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A. P. TERENT'YEV, YE. G. RUKHADZE, G. V. PANOVA and I. G. MOCHALINA

Moscow State University

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POLYMER thioamides, which can be treated as analogues of the widely known polyamides, have still, despite the variety of work in the sphere of polyamides, been very little studied. Only some quite brief information is available in published literature regarding the possibility of synthesizing polymer thioamides from the corresponding thiolactams [1], and also some information on efforts to produce the polymer on the basis of thiourea and diphenylthiourea [2].

In continuation of the work on the synthesis and study of the properties of certain polyamides on the basis of 2,6-lutidine [3], we turned to polyamide analogues, the polythioamides. The works by Porter [4] and Martin [5] on the synthesis and

1560

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study of the properties of a number of bis-(α -thiopicolin amides) are of considerable interest. Martin represents the structure of the thioamides synthesized on the basis of alpha-picolin and benzidine, in the following way:



In the present article we report the results of our studies on the synthesis of thioamides and polythioamides on the basis of alpha-picolin and 2,6-lutidine. These derivatives were produced by the prolonged heating of the corresponding alkyl pyridines, diamines (benzidine, o-tolidine and o-dianisidine) and excess sulphur at 160–200°. Here also, of course, the structure of the thioamides based on alpha-picolin, o-tolidine and o-dianisidine is analogous to I, where R is $-CH_3$ (Ib) and OCH_3 (Ic) respectively. These thioamides are orange-yellow crystals with a melting point around 240°. These derivates were dissolved in pyridine, dimethyl formamide, chloroform and benzene, their solubility diminishing in the order Ia-Ic-Ib. Thus the presence of the methyl and methoxyl substitutes in the phenyl nuclei of the diamine somewhat reduced the solubility of the thioamides. When 2,6-lutidine was used as the alkyl pyridine and the above diamines, the following regularities were found: 1) with a ratio of 1:4 (3 or 2):10 for the reacting diamines 2,6-lutidine and sulphur, one methyl group of 2,6-lutidine enters into the reaction and a derivative is obtained with structure II:

$$H_{3}C - \bigvee_{N} - C = N - \bigvee_{R} - N = C - \bigvee_{R} - CH_{3}$$
II
IIIa R = -H; IIb R = -CH₃; IIc R = -OCH₃

2) with the reacting components in the ratio 1:1:10, the reaction does not occur and the starting materials separate;

3) with the ratio 2:1:10, i.e. surplus diamine, polythioamides are obtained with structure III:



The thiamides with structures I and II, which are polymer homologues, are very similar to one another. This means that the methyl group in the pyridine ring does not cause any marked change in the properties of the thioamides. The polythioamide III has some interesting properties.

A. P. TERENT'YEV et al.

IIIb and IIIc dissolve in most organic solvents, IIIa however, only in dimethyl formamide. When IIIb and IIIc melt (180-190°), a thread can be drawn from the melt; IIIa melts at 350-354°. It seems that this difference in the properties of the derivatives is due to the presence of side substituents in the diamine nucleus, as is seen in the IIIc and IIIb compounds, and this causes looser packing, a reduction in intermolecular interaction and, as a result, an increase in solubility. The difference between the properties of the IIIa, and IIIc and b compounds, may be due to the closer packing of the chains in IIIa. The density determined by the pycnometric method [6], is $d_4^{20} = 1.4742$ for IIIa and $d_4^{20} = 1.3530$ for IIIb, which confirms this suggestion.

The synthesized polythioamides are coloured powder materials; the powder patterns which were taken of some of them show an amorphous structure. The IR spectra taken for polythioamides III, reveal the presence of a thio ureide group. On the basis of these results and the published data [7, 8], it seems to us quite probable that the thioamides and polythioamides may exist in two tautomeric forms.



EXPERIMENTAL

Ia) 4,4'-bis-(α -thiopicolin amido) diphenyl. Into a round-bottomed flask with a feedback cooler, was placed $36\cdot8$ g ($0\cdot2$ M) benzidine, 75 g ($0\cdot8$ M) α -picolin and $72\cdot8$ g ($2\cdot2$ M) sulphur. The mixture was heated over an oil bath at 160° for 20 hours. The excess picolin was distilled off and the sulphur was removed from the solid residue in 150 ml of carbon disulphide and recrystallized three times from the pyridine. The orange needle crystals melt at 236° . Published data: 237° [4]. Yield 45 g (53%).

Ib) 4,4'-bis- $(\alpha$ -thiopicolin amido)-5,5'-dimethyl diphenyl. In the same way, from 10.6 g (0.05 M) o-tolidine, 18.6 g (0.2 M) α -picolin and 16 g (0.5 M) sulphur, to produce a yellow powdery substance, m.p. 223°, yield 4 g. (20%)

Ic) 4,4'-bis-(α -thiopicolin amido)-5,5'-dimethoxy diphenyl. In the same way, from 18.3 g (0.075 M) o-dianisidine, 28 g (0.3 M) α -picolin and 24 g (0.75 M) sulphur, to produce shiny orange crystals, m.p. 233°, yield 11 g (30%).

Found, %: N 11·23; 11·18. C₂₆H₂₂O₂N₄S₂. Calculated, %: N 11·52.

1562

IIa) 4,4'-bis-(α -thio-2,6-lutidine amido) diphenyl. In the same way, from $42\cdot 8$ g (0.4 M), 2,6-lutidine, 18.4 g (0.1 M) benzidine and 36.4 g (1.1 M) sulphur, to produce orange crystals, m.p. 223°, yield 10 g (22%).

