In DSC measurements, a mixture of PHB–8%-HV and PHB–26%-HV may have two melting points, as shown in sample 2. But for the mixture of PHB–30%-HV and PHB–70%-HV, only one melting point is observed because the melting points of the two copolymers are almost the same (see Figure 2). In this case, it is impossible to judge from melting points only whether the PHB–HV sample is a random copolymer or a mixture. On the other hand by NMR analysis of sequence distributions, a mixture of PHB–8%-HV and PHB–26%-HV cannot be distinguished from a PHB–14%-HV random copolymer. But a mixture of PHB–30%-HV and PHB–70%-HV can be easily identified as a mixture from sequence analysis. Both the data for sequence distributions from NMR and the melting points from DSC melting curves are needed to judge whether a PHB–HV sample is a random copolymer or a mixture. Before investigation of physical and mechanical properties of PHB–HV copolymers, the microstructures of the samples must be checked.

Recently, it has been reported[11] that a blend of PHB and PHB–8%-HV has one melting point, which depends on blend composition.

Registry No. (HB)(HV) (copolymer), 119878-76-1.

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Crystalline Structure of Poly(β-benzyl L-aspartate)

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Received November 23, 1988;
Revised Manuscript Received February 14, 1989

Poly(β-benzyl L-aspartate) (abbreviated PBA) is an unusual homopolypeptide since it may exist in three different helical conformations: left-handed α-helix, right-handed α-helix, and ω-helix, as well as a β-pleated sheet.[1] For this reason we decided to study by electron microscopy the crystals of this polymer as grown from solution. Blais and Geil[2] reported that this polymer formed fibrillar aggregates by isothermal precipitation from a saturated solution in either 2-nitropropane or cyclopentanone. In our case we have used hexafluoroisopropyl alcohol as a solvent in order to promote the formation of single crystals of helical PBA, as it is known to happen with the related polymer poly(γ-benzyl L-glutamate).[3]

For our experiments we used a commercial sample (Sigma) of PBA with a nominal molecular weight of 60000. A 0.1% solution of polymer in hexafluoroisopropyl alcohol was prepared at 40 °C. Upon slow cooling to room temperature, crystals appeared in the preparation. A droplet of solvent-containing crystals was deposited onto a carbon-coated copper grid. Excess solvent was removed with filter paper. The grids were then shadowed with Pt–C at an angle of 14°. The grids were observed in a Philips 301 electron microscope.

In order to ascertain that the crystals contained α helices, the X-ray diffraction pattern of a mat of crystals was obtained. Only a sharp ring at 12.7 Å plus a diffuse ring at 4.6-Å spacings were observed. These features coincide with those previously observed by Bradbury et al.[1] and Malcolm[4] for α-helices of PBA.

The crystals that we obtained are shown in Figure 1. They all are about 50 Å thick and display three types of morphologies: (a) triangles, with two sharp and one irregular side (The tip of the triangle opposite to the irregular side is not sharply defined but appears rounded or irregular); (b) hour-glass-like crystals, with sharp sides and irregular bases; (c) complex structures, which appear to be formed by accumulation of the two previous types of crystals.

These morphologies are quite different from other structures observed with the same polymer such as the fibers reported by Blais and Geil[2] or the irregular plates obtained by Masuda et al.[5] using a low molecular weight material.

In spite of the well-developed habit of the crystals apparent from Figure 1, no electron diffraction pattern could be detected. Even at extremely low beam intensities, only an amorphous halo was observed. The absence of diffraction may either indicate that the chains are considerably tilted or that the molecular order has been lost when it was subjected to the vacuum of the electron microscope or even of the evaporator, due to the presence of solvent in the original crystals.

The crystals of PBA in the α-helical conformation, which we have described, show two puzzling features. They are 3 or 4 times thinner than the crystals found in other α-helical polypeptides.[6] Although in a 50-Å thickness it is possible to accommodate a sufficient length of α-helix (about 33 residues in 9 turns), there is no obvious reason to explain why these crystals are so thin. It cannot be excluded that the helical stems are inclined with respect to the crystal, so that a longer helical section might be accommodated in a 50-Å thickness.

Another puzzling feature of these crystals is the hour glass (Figure 1b) or irregular triangular shape (Figure 1a) that we have found. One possible explanation for these shapes would be that the crystals contain a mixture of right-handed and left-handed helices. It was shown by Crick[7] that right-handed α-helices cannot be packed with regularity, whereas alternating layers of left-handed and right-handed helices would have a better interlocking of the helical grooves. In fact Elliot et al.[8] have prepared crystals of 1:1 poly(γ-benzyl L-glutamate) and poly(γ-benzyl D-glutamate) as an equimolecular mixture of right-handed and left-handed helices. In our case regular alternating layers of right-handed and left-handed PBA could be deposited on the two straight crystal faces. It is then not possible to have a regular alternation on a third side, so that in the tip of the triangles and in the irregular edge of the crystals irregular shapes may appear as observed.

