Oxidation of Poly(hexamethylene sulfide) Single Crystals

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ABSTRACT: Oxidation of poly(hexamethylene sulfide) single crystals has been carried out in a dispersion of distilled water at 25 °C using trifluoroacetic acid and H_2O_2 in order to investigate the oxidative attack at different stages of the process and to analyze the properties of the intermediate polysulfones that are obtained. The oxidation takes place in two different stages. The first stage corresponds to preferential formation of sulfoxide groups at the amorphous interface, but if the process takes place at a higher concentration of oxidizing agent, formation of sulfone groups takes place not only at the interface but also in the crystal lamellae. The reaction was followed by analysis of SO and SO_2 groups and infrared spectra of the resulting materials, and changes in crystallinity and melting behavior were followed by X-ray diffraction and calorimetry. Changes in the heat and temperature of melting are related to the different stages of oxidation and to modifications in the crystalline structure.

Introduction

Poly(thioethers) with the general formula $[-(CH_2)_n-S-]_m$ can be obtained by solution polycondensation of the disodium salts of dithiols with dibromoalkanes,[1] by the radical-initiated polyaddition of dithiols to nonconjugated diolefins in solution,[2] by interfacial polycondensation using phase-transfer catalysis,[3] and by anionic and cationic[4–7] ring-opening polymerization of cyclic sulfides. The physical properties of these polymers show important variations as the number of methylene groups increases. The highest melting temperature, T_m, corresponds to $n = 1$[8] and it decreases for the following members, with a minimum for T_m for $n = 3$ and $n = 4$, although there is some important scattering and some confusion of the data in the literature.[2,3,9–11] These differences are presumably due to different molecular weights and distributions and to structural differences originating in the methods of synthesis.

Moreover, structural studies of poly(thioethers) have been carried out for the first three members of this series[12,13] and for poly(pentamethylene sulfide).[14] However, no attention has been paid to the crystallization kinetics from the melt or from solution of these polymers and only the rates of crystallization of poly(methylene sulfide) have been studied for an unfractionated sample.[9]

On the other hand, the oxidation of poly(alkyl sulfides) is a method for obtaining poly(alkyl sulfones) with the general structure $[-(CH_2)_n-SO_2-]_m$. Although poly(ethylene sulfone) is obtained by polymerization of ethylene and sulfur dioxide,[8] poly(methylene sulfones) containing more than two carbon atoms between the sulfone groups are obtained by oxidation. The intermediate stage, poly(methylene sulfoxides) with the structure $[-(CH_2)_n-SO-]_m$, is oxidized to polysulfones and only very few reactions allow selective oxidation of sulfides to sulfoxides.[15–18] The melting temperatures and crystalline structures of some of these polymers have been analyzed and the known data present some dispersion, due mainly to the different degrees of sulfonation and the number of sulfoxide units that can be present in the system.[2,13,19–22] Neither the poly(methylene sulfides) nor the poly(methylene sulfones) are soluble in the oxidizing medium and so a heterogeneous system had to be developed. However, partial solution of the polymer has been reported only at the intermediate sulfoxide stage.[19] Moreover, as in the case of polysulfides, there is no systematic information on the crystallization of polysulfones.

For all these reasons, we have initiated a study of the crystallization of polysulfides and polysulfones with different numbers of methylene groups. Moreover, the fold structure of polymer crystals by chemical reactions has been previously studied by a number of authors. Oxidative attack was the first method used on bulk-crystallized materials and on single crystals,[23–28] and the oxidation of polysulfides to polysulfones is also of interest from the standpoint of determining the nature of the fold surface when the preferential attack takes place in noncrystalline regions.

In this paper we report the results obtained on the oxidations of poly(hexamethylene sulfide) single crystals, with two different purposes: (a) the investigation of the oxidative attack on the crystal in a heterogeneous medium at different stages of the oxidation process in order to analyze where and how it takes place and (b) the study of the properties of the intermediate and final polysulfones that are obtained. These properties are related to the melting behavior and crystalline structure of these polymers.

