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Sulfoalkylation of a Polybenzimidazole with Propanesultone

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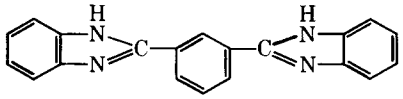
Synopsis

Poly-2,2′-(*m*-phenylene)-5,5′-bisbenzimidazole has been alkylated with propanesultone to yield polymers which are readily dyed with basic dyes. Propanesultone has been used to convert cellulose, starch, phenolformaldehyde resin, and various vinyl copolymers into hydrophilic materials which dye readily or act as ion exchange resins.[1–5] It seemed likely it would react with a polybenzimidazole to make the polymer more water absorptive and readily dyeable with basic dyes. Hence this work was undertaken.

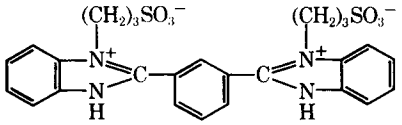
RESULTS

To study the reaction, the model compound,[6] I was treated with propanesultone under a variety of conditions which are listed in Table I.



I

The products obtained were colorless, very hygroscopic, and water soluble with strong infrared bands at 1168 cm^{-1} and 1038 cm^{-1} due to the sulfone anion and weak bands at 1530 cm^{-1} and 1375 cm^{-1}. The band at 3400 cm^{-1} due to the NH group was unchanged from that in the model compound. These data indicate that two of the tertiary nitrogen atoms were quaternized to give product II.



II

Poly-2,2′-(*m*-phenylene)-5,5-bisbenzimidazole,[6] III, was treated with propanesultone in solution and as fibers and cloth. In one case, a dimethylacetamide solution of the polymer was heated at 135–140°C with a

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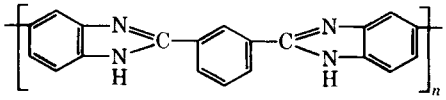
TABLE I
Reaction of (*m*-Phenylene)-5,5′-bibenzimidazole (I) with 1,3-Propanesultone

Exp. no.	Mole ratio of starting materials, I:PS[a]	Solvent[b]	Temp, °C	Time, hr	Elemental analysis, %[c] C	H	N	O	S
MO-1	1:2	DMAc	160–165	3.5	53.47	5.31	9.00	19.59	11.08
MO-2b	1:4	DMAc + toluene (1:2)	115–120	23	55.38	5.08	10.20	18.27	11.21
MO-3b	1:4	DMAc	135–140	22	56.08	4.82	10.20	17.72	12.09

[a] PS = Propanesultone.
[b] DMAc = Dimethylacetamide.
[c] ANAL. Calcd for $C_{26}H_{26}N_4O_6S_2$ (two nitrogen alkylated): C, 56.27%; H, 4.47%; N, 10.11%; O, 17.31%; S, 11.57% (crude product).



III

10 molar excess of propanesultone for 1 hr. This product (P-1) precipitated during the reaction. In another case, some PBI fiber was placed in cold dimethylacetamide and, after it was allowed to swell a few minutes, excess propanesultone was added. The mixture was then heated to 135°C for 1 hr. Some product (P-2) precipitated during this treatment and some of the fiber remained solid (P-3). The two products were similar in analysis and infrared spectra. In a further experiment, the fiber was swelled in a dimethylacetamide sultone mixture by allowing the mixture to stand for 15 min and then slowly heating to 100°C for about 90 min. Then the mixture was maintained at this temperature for 18 hr. Sample P-4 was obtained. Samples P-5 and P-6 were obtained by alkylation of fiber in dimethylacetamide in a more rapid reaction at 160°C. Some sample dissolved and reprecipitated (P-5) and some fiber did not dissolve (P-6).

The elemental analysis and the infrared analysis data on these samples are recorded in Table II. These data show that the degree of alkylation is between one and two propanesultones per recurring unit and that there is little difference in product whether the reaction is started in a homogeneous or heterogeneous media. The sulfoalkylated materials became insoluble in organic solvents (DMF, DMAc, DMSO) and also, although very hygroscopic, they did not dissolve in water or alkali. They were soluble in a 55% $ZnCl_2$ solution in water.

TABLE II
Analytical and IR Data of Alkylated Poly-2,2′-(*m*-phenylene)-5,5′-bisbenzimidazole

Exp. no.	Elemental analysis, %[a] C	H	N	S	Res.	IR bands, cm^{-1}
P-1	58.19	4.86	11.56	8.74	<0.1	(2500–2800, broad shoulder)
P-2	58.92	5.24	10.74	8.37	0.94	(1160–1215),
P-3	58.73	5.35	10.97	9.19	<0.1	(1040);
P-4	59.17	4.75	11.63	7.79	<0.1	(no decrease at 3400)
P-5	56.66	5.06	10.13	11.85	<0.1	
P-6	53.88	5.45	11.74	10.95	<0.1	

[a] ANAL. Calcd for $C_{23}H_{20}N_4O_3S$ (one nitrogen alkylated per polymer unit): C, 63.90%; H, 4.66%; N, 12.92%; S, 7.42%.

ANAL. Calcd for $C_{49}H_{46}N_8O_9S_3$ (1.5 nitrogen alkylated per polymer unit): C, 59.60%; H, 4.70%; N, 11.35%; S, 9.75%.

ANAL. Calcd for $C_{26}H_{26}N_4O_6S_2$ (two nitrogens alkylated per polymer unit): C, 56.27%; H, 4.74%; N, 10.11%; S, 11.57%.