We have also studied the influence of temperature on the structure of such crystals. When they are heated above 150 °C, a transition to the ω-form takes place, as described

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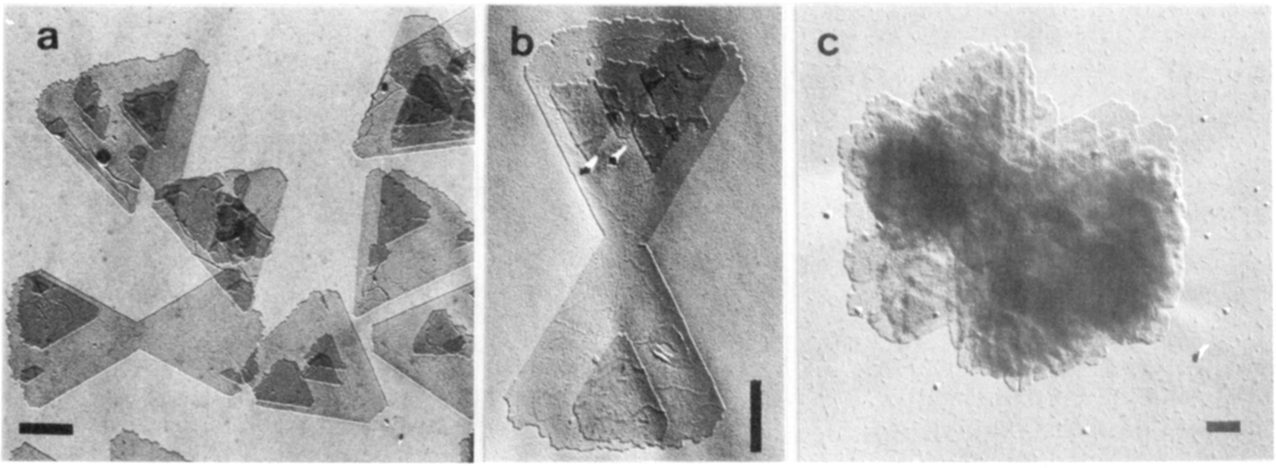

Figure 1. Different types of crystal morphology displayed by PBA when crystallized from hexafluoroisopropyl alcohol: (a) triangles, (b) hour-glass-like crystals, (c) complex structures. All bars equal 1 μm.

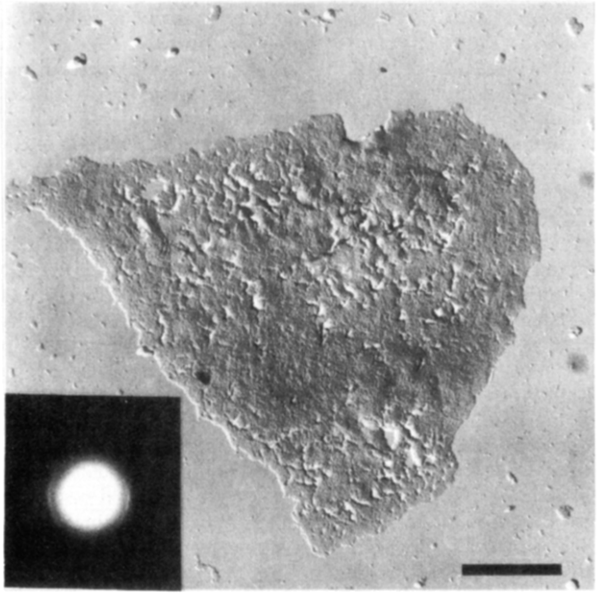

Figure 2. Crystal of PBA heated to 150 °C. The bar corresponds to 1 μm. Inset: Electron diffraction from such a crystal showing a 13.9-Å arc indicative of the ω-form.

by Baldwin et al.[9] The crystals become irregular in contour but maintain an approximate triangular shape (Figure 2). An arced reflection oriented normally to the diagonal can now be detected by electron diffraction. Its spacing is 13.9 Å and agrees with the value found by these authors for the ω-form. Further heating above 170 °C results in a transition to a β-structure characterized by a 17.6-Å spacing in electron-diffraction patterns. Thus heating induces transitions already observed by other investigators[4,5,10] in the following sequence:

$$\alpha\text{-helix} \xrightarrow{150\ ^\circ\mathrm{C}} \omega\text{-helix} \xrightarrow{170\ ^\circ\mathrm{C}} \beta\text{-sheet}$$

Such transitions could also be followed by X-ray diffraction (results not shown) on films cast from hexafluoroisopropyl alcohol. On the other hand, when a powder obtained by precipitation with methanol was used, the sample also showed the α-helical structure at room temperature. Upon heating, the ω-form could not be detected, instead the sample went directly to the β-structure. These results probably indicate that the arrangement of α-helices varies with the solvent used for crystallization. Depending on their organization, the transition to the ω-form may be prevented.

