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# Viscoelastic Relaxations in Oxidized Poly(hexamethylene sulfide)

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ABSTRACT: The dynamic mechanical behavior of several oxidized poly(hexamethylene sulfide) samples has been studied. Two relaxations that have been found and considered were a low-temperature $\gamma$ relaxation of polymethylenic units and a higher temperature $\beta$ transition. The presence and variations of these relaxations have been discussed in relation to the composition of the different samples.

## Introduction

Poly(thioethers) with the general structure $[-(CH_2)_m-S-]_n$ can be obtained by different polymerization methods. For example, poly(hexamethylene sulfide) can be prepared by polymerizing hexamethylenedithiol and biallyl, using ammonium persulfate and sodium metabisulfite to initiate the reaction. Moreover, the oxidation of poly(alkyl sulfides) is a method for obtaining poly(alkyl sulfones) with the general formula $[-(CH_2)_m-SO_2-]_n$.Poly(alkyl sulfoxides), in the intermediate stage of the reaction, are usually oxidized to poly(sulfones), depending on the experimental conditions, and only a few reactions allow selective oxidation of sulfides to sulfoxides.

Different degrees of sulfonation and sulfoxidation can thus be obtained by modifying the experimental conditions. For this reason many of the data on the thermal transitions of these polymers involve some dispersion and confusion due to variations in molecular weight and molecular structure resulting from the method of synthesis.

In a previous paper[1] we reported the oxidation of poly(hexamethylene sulfide) crystallized in very dilute solutions in order to investigate the oxidative attack and the properties of the polysulfone products. Changes in the enthalpy and temperature of melting have been found and correlated with different stages of the oxidation. These stages correspond to different compositions in sulfide, sulfoxide, and sulfone groups, modifying not only the transition temperatures but especially the crystalline structure.

Since the study of dynamic relaxations may lead to a better knowledge of the nature of the fold surface of crystallites because the oxidative attack takes place preferentially in the noncrystalline regions,[2] the aim of this work is to study how the dynamic mechanical relaxations of several oxidized poly(hexamethylene sulfide) samples are changed by the variation in the composition of the resulting polymers.

## Experimental Section

**Materials.** The preparation of poly(hexamethylene sulfide) (PS1) was carried out by polymerization of hexamethylenedithiol and biallyl, using ammonium persulfate and sodium metabisulfite to initiate the reaction, according to the method described by Marvel and Aldrich.[3] The crude polymer product was dissolved in chloroform, and methanol was added as a precipitant. The precipitate was recovered by filtration and dried in a vacuum desiccator. The first precipitated polymer was fractionated with benzene/methanol. The number-average molecular weight was measured in a Hitachi Perkin-Elmer vapor pressure osmometer at 25 °C in chloroform solution. The resulting $\bar{M}_n$ was 9000.

Table I
Composition of Oxidized Poly(hexamethylene sulfide) (PS) with Different Amounts of Sulfoxide (PSO) and Sulfone (PSDO) Groups

| | wt fraction/% | | |
|---|---|---|---|
| sample | PS | PSO | PSDO |
| PS1[a] | 100 | 0 | 0 |
| PS2[a] | 75 | 25 | 0 |
| PS3[a] | 60 | 40 | ca. 0 |
| PS4[a] | 35 | 30 | 35 |
| PS5[a] | 40 | 35 | 25 |
| PS6[b] | ca. 0 | ca. 100 | ca. 0 |

[a] Semicrystalline sample. [b] Amorphous sample.

