Summary

A method for making a complete record of the conductivity throughout moving boundary systems has been developed. It is based on the use of microconductivity cells outside the electrophoresis apparatus and on a careful transport of the boundary system from the apparatus into these cells. On differentiation of the conductivity diagrams, patterns are obtained which are very similar to the optical patterns but also show certain characteristic differences, which have been pointed out and briefly discussed.

UPPSALA, SWEDEN RECEIVED OCTOBER 28, 1949

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Polyalkylene Sulfides. II. Preparation of Polyhexamethylene Sulfide in Emulsion[1]

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The present work on polyhexamethylene sulfide was undertaken to see if means could be found to produce polymers of higher molecular weight than those obtained in the earlier work in this Laboratory.[1] The first changes made in the techniques developed earlier were the use of highly purified cyclohexane as a solvent, use of larger samples to reduce chance of error in exact balance of reacting groups, and elimination of air and oxygen from the reaction flasks. These changes gave slightly higher molecular weight products as judged by intrinsic viscosity than had been regularly obtained before, but no major improvements were noted. It was found, however, that solutions of polymers of an intrinsic viscosity of 0.29 in benzene followed by precipitation with methanol to give fractionation of the polymer gave as much as 50% of the original polymer with an intrinsic viscosity of about 0.5. Such polymers melted very sharply, would cold-draw to give highly oriented fibers, and could be oxidized to higher melting polysulfones.

A more satisfactory method of polymerization was found in the use of the emulsion techniques. The potassium salt of a completely hydrogenated rosin acid[3] as an emulsifier with potassium persulfate as a catalyst gave rapid polymerizations with hexamethylene dimercaptan and biallyl to give good yields of polyhexamethylene sulfides with intrinsic viscosities of 0.34 to 0.44. All products prepared by this method would cold-draw if the intrinsic viscosity was above 0.36. In one run MP-189-EF[4] was used as emulsifier and some sodium hydroxide was added to increase the *p*H. Under these conditions the polyhexamethylene sulfide obtained had a low intrinsic viscosity and had a high sulfur content which indicates that oxidation of –SH group to –S–S– group has occurred with resulting loss of balance between reacting groups.

Since alkaline conditions favor oxidation of mercaptans to disulfides, further work on the polymerization in emulsion was carried out in MP-189-EF emulsions on the acid side. Runs were made using potassium persulfate as a catalyst and copper sulfate and sodium metabisulfite as activators as recommended by Bacon and Morgan for the reduction activation polymerization of acrylonitrile.[5] These polymerizations started rapidly and developed fast. The yield of polymer was high in a very short time, but the intrinsic viscosity of such polymer was always low. However, when the polymerization was allowed to proceed at 30° from one to four days, a few polymers with an intrinsic viscosity of 0.94 to 1.44 were obtained. However, the normal polymer prepared in this manner had an intrinsic viscosity of 0.45 to 0.65. The exact factors responsible for the formation of the high polymers in a few runs have not yet been determined.

The polymers with an intrinsic viscosity of 0.35 or more would yield fibers from a melt and the fibers could be cold-drawn. However, such fibers were very weak unless drawn from a polymer with an intrinsic viscosity of 0.45 or more. Figures 1 and 2 show the X-ray pattern of an unstretched and stretched fiber, respectively, prepared from polyhexamethylene sulfide, having an intrinsic viscosity of 1.44.[6] This high molecular weight polyalkylene sulfide had the same general structure as did the usual polymer made in solution by ultraviolet light activation as shown by a comparison of the infrared patterns of polymer made by each process (Fig. 3).[7]

Some experiments were carried out on the oxidation of polyhexamethylene sulfide in an attempt to prepare polyhexamethylene sulfone. Three oxidizing agents, perbenzoic acid, aqueous

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[1] For the first communication on this subject see Marvel and Chambers, THIS JOURNAL, **70**, 993 (1948).

[2] Monsanto Fellow in Chemistry 1948–1949.

[3] We are indebted to Dr. John Hays of Hercules Powder Company for this material.

[4] MP-189-EF is an electrolyte-free emulsifier which consists essentially of mixed alkane sulfonic acids. We are indebted to Dr. Stanley Detrich of Jackson Laboratory, E. I. du Pont de Nemours and Company, for this material.