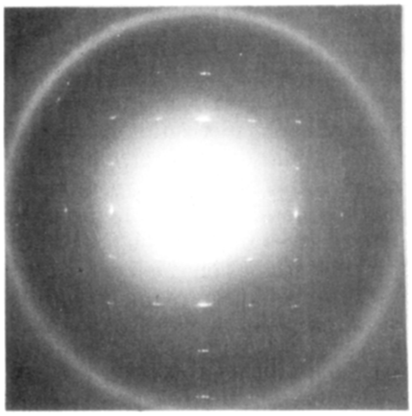

Figure 3. Electron diffraction taken from one crystal of PBA that was shadowed with Pt/C before heating at 170 °C. A single-crystal square pattern appears with a basic spacing of 9.83 Å, which may arise from Pt atoms aligned along the [110] directions of the tetragonal ω-form of PBA. Note that the strongest reflection seen on this picture should correspond to 220. The 110 reflection, although weaker, can be detected on the original picture.

Finally, we also note that during the study of these transition we observed that crystals, which had been shadowed with platinum and were then heated to 170 °C, gave an electron-diffraction pattern that is shown in Figure 3. The rings correspond to diffraction from sparse platinum crystallites formed by condensation of the platium vapors. In fact, rings at 2.25, 1.97, 1.37, and 1.15 Å are seen on the original picture that satisfactorily index as 111, 200, 220, and 222 on the basis of a FCC platinum cell of a_0 = 3.92 Å. Superimposed to this diffraction, there is a well-oriented square pattern with a spacing of 9.83 Å, which we attribute to the polymer. This spacing coincides with the 110 spacing of the ω-form and suggests that platinum atoms are orderly arranged on the surface of the polymer crystal, along [110] crystallographical directions. This question deserves further study.

Acknowledgment. This work has been supported in part by CAICYT Grant PA86-0218-C03-03. C.A. acknowledges a FPI fellowship.

Registry No. PBA, 25248-99-1; PBA (SRU), 25736-41-8.

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Living Polymerization of 1-Chloro-1-alkynes by $MoOCl_4$–*n*-Bu_4Sn–EtOH Catalyst

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Received November 22, 1988

Introduction

Living Polymerization is an excellent method for the preparation of polymers with monodisperse molecular weight distribution (MWD) and controlled structure.[1] While living anionic polymerization has been investigated most extensively, many living polymerizations by other mechanisms have also been developed recently. For example, transition-metal-catalyzed living polymerizations have been achieved for norbornene,[2] propene,[3] and butadiene.[4] Especially, studies on the living polymerization of norbornene have made remarkable progress, expanding into precise preparation of block copolymers.[5] On the other hand, few polymerizations of substituted acetylenes have been claimed to be living systems: (i) 1-chloro-1-octyne/$MoCl_5$–*n*-Bu_4Sn–EtOH,[6] (ii) *tert*-butylacetylene/$MoCl_5$,[7] and (iii) 1-(trimethylsilyl)-1-propyne/$NbCl_5$.[8]

1-Chloro-1-octyne polymerizes with $MoCl_5$–*n*-Bu_4Sn (1:1) catalyst to give quantitatively a polymer whose molecular weight reaches about one million.[9] Recently we have found that a catalyst composed of $MoCl_5$, tetrabutyltin, and ethanol ($MoCl_5$–*n*-Bu_4Sn–EtOH, molar ratio 1:1:0.5) effects living polymerization of 1-chloro-1-octyne.[6] In the presence of this catalyst, the number-average molecular weight ($\bar{M}_n$) of the polymer increases in direct proportion to conversion, and the polydispersity ratio ($\bar{M}_w/\bar{M}_n$) is 1.1–1.3. The $\bar{M}_w/\bar{M}_n$ ratio, however, tends to increase owing to the partial deactivation of the propagating species when additional monomer feed is supplied to a polymerization system in which the initial feed has been consumed.

In the present note, we report on the living polymerization of 1-chloro-1-alkynes effected by $MoOCl_4$–*n*-Bu_4Sn-EtOH (1:1:0.5). This catalyst is featured by high activity and superior living nature, as compared with the corresponding $MoCl_5$-based catalyst. Block copolymers comprising two kinds of substituted acetylenes have been prepared for the first time by using this catalyst.

Experimental Section

$MoOCl_4$ (Strem Chem.) was used without further purification. 1-Chloro-1-alkynes were prepared as described before[9a] and distilled twice at reduced pressure from calcium hydride. Toluene as polymerization solvent was washed by a standard method, distilled twice from calcium hydride, and kept over molecular sieves.