Almost pure poly(hexamethylene sulfoxide) (PS6) was obtained from a PS1 sample ($\bar{M}_n = 10800$) by oxidation in solution. A 0.346-g sample of PS1 was dissolved in 50 mL of chloroform. To this solution, 0.13 mol of 30% hydrogen peroxide was added with vigorous stirring at 25 °C. After 2 h, the solution was evaporated under vacuum, yielding a heterogeneous film, which was dissolved in chloroform and was precipitated by addition of methanol. The white solid was separated by filtration and then was repeatedly washed with ethanol and vacuum-dried. Quantitative elemental analysis of C, H, and S was carried out in a Perkin-Elmer 240 analyzer: C, 54.84; H, 9.20; S, 23.95 (calcd: C, 54.55; H, 9.09; S, 24.24). The infrared spectrum showed the sulfoxide band at 1030 cm$^{-1}$, but not the band at 1130 cm$^{-1}$ for the sulfone group. X-ray diffraction showed no crystallinity. Both the PS1 and PS6 films were cast from chloroform solution.

PS2 and PS3 films were made from preformed samples of PS1, immersed in 50 mL of water, and oxidized at 25 °C with $7 \times 10^{-4}$ and $15 \times 10^{-3}$ M solutions, respectively, of aqueous hydrogen peroxide (30%) under continuous stirring for 24 h. Oxidized films were thorougly washed with ethanol and dried in a vacuum desiccator for 24 h. PS4 and PS5 films were obtained as described above, but with solutions of aqueous hydrogen peroxide (30%) dissolved in aqueous $2.5 \times 10^{-2}$ M trifluoroacetic acid.

The compositions of all the samples are listed in Table I.

**X-ray Diffraction.** X-ray diffraction measurements were made with a Philips X-ray diffractometer. The diagrams were recorded in the $2\theta$ range between 4 and 35°, with nickel-filtered Cu K$\alpha$ radiation.

**Thermal Properties.** The thermal properties were studied in a DuPont DSC-900 calorimeter. The weights of the samples ranged between 3 and 7 mg and the heating rate was 10 °C/min. $T_g$ was taken as the intersection of the base line with the extrapolated sloping portion of the curve produced when a base line shift occurred during the transition.

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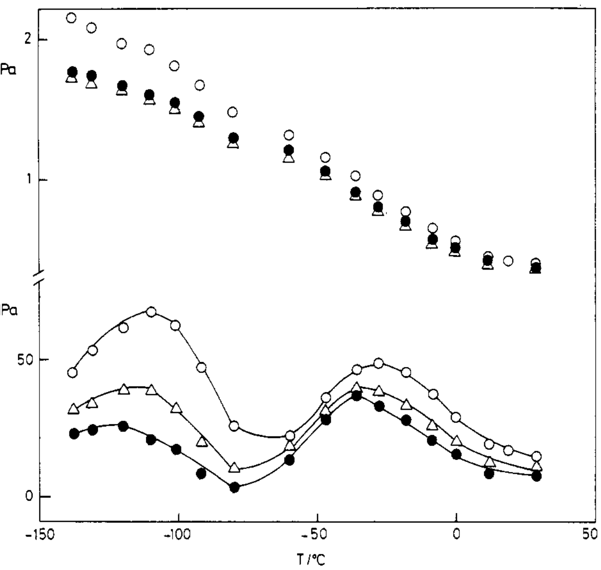

**Figure 1.** Plot of storage ($E'$) and loss ($E''$) moduli against temperature for sample PS1 at different frequencies (Hz): (○) 110; (△) 11; (●) 3.5.

**Dynamic Mechanical Measurements.** Dynamic mechanical properties were measured with a Rheovibron DDV IIB dynamic viscoelastometer from Toyo Measuring Instruments Co. The complex modulus and the loss tangent were determined at 110, 35, 11, and 3.5 Hz in the temperature range between −150 and +50 °C. The films were heated and cooled at a rate of 1 °C/min and checked for thermal history effects, which were negligible as revealed by successive measurements.

## Results and Discussion

The physical properties and thermal transitions of poly(thioethers) show very important variations as the number of methylene groups increases. The highest melting temperature, $T_m$, corresponds to the first term of the poly(methylene sulfide) series[4] and it decreases for the higher members,[5-7] with the lowest values of $T_m$ corresponding to poly(trimethylene sulfide) and poly(tetramethylene sulfide).[8] However, the glass transition temperatures of these polymers have not been reported, except for those members with 2, 3, and 4 methylene units.

