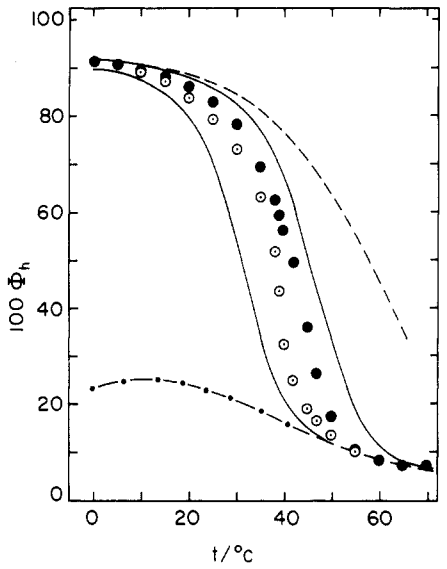

Figure 2. Percent helix vs. temperature for non-cross-linked $\beta\beta$ tropomyosin at pH 7.4: open circles, smoothed data for 0.0100 mg·cm^{-3}; filled circles, smoothed data for 4.72 mg·cm^{-3}. Solid curves are from theory using the best fit algorithm at the corresponding concentrations. Dashed curve is from theory for dimer species using the same algorithm. Dot–dashed curve is from theory for monomer species, i.e. single β-chains. The latter is indistinguishable from the result for single α-chains.

52.328 581 8 (52.627 425 9); A_0 = 15 522.9681 (15 793.4998); A_1 = −348.702 910 (−351.163 555).

It is immediately evident that the interspecies difference in helix–helix interaction free energy is subtle; the shapes of the curves are similar, and numerical values differ by no more than ~55 (and as little as ~30) cal·(mol of block pairs)$^{-1}$. These differences represent only ~10% of the total free energy of interaction. However, as noted previously, this translates to a difference in helix content that is measureable.

The success of this helix–helix interaction in fitting the data is assessed in Figure 2, where the smoothed data points of helix content for each concentration of the $\beta\beta$ species may be compared with the theoreticaly calculated values (solid curves). The fit is very similar to that found in the $\alpha\alpha$ case; i.e., it is semiquantitative.[1] As in the $\alpha\alpha$ case, the theory somewhat overestimates the concentration dependence.

Also shown in Figure 2 are theoretical curves for helix content of the monomer (single-chain) species (dot–dashed curve) and dimer species (dashed curve). The former is virtually indistinguishable from the corresponding curve for α single chains and the low helix content emphasizes once again how important helix–helix interactions are in producing the high values found in the native, two-chain structure.[1] This receives further emphasis from the (dashed) curve for the dimer species, which shows relatively elevated helix content up to rather high temperatures. As in $\alpha\alpha$ species, the loss of helix by $\beta\beta$ species is, in large part, due to chain dissociation.

It remains to be seen whether these subtle changes in interhelix interaction can be interpreted in terms of specific amino acid substitutions at the "a" and "d" positions that are responsible for the hydrophobic portion and the "e" and "g" positions responsible for the electrostatic portion of the interaction. The change from α to β chains entails a change in a total of 11 residues at "a" and "d" sites and a total of 5 at "e" and "g" sites.[4,5] It is unlikely, however, that much insight can be gained by simple inspection of the substitutions involved, because the local changes in helix–helix interaction necessarily interact in a complex manner with local variations in short-range interactions. The net effect on helix content is difficult to intuit.

Acknowledgment. This work was supported in part by Grant No. GM-20064 from the Division of General Medical Sciences, United States Public Health Service and in part by Grant No. PCM-8212404 from the Biophysical Program of the National Science Foundation.

