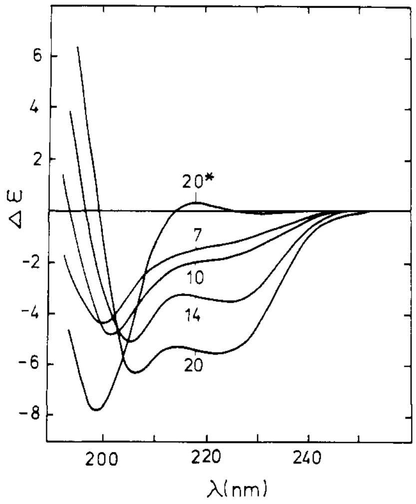

Figure 1. CD spectra of the oligomers **1a** and **1b** for different chain lengths n in water, pH 3.9. (CD spectra were recorded on a dicrograph JASCO J-20 at 25 °C. The concentration was 0.2 mg of peptide/mL in all measurements. The concentration of the samples was determined by conductimetric titration and by amino acid analysis. The content of α-helical structure[4] amounts to about 10% (n = 7), 17% (n = 10), 35% (n = 14), and 60% (n = 20). Curve 20^+ corresponds to the fully neutralized oligomer **1a** with n = 20 and is typical for a random-coil conformation.

in the conformational behavior between **1a** and **1b.** The fully neutralized oligomer with n = 20 shows CD features characteristic of a random-coil structure (curve 20^+ in Figure 1).

Also, the solvent-dependent properties were not changed by the POE group: Both series showed higher ellipticities in the helix-promoting solvent trifluoroethanol (TFE) compared to water, indicating stabilization of the α helix. The addition of increasing amounts of trifluoroacetic acid to **1a** and **1b** resulted in the expected disruption of the helical structure.

During the stepwise synthesis of the γ-benzylic-protected oligomer **2a,** a pronounced relationship between the solubility and viscosity behavior of the POE peptides and the conformation was observed. The low molecular weight oligomers with $5 < n < 10$, for which a β conformation has been found in concentrated solutions of dioxan and dichloroethane,[5] yield highly viscous solutions in methylene chloride. Obviously the high viscosity reflects the formation of a network-like structure, arising from intermolecular hydrogen bonds of the peptide chains. With growing chain length, the viscosity of the POE-oligomer solutions decreases drastically which can only be explained by a conformational transition, e.g., by the onset of a helical structure. Similar observations were made earlier on polydisperse oligomers of this type without macromolecular protecting groups.[5] According to our results, the chain length at which the helical structure begins to predominate over the β form in methylene chloride is approximately 10–12 residues. In the helix-promoting solvent TFE, the helical structure is the prefered conformation event at shorter chain lengths (Table I). Similar to the case of the (L-Glu) oligomers, the formation of a helical structure starts at n = 7 whereas the lower oligomers have random-coil structure in this solvent. Again, identical CD spectra were obtained for the series **2a** and **2b.**

Table I
Characteristic CD Data of the POE-Bound 1a and 2a and the Free Oligomers 1b for n = 20 [a]

Oligomer	$\Delta\epsilon_{207}$ [b]	$\Delta\epsilon_{222}$ [b]	Solvent
1a	−6.3	−5.5	H_2O, pH 3.9
1b	−6.2	−5.4	H_2O, pH 3.9
1b + 10% (W) POE	−6.2	−5.4	H_2O, pH 3.9
2a	−7.1	−6.8	TFE

[a] The minima at λ 207 nm ($\pi \rightarrow \pi^+$) and 222 nm ($n \rightarrow \pi^+$) are typical for an α-helical structure. [b] The ellipticity per amino acid residue is calculated by $\theta = \Delta\epsilon \times 3300$ (deg cm^2)/dmol.

CD studies on hydrophobic oligomers with a preference for extended β conformations indicate that also in this case the POE group has no influence upon the formation of intermolecular β sheets. For example, the same CD data, characteristic for a β structure, were obtained for the oligo-(L-Ala) series with high and low molecular weight ester groups.[2] Preliminary results of POE-bound oligo-(L-Val) and oligo-(L-Ile) confirm this observation.[6] A direct comparison between the POE peptides and the free oligomers is difficult in these series because of solubility problems.[7]

The present investigations show that the conformational behavior of the POE-bound and free peptides is identical. In no case could a disturbance of the conformation of the peptide by the C-terminal blocking group be detected. This important finding can be explained by the conformational properties of the polyoxyethylene chain: Under the experimental conditions, POE has a random-coil structure with extended chain dimensions compared to the ideal state (theta point) due to the effect of the excluded volume.[3,8] Because of the low density and the high flexibility of the POE chain, a specific interaction between the peptide and the POE coil is very unlikely; this was also confirmed by kinetic studies on POE peptides, whereby identical kinetic behavior of both high and low molecular weight peptide esters was found.[9]

We conclude that conformational studies on POE-bound peptides are also relevant for the corresponding free peptides. Preliminary investigations show that beside the measurement of the CD, all other currently used methods such as NMR, IR, or UV can be applied directly to the polymer peptide. Thus, the LPM for peptide synthesis also offers a powerful tool in the field of conformational studies of peptides.