[5] Bacon, *Trans. Faraday Soc.*, **42**, 140 (1946); Morgan, *ibid.*, **42**, 169 (1946).

[6] We are indebted to Mr. R. S. Sprague and Professor G. L. Clark for these X-ray photographs.

[7] We are indebted to Miss E. M. Peterson for the infrared data reported here.

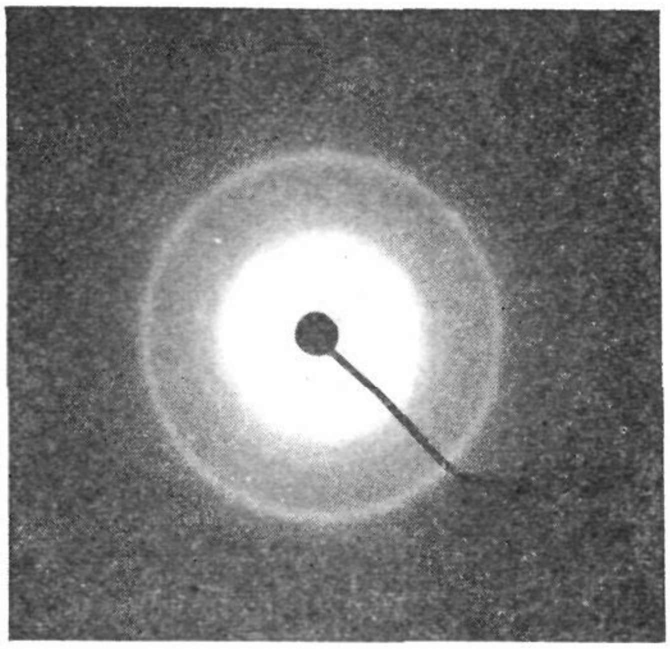

Fig. 1.—Unstretched polyhexamethylene sulfides, $[\eta]$ = 1.44.

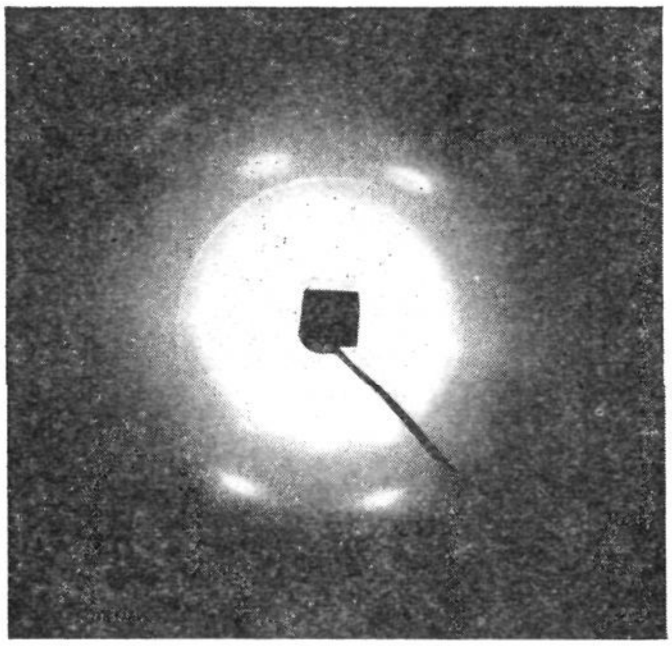

Fig. 2.—Stretched polyhexamethylene sulfides, $[\eta]$ = 1.44.

potassium permanganate and ozone, were used in various runs. Oxidation occurred in all cases, but comparison of the intrinsic viscosities of the polymers before and after oxidation showed that ozone and potassium permanganate caused considerable chain degradation. Perbenzoic acid caused less degradation, but it did not completely oxidize the sulfide units to sulfone. Apparently some sulfoxide units were formed, and this is also indicated by the fact that the oxidized polymers were less stable to heat than would be expected for a polysulfone.[8]

Further work on the development of the emulsion system of polymerizing diolefins and dimercaptans is in progress.