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Field Desorption Mass Spectrometry of Poly(olefin sulfones)

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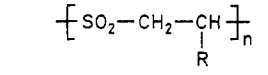
Poly(olefin sulfones) are copolymers of an alkene and sulfur dioxide, which usually have alternating structures (I). Poly(olefin sulfones) are thermally unstable, decom-



(I) R = ALKYL or H

posing to sulfur dioxide and the alkene on heating.[1] It has been reported[2] that the rates of thermal decomposition of several poly(olefin sulfones) show an approximate correlation with the number of hydrogen atoms on the carbon atoms β to the sulfone group. Bowmer and O'Donnell[3] have found that there is a better correlation when both the number of β-hydrogens and the ceiling temperature of the polymer are considered. Bowden et al.[4] have shown that poly(1-butene sulfone) undergoes a two-step degradation, with the initial degradation occurring in the temperature range 130–200 °C and the major degradation taking place at higher temperatures. Bowden et al.[4] suggested that the initial degradation takes place at weak links within the chain. Using a specialized mass spectroscopic technique, we have studied the degradation of poly(1-butene sulfone) and poly(propene sulfone) with a view to elucidating the mechanism of their degradation.

Poly(1-butene sulfone) and poly(propene sulfone) were prepared by the radical polymerization at −78 °C of equimolar amounts of the alkene and sulfur dioxide in the presence of a chain-transfer agent (bromotrichloromethane). The initiator was *tert*-butyl hydroperoxide

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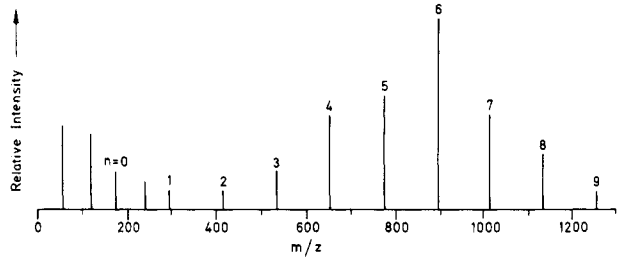


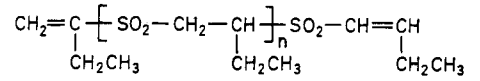
Figure 1. Field desorption mass spectrum of poly(1-butene sulfone). Emitter heating current range 19–25 mA. Isotope peaks have been omitted.

(25% in methanol). The chain-transfer agent was in a ratio of 2:1 to the initiator for the poly(1-butene sulfone) and 50:1 for the poly(propene sulfone).

The technique that has been employed is field desorption mass spectrometry (FDMS).[5] A sample of a poly(olefin sulfone) is placed on an emitter,[6] which is a thin (10-μm diameter) wire covered with carbon microneedles, and introduced into the source of the mass spectrometer. The microneedles serve to support the sample and, when a high potential (10 kV) is placed on the emitter, create a high electric field that ionizes the sample. Ions are desorbed from the emitter by passing through it a gentle heating current and then analyzed directly by mass spectrometry. The mass spectrometer employed has been described.[7,8]

The differences between FDMS and the closely related technique of pyrolysis–FDMS lie only in the emitter temperatures used.[5] In FDMS, emitter temperatures are low (typically <150 °C), and molecular ions are observed in studies of low molecular weight polymers (M < 10 000).[9] There is typically no degradation of the sample in FDMS. Pyrolysis–FDMS is applied to higher molecular weight samples (M > 100 000). Emitter temperatures must be high (typically >200 °C), so as to induce extensive degradation of the sample prior to ionization and desorption. With pyrolysis–FDMS, the ions in the mass spectra typically have low masses [<1000].[10-12] The experiments we report with poly(olefin sulfones) are somewhat intermediate between FDMS and pyrolysis–FDMS as defined above, in that the emitter temperatures used were low but nevertheless there was a degree of degradation of the sample (see below).

The field desorption (FD) mass spectrum of poly(1-butene sulfone) is shown in Figure 1. In a typical run, the heating current through the emitter would initially be near-zero and the mass spectrum would be scanned. The heating current would then be raised by an increment (typically 1 mA) and the mass spectrum rescanned. The heating current would be kept at a fixed value during a scan. This procedure of incremental increases in heating current followed by a scan of the mass spectrum was continued up to a heating current of 30 mA. Ions were observed within the range of heating currents from 19 to 25 mA, and within this range the mass spectra did not depend upon the value of the heating current. No dependence upon the time for which the heating current was held at any particular level prior to scanning the mass spectrum was found. The main series of peaks (n = 0 to n = 9) in the mass spectrum (Figure 1) are assigned to ions $[A + H]^+$, where A has the general formula shown in II. It is proposed that these species A are degradation products of poly(1-butene sulfone). This degradation process must be able to proceed to completion at the highest heating current (25 mA) at which ions were observed, since the sample, which would initially be visible on the emitter, would have disappeared completely at the end of a run.



