BISINDOLES.

32.* SOME ACTIVATED DIESTERS OF 2,2-DIHYDROXY-CARBONYL-BIS-(5-INDOLYL)SULFONE AND POLYAMIDES BASED THEREON

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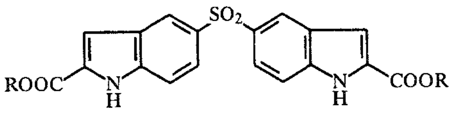
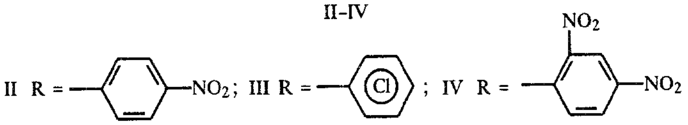
Di-acyl halides of 2,2′-dihydroxycarbonyl-bis(5-indolyl)sulfone, p-nitro-, pentachloro-, and 2,4-dinitrophenol have been used for the synthesis of "activated diesters," polycondensation of which with diamines of different structures yielded polyamides containing indole fragments with free β positions.

For the synthesis of macromolecular polyamides [2, 5] and polyurethanes [6] the "activated diester" method is most often used, this being distinguished from the di-acyl chloride method by the characteristic stability of the starting materials, and by the virtual absence of secondary processes which would lead to a restriction in growth and to "raznozvenost" (different-unit structure) of the polymer chains [7].

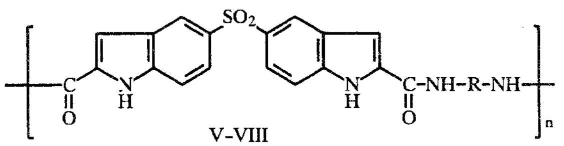
We have previously prepared activated diesters based on the di-acyl chloride of 2,2′-dihydroxycarbonyl-bis(5-indolyl)oxide; polycondensation of these diesters with diamines gave polyamides [8]. In an extension of this work we have carried out the synthesis of activated diesters of 2,2′-dihydroxycarbonyl-bis(5-indolyl)sulfone II-IV by condensation of the di-acyl chloride of 2,2′-dihydroxycarbonyl-bis(5-indolyl)sulfone (I) with p-nitro-, pentachloro-, and 2,4-dinitrophenol at 30°C in the present of triethylamine.



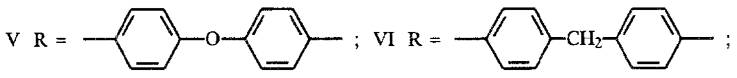
II-IV

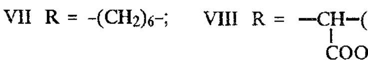


The di-acyl chloride I was prepared by the method of [9] and was converted to the active esters without isolating it from the reaction mixture; this simplified the process of isolating the desired compound.



V-VIII





VII R = $-(CH_2)_6-$; VIII R = $-\underset{\displaystyle COOC_2H_5}{CH}-(CH_2)_4-$

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*For Communication 31, see [1].

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Polyamides V-VIII were prepared by polycondensation of the active esters of II-IV with diamines of different structures. It was established that the yield and viscosity of the polyamides increased with increase in the electrophilicity of the carbonyl group of the diesters II-IV — yields were 48, 84, and 85%; the reduced viscosities (η_{red}) were 0.18, 0.25, and 0.29 dl/g respectively. The best results were obtained using activated ester IV. Polycondensation of diester IV with diaminophenyl oxide, diaminophenylmethane, hexamethylenediamine, and the ethyl ester of N,N'-di(trimethylsilyl)lysine gave polyamides V-VIII respectively (see scheme on previous page).

The reduced viscosity of polyamides V-VII varied over the range 0.25 to 0.29 dl/g.

Polyamides V-VII were shown by x-ray diffraction to have amorphous structure.

EXPERIMENTAL

Infrared spectra were run on a UR-20 spectrometer in KBr disks and PMR spectra on a Varian CFT-20 with a working frequency of 80 MHz in DMSO with TMS internal standard. A Specord spectrophotometer was used for UV spectra with THF as solvent. Monitoring of the progress of the reactions and the purity of the compounds was effected by determining the R_f on Silufol UV-254 plates. The softening temperature of the polyamines were determined from the thermomechanical curves plotted on a Tsetlin instrument.

The results of elemental analyses were in agreement with the calculated figures.

Purification of the starting materials and solvents was carried out by standard methods and the constants were in agreement with literature values.

