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Cross-linked Polythiocarbamate Polymers

THERE is widespread interest in sulphur-containing polymers especially in the higher molecular weight elastomers. We have endeavoured to produce cross-linked materials which would be expected to have enhanced physical properties.

The reactions between the thiol group and an isocyanate, using simple mercaptans, was reported by Petersen¹. The reaction proceeded in a manner similar to that between an isocyanate and either an alcohol or a phenol, but more slowly. This has been the basis of the method described here, using diisocyanates to give chain extension, cross-linking centres being introduced by the use of polyols.

Similar work on the synthesis of linear polythiocarbamates has been discussed recently by Dyer and Osborne², who used diisocyanates and low molecular weight dithiols. These were obtained as white powders.

Schonfeld³ has reported on a sulphur-containing polymer having urethane groups in the chain, prepared by the action of diisocyanates on hydroxy-terminated thiopolyacetals. Thiopolyacetals were prepared with number average molecular weights up to 2,270, and these were reacted with a diisocyanate to give isocyanate terminal groups. Elastomers were then produced by further reaction with mixtures of triols and diols to cross-link and extend the chains.

For the present work a liquid long-chain sulphur-containing polymer, of molecular weight approximately 1,000, having a terminal thiol group at each end of the chain, has been used. This was prepared from the reaction between sodium polysulphide and *bis*(2-chloroethyl) formal. A small percentage of trichloropropane may be added to give thiol groups at intervals along the chain. The number of free -SH groups present was determined by titration of a benzene solution against standard KI₃ (ref. 4). The polymer was reacted with tolylene-2,4,-diisocyanate in a molar ratio of 2 moles diisocyanate/1 mole thiol, using the results obtained from the titration. If the reaction proceeds to completion, each end of the polymer molecule should contain a free isocyanate group available for chain extension or cross-linking. The reaction was carried out at 80° C under dry conditions, and the thiol polymer was slowly added to the diisocyanate over a period of 2 h. Heating was continued for a further 3 h by which time the viscosity of the system had increased considerably. Analysis for free isocyanate, by addition of excess amine and titration of the excess with standard acid, showed that only half the expected extent of reaction had taken place.

If the mixture was cast into a tray at this stage and heated in an oven at 70° C for 24 h, an amber-coloured rubbery solid was obtained, which, however, had little strength.

In an attempt to obtain a cross-linked product, hexane-1,2,6-triol (1 mole to 3 mole thiol polymer) was added to the mixture after time had been allowed for the initial thiol-isocyanate reaction to proceed. After thorough mixing, *in vacuo* to remove bubbles, castings were again made and heated at 60° C for 24 h. Very hard, flexible, clear rubbers were obtained by this method.

Solubility in a range of fifteen common solvents was tested at room temperature, and the samples were found to be unaffected by the majority of these. The samples swelled in dimethyl formamide, and were slightly swollen by chloroform, and isophorone. After immersion in many solvents the rubber changed colour to a very deep yellow, or in some cases a yellow-brown.

Further work is proceeding to examine the reaction process, and the physical properties of the rubber.

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Radiometric Titration of the Hexachloroplatinate (IV) Ion

THE most accurate methods of estimating platinum in the form of PtCl₆⁼ or PtCl₄⁼ in aqueous solutions containing no other platinum metals or gold appear to be precipitation as the metal either by formic acid or by oxalic acid in the presence of mercuric sulphate and sulphuric acid. But if one wishes to estimate PtCl₆⁼ in the presence of PtCl₄⁼ recourse must be made to precipitating the former as (NH₄)₂PtCl₆ or Cs₂PtCl₆, and measures required to avoid co-precipitation make such procedures tedious. Comparable accuracy may be obtained in much less time by labelling the caesium with caesium-137, and using the radioactivity of this isotope as an 'indicator' in a volumetric technique.

The general procedure is to add a fixed volume of standard active CsCl solution to portions of the PtCl₆⁼ solution of increasing volume, remove the fine precipitate by centrifuging or filtering, and assay aliquots of each solution by standard counting techniques. The activity of the solution is plotted against the volume of the PtCl₆⁼ solution, and the end-point taken where the break in the curve occurs. Theoretically¹, for a salt of the low solubility of Cs₂PtCl₆ the plot of activity *v.* volume should be linear. However, since the distinct curvature made an accurate estimation of the end-point difficult in the estimations reported here, a volume of water was added to each sample in a series such that the total volume after the addition of the PtCl₆⁼ was constant. Good straight lines and accurate end points were then obtained. Typical examples are shown in Fig. 1. The presence of the PtCl₄⁼ ion in the solution is seen to have no effect on the accuracy of estimating PtCl₆⁼.

The platinum content of all the solutions was estimated by precipitating the metal with formic acid. Table 1 shows a comparison of the values obtained gravimetrically with those from a typical series of volumetric determinations. These latter values all lie within 2 per cent of the gravimetric values. Hydrochloric acid or sodium chloride up to a concentration of 2 M had no significant effect on the accuracy of the end-point. The lower limit of reactant concentration is set by errors arising from fine particles of precipitate not being removed from the supernatant liquid. For this system, our experience indicates that the lowest concentrations allowed (before mixing) are about 4 × 10⁻³ M. In 5 ml. this yields about 13 mg of precipitate.

Radiometric titration data may be used² to evaluate the solubility product of the salt in question. Using the