(II)

FD mass spectra for poly(propene sulfone) were similar to those of poly(1-butene sulfone). In both poly(1-butene sulfone) (Figure 1) and poly(propene sulfone) spectra there are peaks at low masses. These peaks represent the hydrocarbon of the monomer, the repeat unit of the polymer, two repeat units of the polymer, and sulfur dioxide. The peaks due to sulfur dioxide are small.

To establish firmly that the polymers were breaking up on the emitter, gel permeation chromatography (GPC) was used to estimate the molecular weights of the poly(1-butene sulfone) sample. The gel permeation chromatograph consisted of a Waters Associates Inc. M-45 pump, a UG-K injector, and an Erma 7510 refractive index detector. A Styragel column (10^4 Å) was used with tetrahydrofuran (THF) as the mobile phase. GPC placed the molecular weights in the region 10^3 to 2×10^5. Molecular weight fractions (10^3 to 2×10^4, 2×10^4 to 7×10^4, and 7×10^4 to 1.8×10^5) were taken from the GPC effluent, and mass spectra were obtained for each of these fractions. The mass spectra of these fractions were essentially identical with the spectrum of poly(1-butene sulfone) (Figure 1).

The uncertainty in the absolute temperature of a sample at any given heating current is high (±30 °C), because the sample will not necessarily be at exactly the same temperature as the emitter wire. The *range* of temperatures corresponding to the range of heating currents (19–25 mA) is estimated to be 60 °C. The absolute temperature of the sample at a heating current of 20 mA is estimated to be 140 ± 30 °C. These estimations are based upon measurements of Winkler and Linden,[13] with adjustments to allow for the length of the emitter wire based on calculations of Fraley et al.[14] and our own measurements.[6] The sample temperatures at which ions are observed (roughly 130–190 °C) are above the ceiling temperatures of the poly(olefins sulfones) (90 °C for poly(propene sulfone) and 64 °C for poly(1-butene sulfone)[15]. We therefore conclude that neither radical nor cationic sites are formed during the degradation of the poly(olefin sulfones); otherwise depolymerization as observed in radiolytic degradation would follow, with production of large amounts of the monomers, sulfur dioxide and the alkenes.[16] Depolymerization following homolytic scission of polymer backbones has also been shown to be a general phenomenon in collision-induced dissociation of gaseous polymer ions.[17] We conclude that the degradation products formed in the FD experiments are relatively stable species.

That relatively stable degradation products are formed is supported by the insensitivity of the FD mass spectra to heating current. Peaks were only observed in the FD mass spectra above a heating current of 19 mA. Such onsets are usual in field desorption.[9,18] The mass spectra were, however, largely independent of the heating current in the range in which peaks were observed (19–25 mA). That is to say peaks corresponding to poly(olefin sulfones) with molecular weights of approximately 1000 were always observed. If these degradation products were no more stable than the original polymer, we would have expected an increase in the heating current from 19 to 25 mA (an approximately temperature increase of 60 °C) to have induced further degradation. That the FD mass spectra were largely independent of heating current also means that there was no significant shift to higher masses with temperature, as is observed in FD of intact molecular ions

of stable polymers.[9] This indicates that the peaks in the spectra (Figure 1) are a fair representation of the distribution of masses of the degradation products II.

We propose that the ions observed in the FD mass spectra correspond to the ionized products of the first step in the reported two-stage degradation of poly(1-butene sulfone) and poly(propene sulfone).[4] β-Hydrogen shifts[2,3] to sulfone groups would produce products with the required formula (shown in II). β-Hydrogen shifts have also been suggested to occur in poly(olefin sulfones) by Wellisch et al.[19] If β-hydrogen shifts occurred at the temperatures in question in the regular poly(olefin sulfone) structure as depicted in I, it is difficult to explain why further degradation is not induced on raising the heating current from 19 to 25 mA. We conclude that the degradation products II observed in our experiments are the result of the rupture of weak links in the polymer chain.

Acknowledgment. We thank the Australian Research Grants Scheme for supporting this work.