Experimental Section

Materials. The preparation of poly(hexamethylene sulfide) (PHS) 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.[2] In brief, the monomer mixture consisted of freshly distilled hexamethylenedithiol and biallyl, and the catalyst solution was prepared with ammonium persulfate and sodium metabisulfite, both reagent grade, dissolved in distilled water. Lauryl sulfate in distilled water was used as an emulsifier and the polymerization temperature was 30 °C. The obtained crude polymer was dissolved in chloroform, and methanol was added as a precipitant. The precipitated product was recovered by filtration and drying in a vacuum desiccator. The first precipitated polymer was fractionated using benzene/methanol. Number-average molecular weight, $\bar{M}_n$, was obtained in a Hitachi Perkin-Elmer vapor pressure osmometer at 25 °C in chloroform solutions. The resulting molecular weight was 9000.

Single crystals of PHS were grown isothermally from dilute xylene solutions. The polymer concentration was less than 1% and the crystallization temperature was 40 °C. More than 72 h was necessary for the isothermal crystallization and the crystals were separated from the mother liquor and dried by methods previously described. The crystals were observed by polarizing light microscopy.

Pure poly(hexamethylene sulfone) was obtained from a PHS sample ($\bar{M}_n$ = 13 000) by oxidation in solution. Fifty milliliters of chloroform was used as solvent for 0.2 g of PHS, and 0.1 mL of H_2O_2 (30%) and 0.1 mL of trifluoroacetic acid were added with vigorous stirring at 25 °C. After 24 h, the precipitated polymer was recovered by filtration, washed with ethanol, and dried under vacuum. The IR spectrum shows the typical band at 1130 cm^{-1} for polysulfones, without the band at 1030 cm^{-1} for sulfoxide groups. The elemental analysis was as follows: C, 48.58; S, 21.59; H, 8.17. (Calcd: C, 48.65; S, 21.62; H, 8.11).

Procedures. Oxidation was carried out on PHS single crystals dispersed in distilled water at 25 °C. This dispersion contained

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Table I

sample	$[H_2O_2]$, mol/L	$[CF_3COOH]$, mol/L	% S	percentage S	percentage SO	percentage SO_2
A			27.48	100		
B			27.35	96	4	
1	0.003	0.025	27.25	90	10	
2	0.013	0.025	27.17	80	20	
3	0.065	0.025	26.67	69	28	3
4	0.327	0.025	26.14	65	30	5
5	0.458	0.025	24.96	50	36	12
6	0.981	0.025	24.52	47	33	20
7	1.635	0.024	23.99	40	25	35
8	3.270	0.023	23.38	30	25	45
9	6.540	0.021	22.60	20	20	60

about 0.2 g of crystals per 50 mL of solvent. For the oxidation, trifluoroacetic acid (concentrations between 2.1×10^{-2} and 2.5×10^{-2} M) and H_2O_2 (concentrations between 1.3×10^{-2} and 6.54 M) were used. The mixture was stirred for 24 h and, after the reaction, was allowed to sit at room temperature before the product was isolated. The solid was separated by filtration, repeatedly washed with ethanol, and dried in a vacuum desiccator. Quantitative elemental analysis for C, H, and S was carried out in a Perkin-Elmer 240 analyzer.

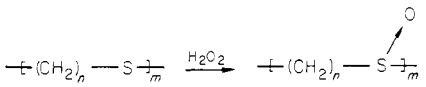
Infrared scans were taken with a Perkin-Elmer 453 instrument, and for the dried crystal, potassium bromide disks were prepared and the spectra were obtained at room temperature. In some cases, solution scans were taken in carbon disulfide in cells 0.1 mm wide.

X-ray diffractograms were obtained with a Geiger counter X-ray diffractometer made by Phillips Co. The diffractograms were recorded in the 2θ range between 4° and 35°, using Ni-filtered Cu Kα radiation. Samples of PHS crystals were obtained under slight pressure at room temperature.