Moreover, the selective oxidation of poly(alkyl sulfides) produces poly(alkyl sulfones), and the thermal transitions of these polymers with 3, 4, and 6 methylene units have been studied along with some of their branched derivatives.[9-11] These data vary somewhat due mainly to the different degrees of sulfonation and the subsequent changes in the number of sulfoxide units introduced in the chain. Intermediate stages in oxidation lead to terpolymers with sulfide, sulfoxide, and sulfone groups associated with corresponding changes in properties especially in the dynamic mechanical relaxations.

In a previous paper[1] we reported the temperature and heats of melting of poly(hexamethylene sulfide) and poly(hexamethylene sulfone). We have now tried to determine their glass transition temperatures by means of DSC; although they are barely detectable, these glass transition temperatures seem to be around −40 and +30 °C, respectively. As revealed by X-ray diffractometry, poly(hexamethylene sulfide) and poly(hexamethylene sulfone) are semicrystalline polymers but poly(hexamethylene sulfoxide) is amorphous.

Table II
Temperatures ($T$/°C) at 3.5 Hz and Activation Energies ($\Delta H$/(kcal/mol)) of Dynamic Mechanical Relaxations of Various Oxidized Poly(hexamethylene Sulfide) Samples

| | γ relaxation | | β relaxation | |
|---|---|---|---|---|
| sample | $T$ | $\Delta H$ | $T$ | $\Delta H$ |
| PS1 | −121 | 13 ± 2 | −36 | 55 ± 11 |
| PS2 | −121 | 15 ± 2 | −46 | >100 |
| PS3 | −130 | 16 ± 3 | −55[a] | |
| PS4 | | | −66 | 20 ± 3 |
| | | | 26 | >100 |
| PS5 | | | −77 | 34 ± 7 |
| | | | 20 | >100 |
| PS6 | | | −72 | >100 |

[a] Shoulder.

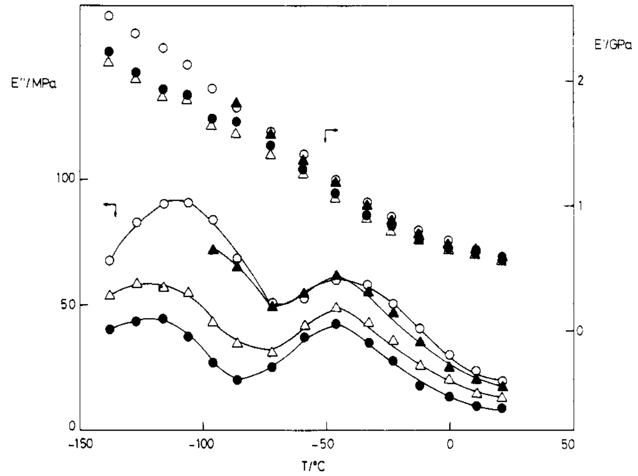

**Figure 2.** Storage ($E'$) and loss ($E''$) parts of the complex modulus as a function of temperature for sample PS2 at different frequencies (Hz): (○) 110; (▲) 35; (△) 11; (●) 3.5.

The dynamic mechanical behavior indicates the main and secondary relaxations of these polymers and relates them to their composition, structure, and crystalline morphology. The starting polymer, poly(hexamethylene sulfide) (PS1), shows two relaxations in the range of temperature and frequency that has been studied (Figure 1). The low-temperature relaxation, $T_\gamma$, is due to movement of methylene units in the amorphous phase, and its activation energy (Table II) lies in the range expected for a γ relaxation. The molecular mechanism responsible for the mechanical damping peaks associated with the γ relaxation is still controversial. Schatzki,[12] Wunderlich,[13] Boyer,[14] and Boyd and Breitling[15] have proposed different types of crankshaft rotations involving several methylene units in the amorphous phase. These proposals have been reviewed and discussed by Cowie.[16] We have found this relaxation in various polyethers and polyethylene[2,17] and have discussed its temperature and apparent activation energy.