Experimental

Solution Polymerization of Hexamethylenedithiol and Biallyl.—Into a 200-ml., carbon dioxide-filled, quartz flask were weighed 20.621 g. (0.1372 mole) of freshly distilled hexamethylenedithiol and 11.276 g. (0.1373 mole) of freshly distilled biallyl. Two hundred milliliters of cyclohexane was added and the tightly stoppered flask was exposed at a distance of about 19 cm. to a source of polychromatic ultraviolet radiation (Hanovia Lamp, type 7420) for sixteen hours. The product which precipitated during the reaction was recovered by filtration. The yield after drying in a vacuum desiccator was 30 g. or 91%. The crude polymer was fractionated before any physical constants were determined.

In the first fractionation the 30 g. of crude polymer was dissolved in 750 ml. of hot benzene and 150 ml. of methanol was added to the hot solution. The solution was allowed to cool to room temperature overnight. The precipitated product weighed 23 g. after recovery by filtration and drying in a vacuum desiccator. The product from the first fractionation was fractionated a second time in the same manner using 650 ml. of benzene with 150 ml. of methanol. Nineteen grams was recovered from this fractionation. This product was treated again as in the first fractionation with 600 ml. of benzene and 160 ml. of methanol. Seventeen grams of polymer was recovered. This amount represented 53% of the theoretical amount for the polymerization. The final product had an intrinsic viscosity of 0.51 in a 0.446% solution in benzene and melted at 76–77°.

Anal. Calcd. for $C_6H_{12}S$: C, 62.00; H, 10.41; S, 27.56. Found: C, 61.95; H, 10.56; S, 27.49.

The polymer described here is the one used in the oxidation experiments described later.

Emulsion Polymerization of Hexamethylenedithiol and Biallyl Using Potassium Persulfate to Initiate the Reaction.—The polymerizations were run in 4-oz. screw-capped bottles which were tumbled end-over-end in a constant temperature bath during the polymerization period. For each polymerization 75 ml. of a solution of 4.2 g. of the potassium salt of hydrogenated rosin acid in 500 ml. of distilled water was put into a carbon dioxide-filled polymerization bottle. The proper amount of a 3% solution of potassium persulfate in distilled water was added and the monomers were weighed into the bottles. The bottles were capped and put on the tumbler in the constant temperature bath. The amounts of each monomer and of catalyst, the time and the temperature for each polymerization are given in Table I.

TABLE I

EMULSION POLYMERIZATION WITH POTASSIUM PERSULFATE

Sample number	Dithiol, g.	Biallyl, g.	Catalyst, ml.	Temp., °C.	Time, days
1	7.0660	3.8795[a]	1.1	30	3.5
2	7.0846	3.8718	2.2	30	3.5
3	7.0868	3.8730	1.1	50	3.5
4	7.5121	4.1055	2.2	50	3.5
5	7.0801	3.8694	1.1	30	7.0

[a] Note the excess biallyl. Theoretical amount is 3.8616 g.

At the end of the polymerization time it was noted that the samples run at 30° had up to 10% of precoagulum. The samples run at 50° were completely precipitated. All of the samples had an odor of biallyl. The portion of the polymer not already precipitated was precipitated with 5 ml. of concentrated hydrochloric acid. After separation by filtration, the polymer was mixed with 50 ml. of 95% ethanol. The ethanol was brought to boiling and the hot mixture was stirred vigorously to extract as much of the emulsifier acids as possible. After cooling the polymer was separated from the ethanol by filtration and dried. The weights of the crude polymers indicated that not all of the ethanol was removed from the polymer during drying or that the extraction to remove the emulsifier acids was not completely successful. In order to purify the crude

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(8) See Gilman, "Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., second edition, 1943, p. 835.