The melting temperatures and melting enthalpies of the samples were measured with a Perkin-Elmer DSC 1B differential scanning calorimeter. The weights of the samples ranged between 3 and 7 mg and the heating rate was 8 °C/min. The instrument was calibrated with indium, benzil, and benzanilide. After melting, the samples were cooled from the melt at room temperature and again the melting temperatures of these melt-recrystallized samples were measured.

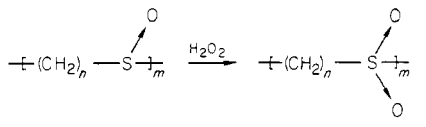
Results and Discussion

The oxidation of polysulfides takes place in two stages. The first stage corresponds to the formation of polysulfoxides according to



(1)

and the second stage corresponds to the formation of polysulfones:



(2)

When the oxidation takes place in a heterogeneous medium, which is generally the case, the initially formed sulfoxides are oxidized to the corresponding sulfones, although this last reaction is much slower than the monooxidation process. If the oxidation takes place in solution, the first stage is completed before the second stage takes place and so sulfides are selectively oxidized to sulfoxides with iodobenzene dichloride in aqueous pyridine as has been reported.[18] An excess of reagent may lead to the formation of sulfones or chlorosulfoxides.

However, when the oxidation takes place on poly(hexamethylene sulfide) single crystals, the reaction may be quite different and the rate and level of oxidation may be related to the coexistence of crystalline and amorphous regions. It has been established that chemical attack in single crystals takes place in a preferential and selective way at the amorphous interface[29] without initial changes in either the crystalline dimensions or the melting and enthalpy values for the crystallites. Hence no evidence for crystal attack and loss of crystallinity was found at low degrees of oxidation.

PHS single crystals grown isothermally at 40 °C have a melting temperature of 78 °C, with an enthalpy of fusion, ΔH, of 28 cal/g for a molecular weight fraction with $\bar{M}_n = 9000$. The degree of crystallinity is about 70%, calculated from X-ray diffractograms. This means that about 25–30% of the chain units are in a nonordered conformation, giving a disordered interfacial structure.

Random oxidation at these interfacial regions can be assumed, as will be shown later, at the beginning of the reaction. In order to follow the process, the oxidized samples were analyzed for S, SO, and SO_2 content, and in Table I the experimental conditions and the percentages of S, SO, and SO_2 obtained for each experiment are summarized. The reaction was carried out at 25 °C for 24 h. When the concentration of oxidizing agent is small, only sulfoxide groups are formed, without formation of sulfone groups, until 30% of SO groups are obtained. At higher concentrations of H_2O_2, the content of SO_2 groups increases very fast until 60% is reached, and the sulfoxide content reaches a maximum of 36% and then decreases, leveling off at about 20%.

The oxidation reaction may be followed by infrared analysis. The IR spectra of pure poly(hexamethylene sulfide) and pure poly(hexamethylene sulfone) are shown in Figure 1. In the case of polysulfide, the absorption band at 1350 cm^{-1} has been assigned to crystallinity since it disappears when the polysulfide is dissolved in CS_2. Moreover, the absorption band at 1030 cm^{-1} corresponds to the sulfoxide groups, and these two bands can be normalized by comparing their optical densities with the one corresponding to the CH_2 groups at 730 cm^{-1}.

The ratio between the optical densities of the bands at 1350 and 730 cm^{-1} does not change until 20–25% oxidation is reached, decreasing very sharply with further oxidation (Figure 2). Moreover, the ratio between the bands at 1030 and 730 cm^{-1} increases monotonically at the earliest stages of the oxidation process, when sulfoxide groups are formed; at later oxidation stages, this ratio levels off. These results agree with the ones obtained by direct elemental analysis and indicate that oxidation proceeds initially with formation of only sulfoxide groups at the interface, without changing the crystallinity of the poly(hexamethylene sulfide).

