^{\mathrm{calc}}$ [deg]	$2\theta^{\mathrm{obs}}$ [deg]
200	very strong	20.23	20.19
120	very weak	34.35	34.37
101	medium strong	15.57	16.16
102	medium (streak)	25.92	26.53
113	medium strong	41.13	41.04

different reflections and a comparison between the observed and calculated 2θ values are presented in Table 4.

Comparison of the unit cell dimensions, together with the dimensions of the unit cells of some other all-carbon backbone macromolecules, reveals some interesting points. In contrast to the starting material polyketone, the dimension of the polyalcohol unit cell in the direction of the fiber axis is slightly less than 3 times the fiber axis unit cell length of polyethylene or poly(vinyl alcohol).

By contrast, in the polyketone (POK-α) crystal structure the strong dipolar interactions between well-arranged adjacent carbonyl groups result in an even slightly denser packing of the chains than observed for polyethylene (see Table 3).[3] Furthermore, the lateral dimensions of the polyalcohol unit cell are significantly larger than those of the poly(vinyl alcohol) unit cell, resulting in a rather low crystalline density.

Even though we have not looked into the detailed molecular arrangement in the polyalcohol crystal structure, it is obvious from the above-mentioned results that the increased intermolecular interactions between neighboring hydroxyl groups cannot compensate for the size plus stereoirregularity of these groups relative to polyketone, in which the latter issue is absent.

To study the development of the tensile modulus with the molecular orientation, tensile tests were performed on a series of films of different molecular weights and drawn to different ratios, up to 9. In Figure 4 the maximum slope in the stress−strain curves (i.e., the maximum tensile modulus) is presented in relation to the tensile strength. Compared with poly(vinyl alcohol) and polyketone fibers, the tensile strength increases at about the same slope with the development of the modulus.

It is also noteworthy that at these rather low degrees of orientation no effect is visible of the molecular weight on the tenacity, which is, among other polymers, also observed for polyethylene fibers. But the properties we obtained by drawing polyalcohol films are significantly below those of the other all-carbon backbone molecules of interest. In fact, we were able to achieve only 20−30% of the values found for both the tensile strength and tensile modulus of oriented gel-spun polyketone fibers.[22,23] Clearly, these poor tensile properties combined with the low melting temperature demonstrate the limited potential of this polymer, and hence, no attention was paid to a further optimization of the fiber preparation conditions.

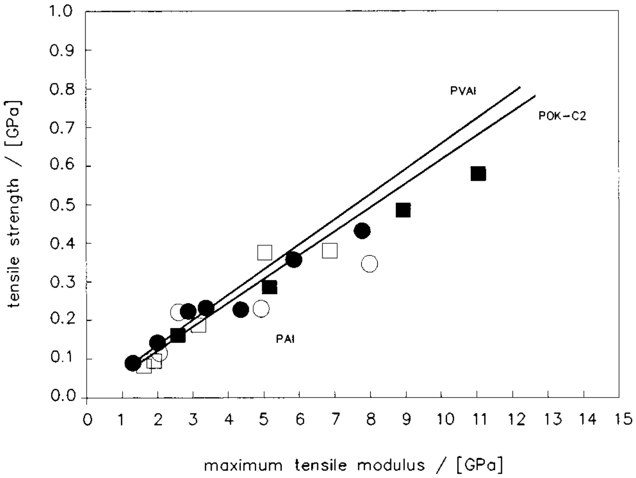

Figure 4. Tensile strength of drawn polyalcohol films cast from solution in NMP vs the maximum tangential modulus. The solid lines represent the correlations found for polyketone (POK-C$_2$) and poly(vinyl alcohol) (PVA*l*) fibers ((□) M_w = 47 000 kg/kmol; (■) M_w = 180 000 kg/kmol; (●) M_w = 320 000 kg/kmol; (○) M_w = 470 000 kg/kmol).

Notwithstanding these particular drawbacks, a comparison between the attainable degree of drawing induced molecular orientation of this polymer and polyketone and poly(vinyl alcohol) is instructive, when looking at the related chain polarities. In further contributions, we will describe the results obtained in our study into the influence of the drawing temperature on the drawability of these flexible polymers with intermediate polarity.[24]

Conclusions

An atactic 1,4-polyalcohol is synthesized by reduction with sodium borohydride of the perfectly alternating ethylene−carbon monoxide copolymer. Oriented semicrystalline samples are prepared by drawing solution cast films at 110 °C. These samples were studied by means of X-ray diffraction techniques. The low melting temperature (137 °C) is attributed to the low packing density of the chains in the crystal lattice. Some streaking is observed, especially on the second layer line, which indicates that the side-by-side packing of the chains is distorted due to the different orientations of the slightly bulky hydroxyl side groups. The 1,4-arrangement of the hydroxyl substituents results in a significantly lower crystalline density than for atactic poly(vinyl alcohol), which has a 1,3-arrangement of the hydroxyl substituents.

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