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The Preparation and Cyclopolymerisation of *cis*-1,3-Di-isocyanatocyclohexane

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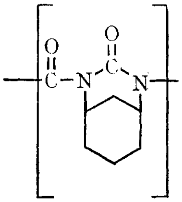
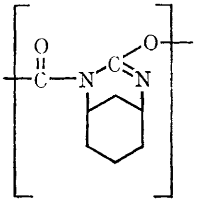
If two unsaturated, polymerisable groups of similar reactivity are arranged in *cis*-1,3-positions on a cyclohexane structure it might be expected, because of the di-axial conformation which could be assumed, that polymerisation would occur by the alternating intramolecular–intermolecular or "cyclopolymerisation"[1] mechanism. *cis*-1,3-Di-isocyanatocyclohexane was obtained from cyclohexane-*cis*-1,3-dicarboxylic acid by converting it into the dimethyl ester and hence *via* the dihydrazide to the diazide in the usual way for the Curtius reaction. The diazide was decomposed in dilute benzene–carbon tetrachloride solution to afford, after fractional distillation, the di-isocyanate as a colourless lachrymatory liquid, b.p. 102°/1·7 mm., n_D^{20} 1·4787, giving a single peak in a vapour-phase chromatogram, and confirmatory analytical and spectral data. Hewgill and Jefferies[2] have shown that this Curtius reaction is stereochemically specific and the *cis*-arrangement of the groups is retained. These workers did not isolate the di-isocyanate but converted it *in situ* into derivatives of provable configuration.

The di-isocyanate was polymerised in dry dimethylformamide solution at −60°, under nitrogen, using sodium cyanide as initiator. The polymers were obtained in high yield, as white powders (after precipitation and extraction) with melting points varying from 224° to 265°, and [η] in formic acid (98—100%), of about 0·1 dl./g. The polymers, from their infrared spectra, did not contain any residual isocyanate groups, and were soluble in, for example *m*-cresol and formic acid (98—100%), being recovered unchanged from such solutions. Thus the polymers have a linear structure and cyclopolymerisation must have occurred. Two different structural units (I and II) appear to be possible, depending upon whether polymerisation occurs through the N=C or the C=O group in the intramolecular step. The infrared spectra of the polymers show absorption bands at 1675 and 1635 cm.$^{-1}$ which could correlate with either of these structures. We have estimated the proportion of (II) units by a quantitative aminolysis with di-n-butylamine, similar to the method developed by Iwakura *et al.*[3] A mixture of the polymer and dry dimethylformamide containing sodium cyanide was treated with excess of di-n-butylamine at 25° and aliquots of the mixture


(I)


(II)

titrated over a period of several days, to determine the amount of the amine which had reacted with the polymer. A relatively fast reaction occurred over the first ten hours, followed by an extremely slow reaction continuing up to, and beyond, 100 hr. By analogy with compounds containing similar groups, the rapid uptake of the amine is believed to correspond with the reaction of the grouping $-N{=}\underset{|}{C}-O-CO-$ with one mole of the amine, leading to fission of the oxygen–carbonyl bond and the slow uptake with reaction of the grouping $-CO-\underset{|}{N}-CO-\underset{|}{N}-$ with fission of the nitrogen–carbonyl bond. Our results suggest that the structures (I) and (II) are present in the polymer in the ratio of 65 : 35.

The polymerisation of the corresponding *trans*-1,3-di-isocyanate is being examined.

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[1] J. K. Stille, "Introduction to Polymer Chemistry", John Wiley and Sons, Inc., Ch. 12.

[2] F. R. Hewgill and P. R. Jefferies, *J. Chem. Soc.*, 1956, 805.

[3] Y. Iwakura, K. Uno, and K. Ichikawa, *J. Polymer Sci., Part A, General Papers*, 1964, **2**, 3387.