The other relaxation, denoted here as the β transition, takes place at −36 °C (3.5 Hz) and is considered the glass transition of the polymer because of its high activation energy. The activation energies for the relaxations were calculated from the frequency shift of the maxima, and their absolute errors were obtained with the assumption of a variation of ±1 °C in the temperature of the maxima of loss modulus plotted as a function of temperature.

As previously reported[1] the oxidation of poly(hexamethylene sulfide) takes place in two stages; the first one corresponds to the formation of polysulfoxide and the second one corresponds to the formation of polysulfone. The level of oxidation may be related to the crystalline and amorphous regions, and random oxidation of the interfacial region can be assumed at the beginning of the reaction.

Both sulfoxide and sulfone groups will be present in different amounts (samples PS2, PS3, PS4, and PS5), depending on the oxidation conditions. When the con-

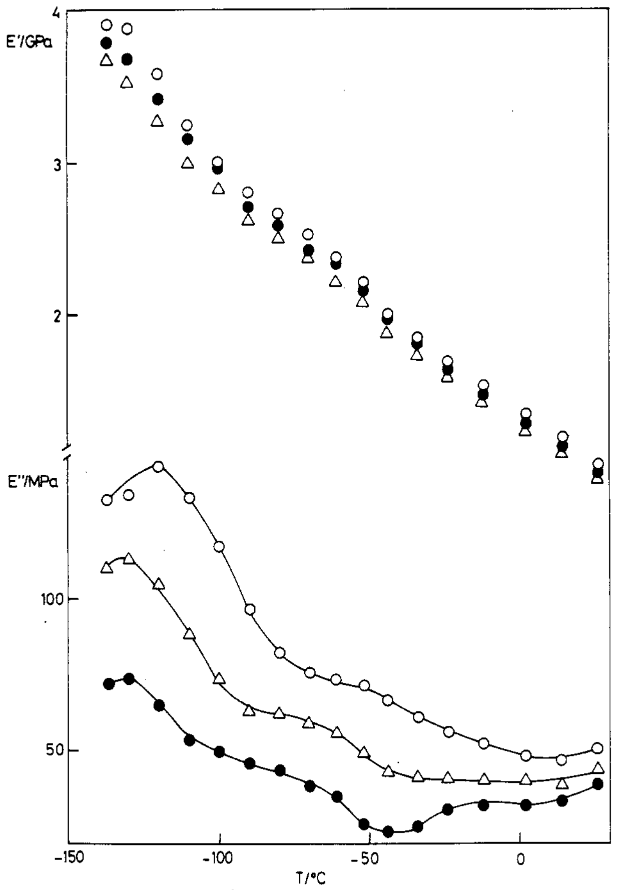

**Figure 3.** Storage ($E'$) and loss ($E''$) moduli against temperature for sample PS3 at different frequencies (Hz): (○) 110; (△) 11; (●) 3.5.

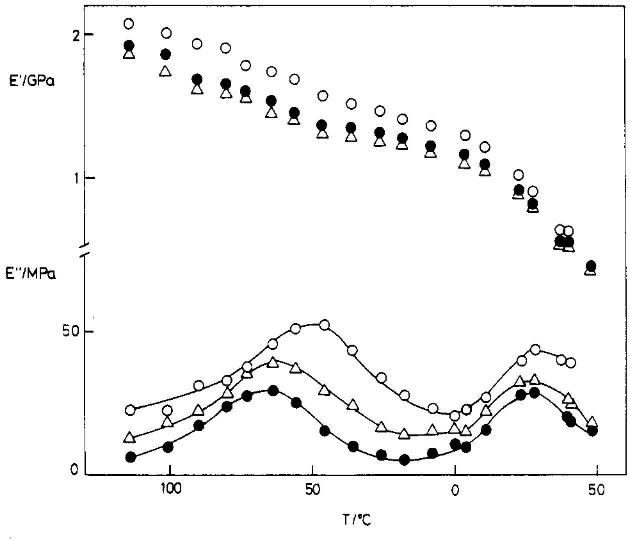

**Figure 4.** Storage ($E'$) and loss ($E''$) parts of the complex modulus as a function of temperature for sample PS4 at different frequencies (Hz): (○) 110; (△) 11; (●) 3.5.