Registry No. Poly(1-butene sulfone) (SRU), 77464-94-9; (1-butene)·(sulfur dioxide) (copolymer), 25104-10-3; poly(propene sulfone) (SRU), 77450-82-9; (propene)·(sulfur dioxide) (copolymer), 30475-44-6.

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X-ray Study on Lattice Thermal Expansion of Fully Extended Aromatic Polyamide Fibers

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As is well-known, highly oriented poly(*p*-benzamide) (PBA) and poly(*p*-phenyleneterephthalamide) (PPTA) fibers are composed of so-called fully extended rigid-rod chains.[1,2] For these fibers macroscopic properties such as elastic modulus and thermal expansibility are expected to reflect directly the behavior of the extended chain,[3–5] whereas for usual crystalline polymers consisting of flexible chains, the inherent contribution of the extended chain in the crystalline region is obscured in such macroscopic properties by the presence of more deformable noncrystalline parts, including bent or folded molecular conformations.[6,7] Therefore, these rigid-rod polymers are suitable materials for understanding the characteristic role of the extended-chain structure in macroscopic properties.

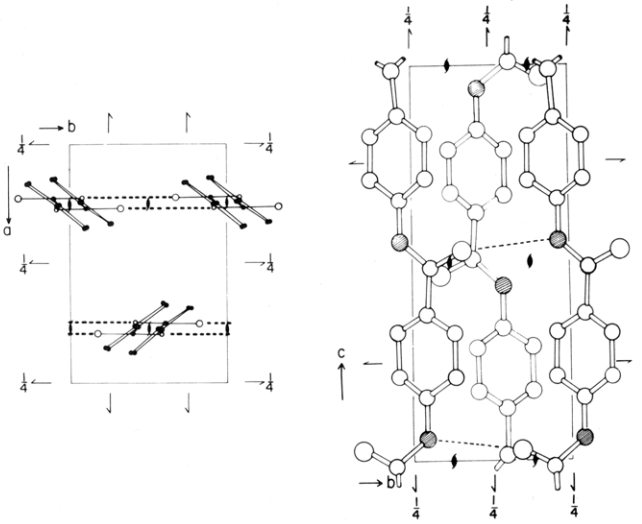

Figure 1. Crystal structure of PBA.[12]

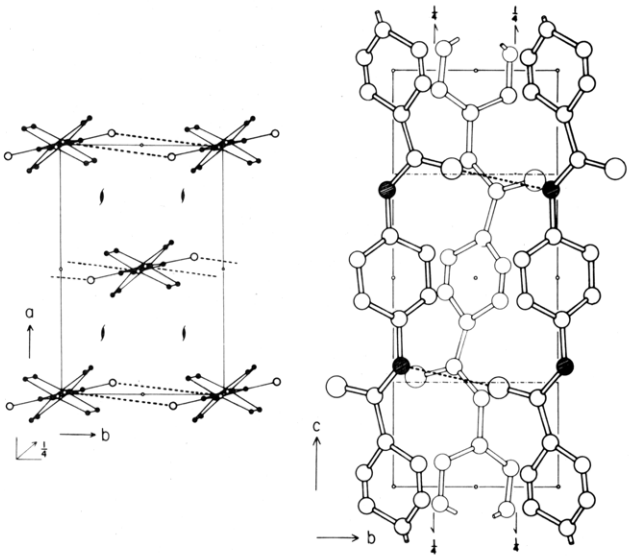

Figure 2. Crystal structure of PPTA.[12,13]

Here we focus our attention on the problem of thermal expansion. For many crystalline polymers, including polyethylene, negative thermal expansion (thermal contraction) of the fiber period has been observed by means of X-ray diffraction and ascribed to thermal fluctuation of the molecular chain moving perpendicular to the chain axis.[8–10] On the other hand, the thermal expansion behavior in the macroscopic dimension is rather complex, and its coefficient varies from positive to negative according to the sample preparation conditions and the measuring temperature.[7] In a previous paper,[11] we reported thermomechanical properties of PBA and PPTA fibers and showed that these fibers exhibit a macroscopic thermal contraction of the order of 10^{-5} K^{-1} along the fiber direction. Taking into account the fully extended molecular

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