In order to accumulate more evidence, changes in crystallinity during reaction can be followed by X-ray diffraction and by calorimetry. The diffractograms of pure poly(hexamethylene sulfide) single crystals show well-de-

Table II[a]

sample	T_{m_1}, °C	T_{m_2}, °C	T_{m_3}, °C	molar fractions x_S	x_{SO}	x_{SO_2}	ΔH_u, cal/(g of initial PHS)	ΔH_u, cal/(g of residual PHS)
A	76			1.0	0	0	28.2	28.2
B	76			0.965	0.035	0	28.1	28.7
1	81	81		0.910	0.089	0	28.1	31.2
2	85	84		0.819	0.180	0	27.9	34.8
3	86	83	162	0.719	0.256	0.024	25.5	37.0
4	88	85	165	0.682	0.276	0.041	23.9	36.8
5	90	84	172	0.548	0.348	0.104	18.0	36.0
6	92	84		0.517	0.303	0.180	15.0	33.3
7	94	86		0.458	0.286	0.256	10.5	30.0
8	97	83	200	0.344	0.251	0.404	5.5	18.3
9	100	82	206	0.236	0.208	0.556	2.5	12.5

[a] T_{m_1} = melting temperature of PHS oxidized single crystals; T_{m_2} = PHS after melt recrystallization; T_{m_3} = polysulfone.

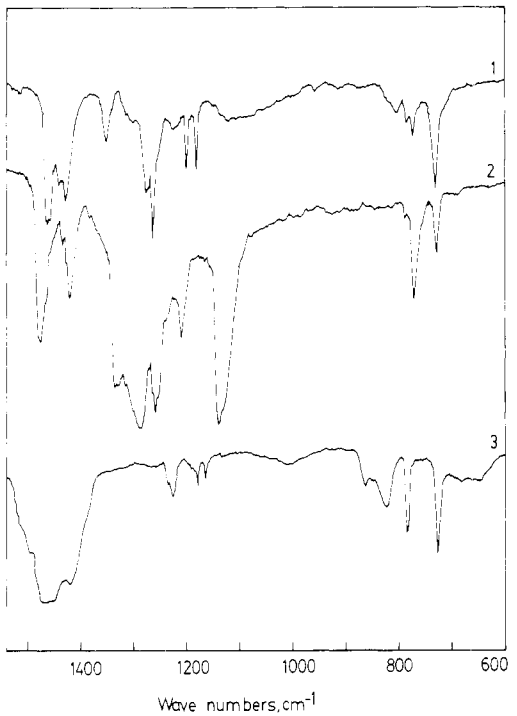


Figure 1. Infrared absorption of poly(hexamethylene sulfide) (1), poly(hexamethylene sulfone) (2), and poly(hexamethylene sulfide) in a solution of carbon disulfide (3).

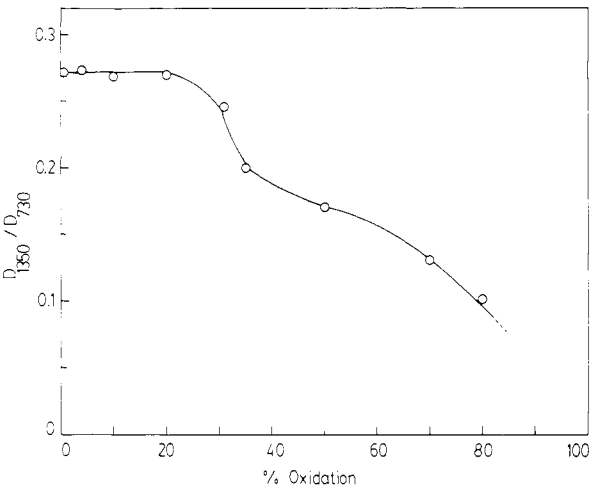


Figure 2. Ratio between optical densities at 1350 and 730 cm^{-1} vs. percent oxidation.