2,2'-Di(p-nitrophenoxycarbonyl)-bis(5-indolyl)sulfone (II). To a solution of 0.28 g (2 mmoles) p-nitrophenol and 0.28 ml (2 mmoles) triethylamine in 5 ml dry dioxane was added, with stirring, 0.42 g (1 mmole) di-acyl chloride I. After 1 h the precipitated triethylamine hydrochloride was filtered off and washed with dioxane. Compound II was precipitated from the filtrate with hexane. Yield 0.46 g (74%), mp 273-275°C (from 1:2 DMF—water). R_f 0.64 (1:4 benzene—ether). IR spectrum (cm^{-1}): 3330, 3420 (NH), 1750 (C=O). UV spectrum (λ_{max} nm (log ε)): 264 (4.71), 317 (4.70). PMR spectrum (δ, ppm, J, Hz): 12.5 (1H, br.s), 7.63 (3H, d), 8.43 (4H, d), 7.78 (6H, d.d), 7.60 (7H, d), 7.60 (*a*-H, d), 8.30 (b-H, d), 8.30 (c-H, d), J_{13} = 0.7, J_{46} = 1.4, J_{67} = 9.0, J_{ab} = J_{cd} = 9.2.

2,2'-Di(pentachlorophenoxycarbonyl)-bis(5-indolyl)sulfone III was prepared from 0.42 g (2 mmoles) pentachlorophenol by a method similar to that for compound II. Compound III was precipitated with water. Yield 0.7 g (79%), mp 327°C (from 5:1 THF—ether), R_f 0.50 (3:1 benzene—ether). IR spectrum (cm^{-1}): 3360 (NH), 1760 (C=O). UV spectrum, λ_{max} nm (log ε): 232 (4.68), 250 (shoulder) (4.72, 310 (4.57). PMR spectrum (δ, ppm, J, Hz): 12.7 (1H, br.s), 7.74 (3H, d), 8.45 (4H, d), 7.81 (6H, d.d), 7.61 (7H, d), J_{13} = 1.2, J_{46} = 0.8, J_{67} = 8.5.

2,2'-Di(2,4-dinitrophenoxycarbonyl)-bis(5-indolyl)sulfone IV was prepared from 0.42 g (1 mmole) di-acyl chloride I and 0.38 g (2 mmoles) 2,4-dinitrophenol by a method similar to that for compound II. The product was purified on a column with 3:1 benzene—acetone eluent. Yield 0.61 g (85%), decomp. 183-185°C, R_f 0.52 (2:1 benzene—acetone). IR spectrum (cm^{-1}): 3300, 3800 (NH), 1760 (C=O). UV spectrum, λ_{max} nm (log ε): 259 (4.76), 315 (4.54). PMR spectrum (δ, ppm, J, Hz): 12.7 (1H, br.s), 7.62 (3H, br.s), 8.48 (4H, d), 7.80 (6H, d.d), 7.19 (7H, d), 8.90 (*a*-H, d), 8.62 (b-H, d.d), 7.94 (c-H, d), J_{ab} = 2.3, J_{bc} = 8.7. J_{13} was not observed because of rapid NH → ND exchange.

Polyamides V-VIII.* To a solution of 1 mmole activated ester IV in HMPA was added 1 mmole diamine (monomer concentration 0.6 mole/liter) and the mixture stirred 6 h at 80°C (30°C for compound VIII). The polymer was precipitated with water, filtered off, and extracted with ethanol.

Polyamide V, from Diester IV and Diaminodiphenyl Oxide. Yield 84%, η_{red} 0.29 dl/g, decomp. 300°C. IR spectrum (cm^{-1}): 3300-350 (NH), 1660 (C=O).

Polyamide VI, from Diester IV and Diaminodiphenylmethane. Yield 81%, η_{red} 0.26 dl/g, decomp. 300°C. IR spectrum (cm^{-1}): 3410 (indole NH), 3240 (amide), 1650 (C=O), 1560 (amide).

Polyamide VII, from Diester IV and Hexamethylenediamine. Yield 84%, η_{red} 0.23 dl/g, decomp. 300°C. IR spectrum (cm^{-1}): 3375 (indole NH), 3230 (amide), 1650 (C=O), 1560 (amide).

Polyamide VIII, from Diester IV and the Ethyl Ester of N,N'-Di(trimethylsilyl)lysine. Yield 74%, η_{red} 0.25 dl/g, decomp. 170°C. IR spectrum (cm^{-1}): 3410-3200 (NH), 1630 (C=O), 1540 (amide).

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*Polyamide VII was prepared in the presence of 2 mmoles triethylamine.

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*Different-unit structure, heterochain structure.