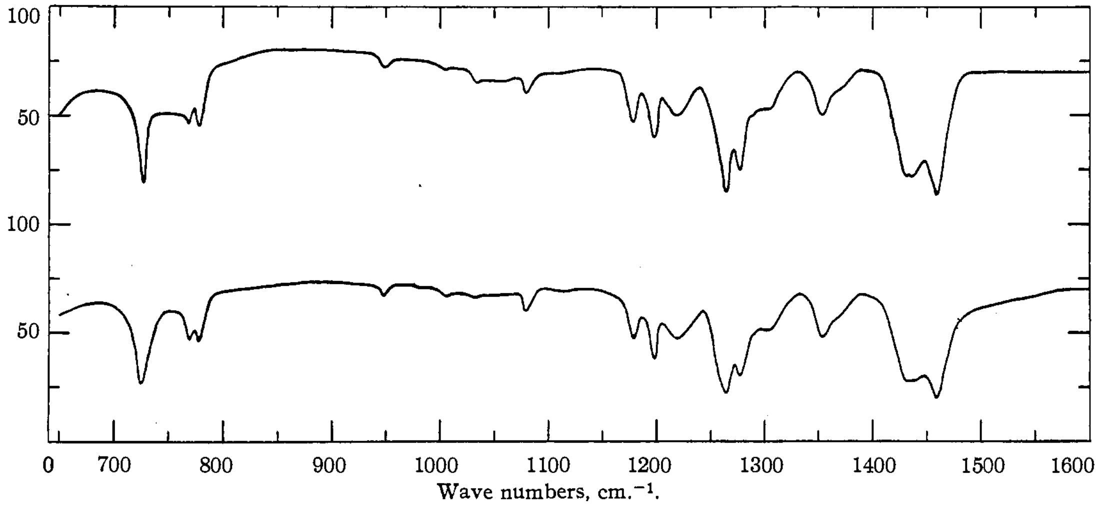

Fig. 3.—Infrared absorption of polyhexamethylene sulfide: upper curve, Polymer ([η] = 0.51) produced in cyclohexane solution by ultravolet catalysis; lower curve, Polymer ([η] = 1.44) produced by emulsion polymerization technique.

polymers each was dissolved in 225 ml. of boiling benzene, and 90 ml. of methanol was added to the boiling solution. The solutions were allowed to cool overnight. The precipitated polymers were recovered by filtration and dried. The following table summarizes the yields and intrinsic viscosities for the crude and purified polymers.

TABLE II

POLYMERS OBTAINED FROM EMULSION POLYMERIZATION WITH POTASSIUM PERSULFATE

Sample number	Crude			Purified		
	Yield, %	[η]	In % solution[b]	Yield, %[a]	[η]	In % solution[b]
1	100	0.26	0.316	54	0.34	0.312
2	101	.31	.316	64	.43	.384
3	106	.23	.300	47	.38	.288
4	104	.18	.300	34	.41	.300
5	114	.39	.336	78	.44	.312

[a] The percentage yield for the purified product is based upon the theoretical amount for the polymerization. [b] Under this heading is found the percentage concentration of the benzene solutions used for the intrinsic viscosity determinations.

Anal. (Sample 5). Calcd. for $C_6H_{12}S$: C, 62.00; H, 10.41; S, 27.52. Found: C, 62.13; H, 10.45; S, 27.52.

Emulsion Polymerization of Hexamethylenedithiol and Biallyl Using Benzoyl Peroxide to Initiate the Reaction.—A series of polymerizations was run to determine the utility of benzoyl peroxide as an initiator for the polymerization of hexamethylenedithiol and biallyl. The technique used was the same as that for potassium persulfate except that solid benzoyl peroxide was substituted for the potassium persulfate solution. The time, the temperature, and the amount of catalyst were the same. The results were generally poor. In some cases no polymer was obtained at all. In the best polymerization 7.0820 g. (0.04712 mole) of hexamethylenedithiol, 3.8714 g. (0.04713 mole) of biallyl and 0.033 g. of benzoyl peroxide were tumbled with 75 ml. of the solution of the potassium salt of hydrogenated rosin acid for three and one-half days at 30°. The crude polymer weighed 10.2 g. or 93% of the theoretical amount and had an intrinsic viscosity of 0.08 in a 0.308% benzene solution. The purified polymer weighed 3.6 g. or 33% of the theoretical amount for the reaction and had an intrinsic viscosity of 0.25 in a 0.316% benzene solution.