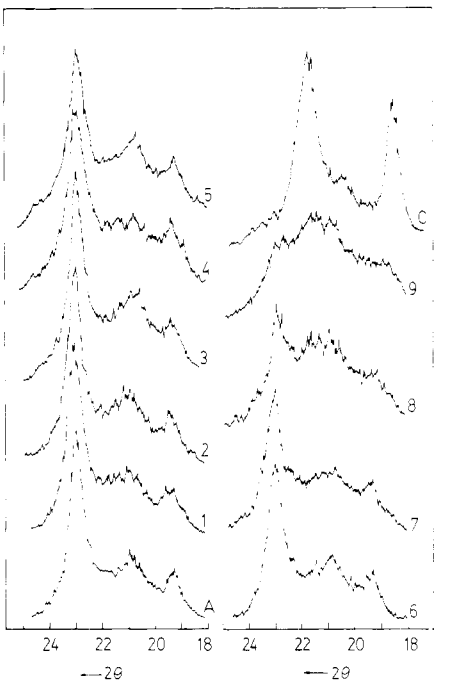


Figure 3. X-ray diffraction curves of single crystals at different oxidation levels (Table I). C corresponds to 100% polysulfone.

fined peaks at 2θ = 19.5°, 21.0°, and 23.0°, and pure poly(hexamethylene sulfone) crystallized from solution shows a diffractogram with well-defined peaks at 2θ = 22.0° and 18.6° while that crystallized from the melt shows only one peaks at 2θ = 21°.

The diffractograms change at different levels of oxidation and Figure 3 shows these variations during the oxidative attack. For samples 1–3, in which only sulfoxide groups are formed, the three peaks corresponding to PHS are clearly defined without any apparent modification. As the oxidation progresses (samples 6–9) the peaks corresponding to PHS decrease, but only at very high levels of oxidation (70–80%) do the peaks disappear. This means that after oxidative attack at the interface, oxidation takes place in the crystalline array, destroying the crystallinity and leaving no possibility for obtaining polysulfone single crystals.

If the single crystals are melted and further recrystallized from the melt, the diffractograms shown in Figure 4 are obtained. When sulfone groups are present, the peak at 2θ = 23.0° decreases when the content of SO_2 increases and a new peak at 2θ = 20.5–21° appears. This peak corresponds to the one found in pure polysulfone when it is crystallized from the melt.

Results of the DSC measurements are summarized in Table II. When the oxidized single crystals are melted for the first time, the first peak in the thermogram is

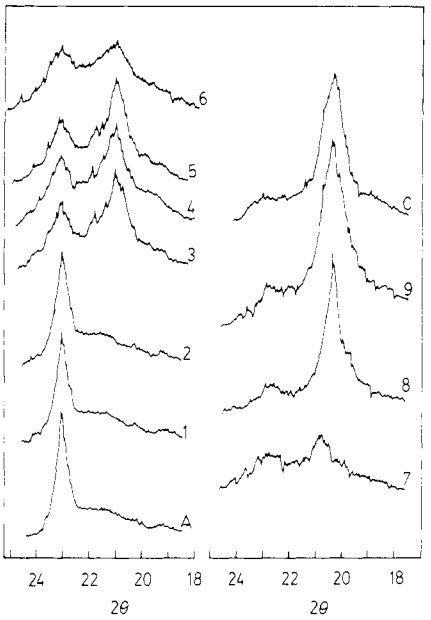


Figure 4. X-ray diffraction curves of samples recrystallized from the melt at different oxidation levels (Table I). C corresponds to 100% polysulfone.