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Hypersonic Relaxation in Poly(ethylene oxide)

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The observation and interpretation of the glass–rubber relaxation in semicrystalline polymers is subject to consid-

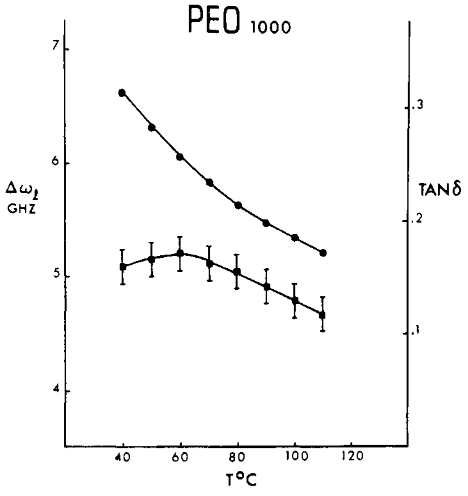

Figure 1. Brillouin frequency $\Delta\omega_l$ (●) and tan δ (■) vs. T for 1000 mol wt poly(ethylene oxide).

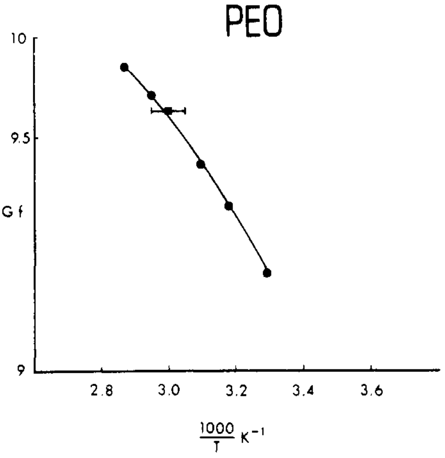

Figure 2. Comparison of dielectric relaxation (●) and hypersonic relaxation (■) in PEO. Log f is plotted vs. $1/T_{\max}$.

erable debate.[2,3] One way to gain insight into the amorphous loss processes observed in the semicrystalline state is to measure the loss at high frequencies in the molten state. This approach has been used successfully by Boyd[1,4,5] and coworkers for several highly crystallizable polymers. They found that the temperatures of maximum dielectric loss in the gigahertz frequency range were indeed above the melting point for poly(ethylene oxide). The present study was undertaken to test this result using dynamic mechanical spectroscopy in the hypersonic region. Brillouin scattering was used to obtain the loss data. A value of the frequency and tan δ were determined for longitudinal acoustic phonons as a function of temperature.

Experimental Section

Poly(ethylene oxide) of nominal molecular weight 1000 was obtained from Polysciences, Inc. This polymer was chosen to lower the melting point to T_m = 40 °C while maintaining the hypersonic loss maximum at its asymptotic value.

Brillouin spectra were obtained as described previously.[6,7] The incident wavelength was 5145 Å and the scattered light was observed at 90°.

Results

The values of $\Delta\omega_l$ (in GHz) and tan δ are plotted vs. temperature in Figure 1. The maximum loss is observed at 60 °C and a frequency of 6.06 GHz. Depression of the melting point allowed measurements down to 40 °C.

The present results are compared to those reported by Porter and Boyd[1] using dielectric relaxation in Figure 2. The log of the frequencies is plotted vs. the reciprocal of the temperatures of maximum loss. The agreement is very good, even on the expanded scale shown here. The loss process is confirmed to be the glass–rubber relaxation.

Observation of a temperature of maximum loss in the hypersonic range above the melting point has previously been reported for bisphenol-A polycarbonate.[7] A dielectric loss maximum has also been observed in molten Nylon 6–10.[4] Examinations of many other crystallizable polymers in the molten state are in progress.

It has been suggested[8] that the frequency of maximum loss at the melting point should be near 10^{12} Hz for the glass–rubber relaxation. For linear polyethylene it appears that this is the case. However, there is no fundamental reason why the melting point should be correlated with the glass–rubber relaxation and the examples cited above serve to illustrate the range of frequencies of maximum loss that are observed near T_m. The present results also suggest that the use of GHz relaxation techniques will be very important in the study of the amorphous loss processes in highly crystallizable polymers.

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Asymptotic Behavior of the Number of Self-Avoiding Walks Terminally Attached to a Surface to which They Never Return

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The effect of excluded volume on the properties of a polymer interacting with a plane surface was first considered by Silberberg,[1] using a theory which was essentially "mean field" in character. One of the parameters needed in this treatment was the exponent which characterized the number of self-avoiding walks which originate at the interface but never return there. This exponent has been estimated by various groups of workers[2–4] using exact enumeration techniques for a variety of lattices. If we consider any three-dimensional lattice in which the surface is represented by a lattice plane, we can write the number of n-step self-avoiding walks which start at an origin in this plane and are then confined to the half space on one side of this plane, as $(n,1)_S$. (The 1 indicates that there is only one vertex in the surface plane.) It has been shown elsewhere[5] that

$$\lim_{n\to\infty} n^{-1}\log(n,1)_S$$

exists and is equal to the connective constant of the lattice, log μ. In addition there are good reasons to believe that[4]

$$(n,1)_S \sim n^{-\xi}\mu^n$$

Lax and others[2,3] have investigated the value of ξ for the four