Emulsion Polymerization of Hexamethylenedithiol and Biallyl Using Benzoyl Peroxide, Ferrous Ammonium Sulfate and Sodium Pyrophosphate to Initiate the Reaction.—For this experiment the polymerization medium consisted of 75 ml. of a 1.2% solution of the potassium salt of hydrogenated rosin acid and 20 ml. of methanol as an antifreeze. To this mixture under a carbon dioxide atmosphere in a 4-oz. polymerization bottle were added 7.1083 g. (0.04730 mole) of hexamethylenedithiol and 3.8848 g. (0.04730 mole) of biallyl. The bottle was capped and cooled to 0°. Then 10 ml. of an aqueous suspension of 0.15 g. of ferrous ammonium sulfate hexahydrate and 0.15 g. of sodium pyrophosphate decahydrate was added together with 0.033 g. of benzoyl peroxide. The mixture was tumbled end-over-end in a 0° constant temperature bath for three and one-half days. At the end of that time the polymer was coagulated with 5 ml. of concentrated hydrochloric acid and recovered by filtration. The coagulated polymer together with a small amount of precoagulated polymer was extracted with 50 ml. of boiling ethanol. After cooling the mixture the polymer was recovered by filtration and dried. This rather crude polymer had a light green color which was probably due to the presence of the iron salt of the emulsifier acids. The polymer weighed 9.5 g. or 86% of the theoretical amount and had an intrinsic viscosity of 0.08 in a 0.320% benzene solution. When this polymer was dissolved in 225 ml. of hot benzene, 2.15 g. or 20% of the theoretical amount for the reaction was recovered after adding 90 ml. of methanol and cooling the solution overnight. The purified polymer was light green and had an intrinsic viscosity of 0.17 in a 0.348% solution in benzene.

Emulsion Polymerization of Hexamethylenedithiol and Biallyl Using Ammonium Persulfate, Sodium Metabisulfite and Copper Sulfate as Initiator.—The monomer mixture used for this experiment consisted of 49.220 g. (0.3275 mole) of freshly distilled hexamethylenedithiol and 26.901 g. (0.3275 mole) of freshly distilled biallyl. Ten milliliters of this mixture weighed 8.67 g. The monomers were kept under a nitrogen atmosphere until weighed. The monomer mixture was used as soon as possible after the weighing into a nitrogen-filled cork-stoppered flask was complete. The catalyst solutions were made up about five hours before use. One catalyst solution consisted of 1.46 g. of ammonium persulfate (Baker and Adamson, reagent grade) dissolved in 20 ml. of distilled water. A second catalyst solution consisted of 0.37 g. of sodium metabisulfite (Baker and Adamson, C. P. grade) dissolved in 10 ml. of distilled water. The third catalyst solution consisted of 0.37 g. of copper sulfate (Baker and Adamson, reagent grade crystals) dissolved in 100 ml. of distilled water. The emulsifier solution consisted of 5 g. of MP-189-EF dissolved in 500 ml. of distilled water.

TABLE III

POLYMERIZATION IN EMULSION WITH ACTIVATED SYSTEMS

Bottle number	Monomer mixture ml.	g.	Catalyst solutions, ml. $(NH_4)_2S_2O_8$	$CuSO_4$	$K_2S_2O_8$	Reaction time, days	Yield, g.	Yield, %	[η]	Grams/ 100 ml.[a]
1	9.0	7.8	1/2	1/2	1/2	1	7.4	95	0.94	0.280
2	8.4	7.3	1	1	1	1	7.0	95	0.65	.360
3	8.4	7.3	1	1	1	2	6.4	88	0.43	.328
4	8.4	7.3	1	1	1	4	6.6	90	0.45	.356
5	8.4	7.3	1	0	1	4	7.0	95	1.44	.416
6	8.4	7.3	1	0	0	4	6.6	90	0.29	.280
7	8.4	7.3	1/4	0	0	4	6.0	82	0.31	.340

[a] Refers to the concentration of the polymer in the benzene solution used for the determination of the intrinsic viscosity.

Fifty milliliters of the emulsifier solution was pipetted into each of seven 4-oz. polymerization bottles. The air above the solution was replaced with nitrogen and the bottles were capped. The capped bottles were cooled to 2°. The specified amounts of monomer mixture and catalyst resolutions were added from suitable burets. Each bottle was filled, capped and put on the tumbler in the 30° constant temperature bath as rapidly as possible. In Table III are summarized the data for each run.

At the end of the reaction time the polymer was precipitated by adding the emulsion to 15 ml. of a solution made by dissolving 50 g. of potassium aluminum sulfate in 50 ml. of concentrated hydrochloric acid and 500 ml. of distilled water. After the precipitated polymer was separated by filtration, it was dissolved in 100 ml. of benzene. The wet benzene solution was filtered into 200 ml. of methanol. The precipitated polymer was recovered by filtration, dried and weighed. An intrinsic viscosity determination was made for each sample. The results are summarized in Table III.