Polymerizations were carried out under dry nitrogen in a baked glass tube equipped with a three-way stopcock. The following procedure is exemplary (see Figure 2 for results): A glass tube was charged with 1-chloro-1-octyne (1.0 mmol, 145 mg, 0.159 mL), dodecane [0.050 mL, as internal standard for gas chromatography (GC)], and toluene (3.8 mL). In a separate glass tube were placed $MoOCl_4$ (0.50 mmol, 127 mg), toluene (11.3 mL), and a toluene solution (2.5 mL) of *n*-Bu_4Sn (200 mM), and the mixture was allowed to age at 30 °C for 15 min. To this was added a toluene solution (1.25 mL) of EtOH (200 mM), and the mixture was aged at 30 °C for another 15 min. Polymerization was initiated by adding 6.0 mL of this catalyst solution to the above monomer solution at 30 °C. The second, third, and fourth monomer feeds (1.0 mmol each) were injected as toluene solutions (toluene, 2 mL) after every 5 min. The polymerization was terminated with a mixture (1 mL) of methanol and toluene (1:4 volume ratio) after 5 min from the final monomer addition. The monomer had totally reacted according to GC (silicone DC 3m, 150 °C). Further, it was confirmed by GC in control experiments that the monomer had been completely consumed at each step. The polymerization mixture was diluted with toluene (30 mL) and poured into methanol (1 L) under stirring. The polymer precipitate was filtered off and dried to a constant weight. Triblock copolymerizations were carried out in a similar way.

The $\bar{M}_w$ (weight-average molecular weight) and $\bar{M}_n$ values of polymes were tentatively determined by gel permeation chromatography (GPC).[10] GPC curves were observed on a Jasco Trirotar chromatograph (eluent $CHCl_3$; columns, Shodex A804, A806, and A807 polystyrene gels; sample 0.10 wt % solution; polystyrene calibration).

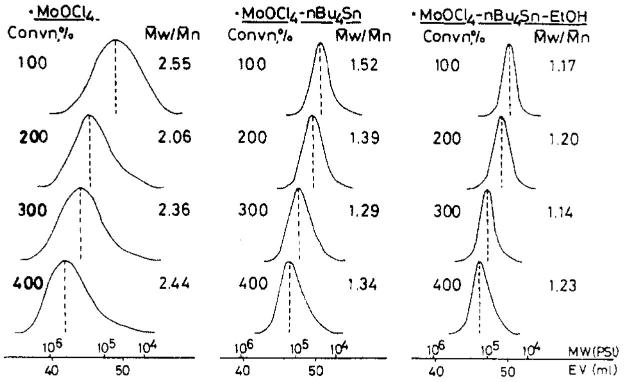

Figure 1. MWD curves of poly(1-chloro-1-octyne)s obtained with $MoOCl_4$-based catalysts (polymerized in toluene at 30 °C for 5 min for each monomer feed; $[M]_0 = [M]_{added} = 0.10$ M, $[MoOCl_4] = 20$ mM).

Results and Discussion

Living Polymerization of 1-Chloro-1-octyne. Polymerization of 1-chloro-1-octyne was studied by use of three kinds of $MoOCl_4$-based catalysts, that is, $MoOCl_4$ alone, $MoOCl_4$–*n*-Bu_4Sn (1:1), and $MoOCl_4$–*n*-Bu_4Sn–EtOH (1:1:0.5). When carried out in toluene at 30 °C, the polymerization was very quick with each catalyst, being finished within 5 min. Then monomer was repeatedly supplied every 5 min three times and was completely consumed each time.

Figure 1 shows MWD curves of the poly(1-chloro-1-octyne)s obtained in these polymerizations. Among the three $MoOCl_4$-based catalysts, the $MoOCl_4$–*n*-Bu_4Sn–EtOH catalyst produced a polymer whose $\bar{M}_w/\bar{M}_n$ ratio was 1.15–1.25, being close to unity. Furthermore, the polymer molecular weight increased progressively with each further supply of monomer, whereas the MWD remained narrow throughout this procedure. These results manifest that this polymerization is a living polymerization. In contrast, the $\bar{M}_w/\bar{M}_n$ ratio for $MoOCl_4$–*n*-Bu_4Sn was 1.3–1.5, and that for $MoOCl_4$ alone was as large as 2.1–2.6. The polymer molecular weight also increased with additional supplies of monomer in these latter polymerizations, suggesting the presence of long-lived propagating species in these systems.

As seen in Figure 2, the $\bar{M}_n$ of the polymer increased in direct proportion to the amount of monomer supply, and in turn monomer consumption, in the polymerization of

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