centration of oxidizing agent is small, only sulfoxide groups are formed, without formation of sulfone groups, until about 30% of sulfoxide groups are obtained. At higher concentrations of oxidizing agent, the content of sulfone groups increases.

The oxidation from sulfur to sulfoxide groups is not exhaustive for PS2 and PS3 samples. Moreover, absolute exclusion of traces of sulfone groups cannot be assured for sample PS3 (Table I). The crystallinity levels of samples PS2 and PS3 are about 50%, measured by X-ray diffractometry. Because of this low degree of crystallinity, the disordered amorphous phases of samples PS2 and PS3 have not been completely attacked, and consequently these samples exhibit a $\gamma$ relaxation, as shown in Figures 2 and 3. The apparent increasing intensity of the relaxation from PS1 to PS3 samples is due to storage modulus increases, but the damping is actually the same for the three polymers. The persistence of the $\gamma$ relaxation again confirms the early formation of sulfoxide groups in the amorphous phase, as pointed out in a previous paper.[1]

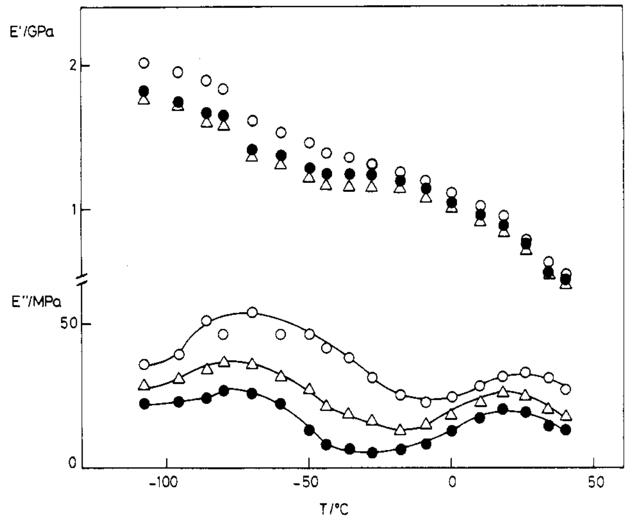

**Figure 5.** Plot of storage ($E'$) and loss ($E''$) moduli against temperature for sample PS5 at different frequencies (Hz): (○) 110; (△) 11; (●) 3.5.