Anal. Calcd. for $C_6H_{12}S$: C, 62.00; H, 10.41; S, 27.59. Found, Sample 1: C, 61.87; H, 10.53; S, 27.81. Found: Sample 4: C, 61.95; H, 10.47; S, 27.65.

In a melting point determination samples 1 and 4 were found to change from a white opaque material to a colorless transparent substance at 75–77°.

Oxidation with Potassium Permanganate.—To a solution of 1.16 g. of polyhexamethylene sulfide ([η] = 0.51) in 60 ml. of benzene was added a mixture of 50 ml. of acetone, 3 ml. of glacial acetic acid and 2 ml. of distilled water. Then, 3.5 g. of potassium permanganate crystals were added over a period of fifteen minutes while the mixture was stirred and refluxed. The refluxing and stirring were continued for two hours and the mixture was allowed to sit at room temperature for about forty-four hours before the product was isolated. The dark colored solid was separated by filtration and then dispersed in 200 ml. of distilled water. Gaseous sulfur dioxide was bubbled through the water dispersion until only a white solid remained. This solid was separated by filtration and then extracted in a Soxhlet extractor for three hours with water, for four hours with acetone, and for four hours with benzene. After drying, the product weighed 1.28 g. and melted at 183–195°. The yield was 86% of the theoretical amount. The product was soluble in *m*-cresol, sulfuric acid, and hot dimethylformamide. It had an intrinsic viscosity of 0.32 in sulfuric acid and 0.58 in *m*-cresol.

Anal. Calcd. for $C_6H_{12}SO_2$: C, 48.62; H, 8.16; S, 21.63. Found: C, 50.60; H, 8.64; S, 21.43.

Oxidation with Ozone.—Ozone (approximately 2%) was bubbled through a solution of 1.16 g. of polymer in 100 ml. of chloroform at the rate of 0.00028 mole per minute for about four hours, then the flow of ozone was stopped and the product which had begun to precipitate twenty to thirty minutes after the ozone was started was recovered by filtration. The dried product weighed 1.49 g. or 101% of the theoretical amount. It melted at 195–198° and was soluble in *m*-cresol, sulfuric acid and hot dimethylformamide. The intrinsic viscosity was 0.27 in sulfuric acid and 0.30 in *m*-cresol.

Anal. Calcd. for $C_6H_{12}SO_2$: C, 48.62; H, 8.16; S, 21.63. Found: C, 47.30; H, 7.93; S, 23.50.

Oxidation with Perbenzoic Acid.—A solution of 1.16 g. of polymer dissolved in 50 ml. of chloroform was cooled in a 250-ml. volumetric flask to −5°. Fifty milliliters of a perbenzoic acid solution containing 0.00054 mole of perbenzoic acid per ml. was cooled to about 7° and added to the chloroform solution of the polymer. A white precipitate formed almost as soon as the perbenzoic acid was added. The mixture was diluted further with 100 ml. of cold chloroform and kept at about −5° for one and one-half hours with occasional shaking. The mixture was stored in the refrigerator at about 4° for fifteen hours. After warming to room temperature the mixture was diluted to 250 ml., and the excess perbenzoic acid (5%) was determined by titration. The white precipitate was separated from the liquid by filtration. After drying the product weighed 1.47 g. or 99%. The product melted at 201–206° with slight discoloration. After extracting in a Soxhlet extractor for seven hours with acetone and twelve hours with benzene, the product melted at 202–205° without discoloration. The product would discolor at a few degrees above its melting point. The oxidized polymer was soluble in *m*-cresol, sulfuric acid and hot dimethylformamide. The intrinsic viscosity was 0.69 in sulfuric acid and 0.83 in *m*-cresol.

Anal. Calcd. for $C_6H_{12}SO_2$: C, 48.62; H, 8.16; S, 21.63. Found: C, 48.52; H, 8.29; S, 22.10.

Summary

Samples of polyhexamethylene sulfide with intrinsic viscosities as high as 1.44 have been obtained by the reaction of hexamethylenedithiol with biallyl in emulsion systems. These polymers give orientable fibers on cold drawing.

These polymers have been oxidized to polysulfones. No oxidizing agent thus far tried is entirely satisfactory as some degradation of the polymer seems to occur during oxidation and there is evidence some sulfoxide links are present in the oxidized polymer due to incomplete oxidation.

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