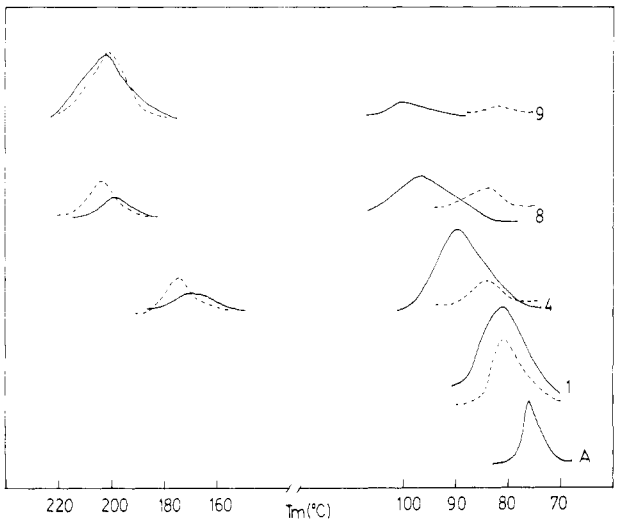


Figure 5. DSC curves at a heating rate of 8 °C min: (—) oxidized single crystals; (- - -) after recrystallization from the melt at 50 °C.

related to the melting of PHS although these peaks appear at temperatures slightly greater than the one of pure PHS.

As oxidation increases, this melting temperature increases and the trend is very apparent from Figure 5. There is no direct explanation for this fact and the only plausible statement on this point is that some SO_2 groups are included in the crystals. In other words, when oxidation increases, not only the interface is changed but also the crystal surfaces are oxidized although internal regions are less accessible. This fact does not modify substantially the diffractograms corresponding to PHS, as was shown in Figure 3, and only when oxidation is equal to or higher than 50% is the crystalline array of PHS distorted.

Isomorphic replacement has been reported in different polymers, although rules for the factors that favor cocrystallization have not been developed.[30] The introduction of random isomorphous units causes a continuous variation of the melting point, which assumes values intermediate between those of the homopolymers, and the melting point is a linear function of composition,[31] quite different from the melting temperature–composition relations for random or ordered copolymers.

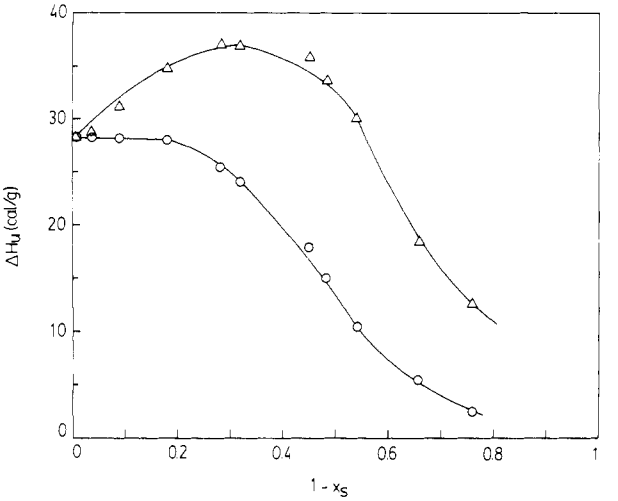


Figure 6. Melting heat, ΔH_u, against mole fraction of oxidized units for poly(hexamethylene sulfide): (○) ΔH_u in cal/g initial of polysulfide; (△) ΔH_u in cal/g of residual polysulfide.

It can, thus, be concluded that the increase of T_m for oxidized PHS may correspond to the random introduction of SO_2 units in the crystal, although the simultaneous presence of SO groups and amorphous character is a complicating factor that depresses the melting temperature expected for poly(hexamethylene sulfide)–poly(hexamethylene sulfone).

At this point, it is very important to comment that at higher temperatures, a second peak appears in the thermogram. These melting temperatures are on the order of the melting temperatures of the polysulfone. When oxidized PHS is melted, a new arrangement is obtained and crystallization of the polysulfone takes place. The melting temperature for this second peak is related to the content of SO_2 groups in the polymer, increasing when SO_2 content increases. The value expected for the pure polysulfone corresponds to 218 °C.

When oxidized single crystals are melted and further recrystallized, the melting temperatures are slightly lower and this depression becomes greater as oxidation increases. Moreover, the area under the peak is very small compared with the initial one and this result means that the recrystallization of the polymer with sulfoxide and sulfone groups takes place to a very limited extent. The reduction of melting heat, as will be commented below, is consistent with the depression of the melting temperature.