TABLE III
Alkylation of PBI Cloth with Propanesultone

Exp. no.	Reaction conditions: Time, min	Reaction conditions: Temp, °C	Elemental analysis, %: C	H	N	S	Res.	Calcd degree of alkylation
V	30	26	74.38	4.10	17.39	0.18		about one nitrogen
	20	26–80						alkylated per 50
	15	80						polymer units
VI	30	26	70.53	4.45	15.58	2.61		
	35	26–80						about one
	180	100						nitrogen
I	30	26	67.44	4.04	15.03	2.24		alkylated per
	30	26–100						four polymer
	10	100						units
IV	10	100	70.61	4.50	15.25	2.45		
VII	30	26	61.24	5.32	13.49	6.04		
	35	26–80						
	180	100						about one
II	30	26	58.91	4.85	11.72	7.43	1.94	nitrogen
	60	26–100						alkylated per
	30	100–140						polymer
	30	140						unit
III	30	26	56.54	5.43	11.46	10.18		about two nitrogens
	60	26–100						alkylated per
	30	26–140						polymer
	24 hr	140						unit

Table III shows results of sulfoalkylation of a piece of PBI cloth in a mixture of dimethylacetamide and propanesultone (4:1 wt ratio) containing about 40 times the molar amount of sultone to PBI recurring unit.

Alkylated cloth with about 6% sulfur content and higher became insoluble in strong polar organic solvents, such as DMF, DMAc, and DMSO, even at boiling temperature. Samples with 2–2.5% sulfur content and lower are partly soluble. Samples with a high degree of alkylation are very hygroscopic.

It was expected that alkylated PBI fibers would become dyeable with basic (cationic) dyes. The dyeing of alkylated cloth with different degrees of alkylation was carried out with the cationic dye Basic Blue 4 (Sevron Blue 5G) (*Color Index*, Vol. 3, 2nd ed., #51004, 1956, p. 3423) in boiled water at pH 4–4.5. After 3 hr of dyeing, samples with 6% sulfur content and higher became very deep blue and those with about 2–2.5% sulfur showed intermediate shades. A sample with 0.18% sulfur and the unalkylated material affixed practically no dye.

This process of converting polyaromatic heterocycles to dyeable and hydrophilic products can undoubtedly be used generally for polymers which contain secondary and tertiary basic nitrogen atoms. Other alkylsultones, as for example 1,3- and 1,4-butanesultone, could undoubtedly be used for this purpose of rendering polyaromatic heterocycles dyeable and hydrophilic.

EXPERIMENTAL

The model compound I and the polymer III used for alkylation reactions were prepared earlier in this laboratory[6]; the polybenzimidazole fiber was obtained from the Celanese Corporation.

1,3-Propanesultone (mp 35–36°C) was purchased from Aldrich Chemical Company.

Alkylation of (*m*-Phenylene)-5,5′-bibenzimidazole (I) with 1,3-Propanesultone

A typical solution reaction of the model compound is the following: A solution of 1.55 g (0.005 mole) of I and 1.22 g (0.01 mole) of propanesultone in 4.5 ml of DMAc was refluxed for 3.5 hr. After standing overnight at room temperature, the white precipitate was collected and boiled twice with 20 ml of toluene, washed with benzene, and dried in a vacuum oven at 55–60°C. The product, after a few minutes, became sticky in the air (very hygroscopic).

Alkylation of Poly-2,2′-(*m*-phenylene)-5,5′-bisbenzimidazole with 1,3-Propanesultone

A typical alkylation reaction on the polymer in solution is the following: In 1 ml of dimethylacetamide was dissolved, at 40–50°C, 18 mg (0.06 mmole) of polybenzimidazole film (η_{inh} = 0.8, determined in 0.5% DMSO)

and the solution was added to the solution of 72 mg (0.6 mmole) of propanesultone. The solution was heated for 20 min to 140°C and maintained at 135–140°C for 1 hr. After about 15 min, the alkylated product precipitated and the reaction mixture grew stiff. In the next 18 hr, the temperature was kept at 100–105°C. The pale-yellow product was collected by filtration and washed several times with warm DMAc and benzene and dried in a vacuum oven at 60–70°C. The yield was 25 mg.

Alkylation of Cloth

A typical alkylation of a cloth sample is as follows: In a mixture of 25 g (~0.2 mole) of propanesultone and 100 ml of DMAc were placed three pieces of cloth (Celanese product) (about 0.5 g of each). The reaction mixture was first kept at room temperature (26°C) for 30 min. In the next 30 min, the temperature was raised to 100°C. After 10 min, the first piece of cloth (I) was removed. The temperature of the reaction mixture was maintained at 100°C for a further 20 min. Then the temperature was raised to 140°C during 30 min. After 30 min, the second piece of cloth (II) was removed and after 24 hr reaction time at this temperature, the third piece of cloth (III) was removed.

Immediately after reaction, all of the pieces of cloth were washed several times with hot DMAc and benzene and then dried in the vacuum oven at 70°C.

Dyeing Procedure

To 150 ml of distilled water were added 0.1 g sodium acetate, three drops of acetic acid to adjust the pH to 4.0–4.5, and finally 0.1 g of the cationic dye Sevron Blue 5G. The mixture was heated to full boiling, then the samples were added: the alkylated cloths and an unreacted sample to compare, with a total weight of about 1.5 g. The boiling was continued for 3 hr. Subsequently, the samples were rinsed with water and dried.

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