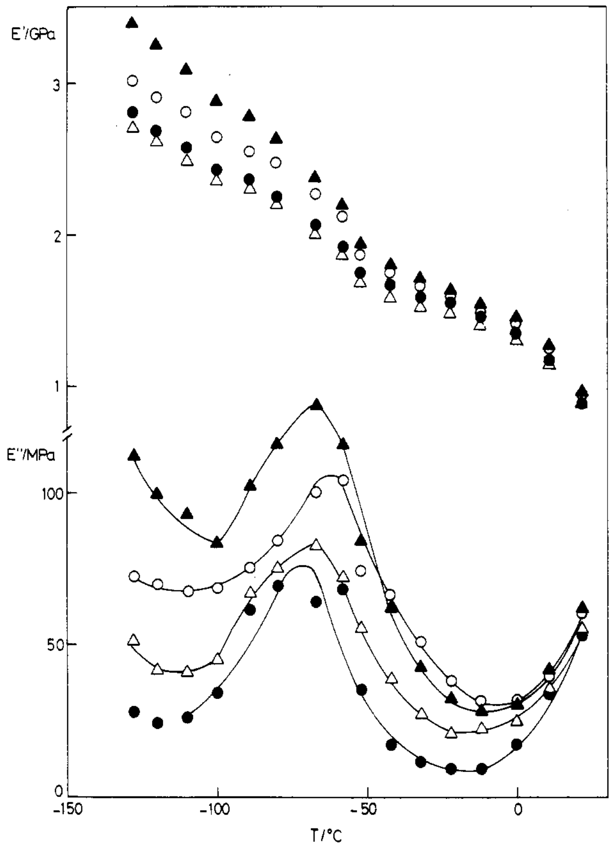

**Figure 6.** Storage ($E'$) and loss ($E''$) parts of the complex modulus as a function of temperature for sample PS6 at different frequencies (Hz): (○) 110; (▲) 35; (△) 11; (●) 3.5.

The presence of a relaxation due to sulfone groups is indicated by the trend in loss modulus variation of sample PS3 (Figure 3). The dynamic mechanical spectrum of this polymer, which presents traces of sulfone, shows a steady

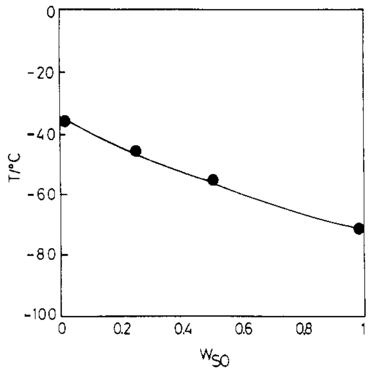

**Figure 7.** Variation in glass transition temperatures of samples PS1, PS2, PS3, and PS6 as a function of weight fraction of sulfoxide groups.

increases in the loss modulus at the highest temperatures, in contrast with the decrease found in sample PS2 (Figure 2). Thus the absence of sulfone groups determined by elemental analysis and dynamic mechanical behavior confirms the presence of only sulfide and sulfoxide groups in PS2.

Another transition due to the polysulfone groups is shown in Figures 4 and 5 corresponding to samples PS4 and PS5. The transitions of polymers with sulfoxidized and sulfone units take place around −70 and +25 °C, respectively. The activation energies for sulfone groups are higher than 100 kcal/mol and somewhat lower for sulfoxidized groups because the presence of two maxima in copolymers leads to activation energies much lower than those calculated for relaxation at low temperature.[18,19]

The nearly constant relaxation taking place at higher temperatures, 26 and 20 °C in samples PS4 and PS5, respectively, led to the assignment of this relaxation to a $\beta$ transition in the sense recently discussed by Popli and Mandelkern.[20] It was shown by these authors that the $\beta$ transition can be produced by segmental motion within the interfacial region (different from the amorphous phase wherein the chain units interconnect crystallites). The $\beta$ transition is greatly enhanced by random copolymerization.[21,22] It is important to note that the final stages in the oxidative attack of poly(hexamethylene sulfide) when both the amorphous layer and the crystalline arrays have been sulfoxidized occur randomly in samples PS4 and PS5.

Finally, in Figure 6, the main relaxation in the dynamic mechanical response of poly(hexamethylene sulfoxide) occurs at −72 °C (3.5 Hz) and also two smooth increases in the loss modulus take place at around −130 and +20 °C. These trends may be due to the small concentrations of sulfide and sulfone groups, which cannot be disregarded in PS6 sample (Table I). The main relaxation can be attributed to the glass transition, because the rising loss near 20 °C, due to sulfone groups, prevents a strong decrease of the loss modulus at temperatures far above $T_g$. If the main relaxation at −72 °C in the PS6 sample is considered to be the $T_g$ of this polymer, the glass transition temperature decreases in the series of polymers PS1, PS2, PS3, and PS6 (Figure 7), in accordance with the general Wood equation for random copolymers.[23]

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