Found, %: S 13·35; 13·36; N 12·23. C₂₈H₂₂N₄S₂. Calculated, %: S 14·11; N 11.32.

IIb) 4,4'-bis-(α -thio-2,6-lutidine amido)-5,5'-dimethyl diphenyl. In the same way a mixture of 32·1 g (0·3 M) 2,6-lutidine, 21·2 g (0·1 M) o-tolidine and 32 g (1 M) sulphur was heated at 170° for 20 hours. The resulting mass was dissolved by heating in pyridine. On cooling the precipitated deposit was filtered off, washed in 150 ml of carbon disulphide and recrystallized three times from the pyridine. A green powder was obtained, m.p. 247°, yield 25 g (52%).

Found, %: S 13.00; 13.34; N 11.16; 11.19. C₂₈H₂₆N₄S₂. Calculated, %: S 13.29; N 11.61.

IIc) 4,4'-bis-(α -thio-2,6-lutidine amido)-5,5'-dimethoxy diphenyl. In the same way, but heating was carried out at 180° for 20 hours, for a mixture of 21·4 g (0·2 M) 2,6-lutidine, 24·4 g (0·1 M) o-dianisidine and 32 g (1 M) sulphur, to produce a yellow powder, m.p. 282°, yield 33 g (65%).

 $\label{eq:cond} \begin{array}{c} Found, \ \%: \ S \ 12 \cdot 06; \ 12 \cdot 17; \ N \ 10 \cdot 75; \ 11 \cdot 39. \\ C_{28}H_{28}N_4O_2S_2. \ Calculated, \ \%: \ S \ 12 \cdot 48; \ N \ 10 \cdot 89. \end{array}$

IIIa) Poly-4,4'-bis-(α -thio-2,6-lutidine amido) diphenyl. In the same way, from a mixture of 5.3 g (0.05 M) 2,6-lutidine, 18.4 g (0.1 M) benzidine and 16 g (0.5 M) sulphur, to produce a mass which was washed in 150 ml of carbon disulphide and 100 ml hot pyridine. A yellow powder was separated, m.p. 350-354°, yield 10 g (62%).

Found, %: C 65·45; 65·61; H 3·56; 3·48. (C₁₉H₁₃N₃S₂)_n. Calculated, %: C 65·67; H 3·77.

IIIb) Poly-4,4'-bis-(α -thio-2,6-lutidine amido)-5,5'-dimethyl phenyl. In the same way, from a mixture of 5.3 g (0.5 M) 2,6-lutidine, 21.2 g (0.1 M) o-tolidine and 16 g (0.5 M) sulphur, to produce a yellow powder. This was purified by precipitating it in methanol from the pyridine solution, followed by washing in carbon disulphide. The operation was repeated three times. A material was obtained with m.p. 190-192°, yield 10 g (52%).

Found, %: C 68·10; 67·84; H 4·81; 4·78. (C₂₁H₁₇N₃S₂)_n. Calculated, %: C 67·17; H 4·56.

IIIc) Poly-4,4'-bis-(α -thio-2,6-lutidine amido)-5,5'-dimethoxydiphenyl. From a mixture of 5.3 g (0.05 M) 2,6-lutidine, 24.4 g (0.1 M) o-dianisidine and 16 g (0.5 M) sulphur using the same method, to produce an orange powder, m.p. 179–180°, yield 12 g (60%).

Found, %: N 10.75; 10.67; S 16.00; 15.80. $(C_{21}H_{17}N_3O_2S_2)_n$. Calculated, %: N 10.31; S 15.73.

CONCLUSIONS

(1) Thioamides and polythioamides have been synthesized based on α -picolin and 2,6-lutidine and a number of diamines: benzidine, o-tolidine and o-dianisidine.

(2) On the basis of the results obtained and of published data, it is suggested that thioamides and polythioamides may exist in two tautomeric forms.

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K. A. KOCHESHKOV et al.

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POLYMERS OF ETHYLENE PRODUCED WITH THE AID OF ORGANOCADMIUM-TITANIUM TETRACHLORIDE MIXTURES*

K. A. KOCHESHKOV, V. A. KARGIN, N. I. SHEVERDINA, T. I. SOGOLOVA, I. YE. PALEYEVA and O. A. PALEYEV

Physico-Chemical Institute

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THE influence of the organometallic compound in a mixed catalyst of the Ziegler-Natta type on the process and products of α -olefine polymerization has been repeatedly remarked by a number of different investigators [1-3,11]. We have also reported the use of organocadmium compounds as components of mixed catalysts and we have studied the properties of the ethylene polymer obtained in the presence of a catalyst on the basis of diethyl cadmium [2, 3]. In a patent Beauchamp [4] later described the polymerization of ethylene in the presence of diethyl cadmium and titanium tetrachloride in a medium of petroleum ether at a pressure of 17-21 atm. In some studies by Japanese authors [5, 6], dimethyl cadmium and diethyl cadmium were used as the direct catalyst for polymerizing vinyl acetate, acrylonitrile, methyl metacrylate, vinyl chloride and styrene.

We were interested in studying the process of ethylene polymerization on mixed catalyst (titanium tetrachloride-organocadmium). It was suggested, not only that some distinctive ethylene polymerization products should be produced

1564

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