The changes in the heat of melting are plotted in Figure 6. When ΔH_u is expressed in cal/g of initial polymer, the ΔH_u values are practically constant until 25% oxidation is reached and then decrease very fast as oxidation increases. The reduction of the melting heat is a consequence of oxidation in the crystals. If ΔH_u is expressed in cal/g of residual polysulfide $[-(CH_2)_6-S-]_m$, ΔH_u values increase up to 30–35% oxidation, where ΔH_u = 38 cal/g. This value corresponds, approximately, to that of the perfect crystal; i.e., oxidation of the amorphous interface is completed and the crystalline part is unchanged.

An increase in oxidation leads to a drastic reduction of the melting heat as a consequence of attack on the crystals. From these data, it can be concluded that the first stage of oxidation takes place at the amorphous interface, with initial formation of sulfoxide groups but without alteration of the lamellar crystallites. When the S atoms in this interface are oxidized (prior to it, no significant changes in crystallinity occur), attack at the crystallite surface takes place. Now there are two competitive processes: formation

of new SO groups and formation of sulfone groups. These groups increase continuously, but the sulfoxide content slightly decreases.

In summary, from the reported experimental data it may be concluded that oxidation of PHS crystals takes place in two different stages. The first corresponds to a preferential and selective formation of sulfoxide groups at the amorphous interface of the single crystals. At a given sulfoxide content, about 30 wt % for $\bar{M}_n$ = 9000, the structure corresponds to the original lamella with a sulfoxidized interface and, consequently, with a higher interfacial free energy. However, the PHS crystalline structure is not affected and the heat of fusion is practically constant. This result is not surprising because it corresponds with the behavior of halogenated[29] or oxidized[23-28] polyethylene single crystals. Moreover, if oxidation takes place at a higher concentration of oxidizing agent, the second stage, formation of sulfone groups, takes place and this attack occurs not only in the interface but also in the crystal lamellae, with partial destruction of the polysulfide crystalline array. When the oxidized PHS crystals are melted and further recrystallized, the melting temperatures show a bigger depression, which corresponds to the behavior of a random copolymer.

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Registry No. Poly(hexamethylene sulfide), 57514-74-6; hexamethylenedithiol–biallyl copolymer, 77932-15-1.

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Structural Analysis of Ethylene–Maleic Anhydride Copolymer, Ammoniated Ethylene–Maleic Anhydride Copolymer, and Carboxyimamidate by ^{13}C and ^{1}H NMR

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ABSTRACT: ^{1}H and ^{13}C NMR have been used to probe the details of the micromolecular structure of carboxyimamidate and its intermediates: low molecular weight ethylene–maleic anhydride copolymer (EMA) and ammoniated ethylene–maleic anhydride copolymer (AEMA). With the aid of shift calculations and numerous model compounds, the complete structure of each polymer has been defined, including end groups, sequencing, and tacticity.

In 1977, a derivative of low molecular weight ethylene–maleic anhydride copolymer (EMA), carboxyimamidate,[1] was reported to be active in reducing metastasis of malignant methylchloanthrene-induced bladder carcinoma in F344 strain rats.[2] Since then, numerous polymeric analogues of carboxyimamidate have been synthesized and submitted for screening, but only a few have shown as much promise as the original lead. Therefore, to define the active site of the copolymer and obtain a better understanding of the nature of the activity, it became important to systematically prepare specific portions of the drug. Very little was known about its specific structure, however, even though considerable data had been collected that defined its physical properties. To avoid synthesizing all possible combinations of the functionalities known to be present in carboxyimamidate, it became imperative to define, as narrowly as possible, the complete structure of the copolymer. Hence ^{13}C NMR was investigated and was found, as indicated in this paper, to be a very sensitive analytical tool. In fact, it was found to be so efficient and reliable in characterizing and differentiating various polymers that it represents a significant advancement in

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