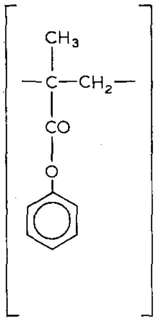
Letters

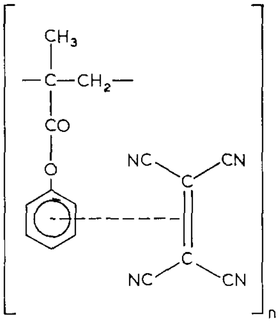
Structure Building in Tetracyanoethylene Complexes of Polymers

The donor-acceptor complexes of polymers containing electron-donating units and acceptors of low molecular weight have been investigated both in solution and in the solid state, with the purpose of investigating their optical and electrical properties [1-5].

Certainly, electrical and physical behaviour depends upon the degree and the nature of supermolecular arrangement of the polymer complex. Consequently, an attempt has been made to perform an electron-microscopic study of the donor-acceptor complexes of tetracyanoethylene (TCE) with polymers which contain electron-donating substituents, e.g. polyphenyl methacrylate (PPM), poly-2-naphthyl methacrylate and polyvinyl carbazole. The optical properties and stability of these complexes in solution had been investigated earlier [6].

PPM (I) was prepared by radical polymerisation in benzene, in the presence of azobisisobutyronitrile as initiator [6]. After reprecipitation from benzene with alcohol, PPM had an intrinsic viscosity of 0.26 dl/g (benzene, 20° C).


I


II

The TCE complex (II) of PPM was obtained by mixing chloroform solutions of the polymer and TCE in concentrations of 1×10^{-2} mole/l, in a mole ratio 1:1 between the polymer donor unit and the TCE acceptor.

Samples for electron microscopic observation were prepared by dropwise application of the chloroform solution of the polymer or the polymer complex on fresh slices of mica. After the solvent had evaporated, the samples were shadowed with Pt-C and the coatings removed with water in the conventional manner.

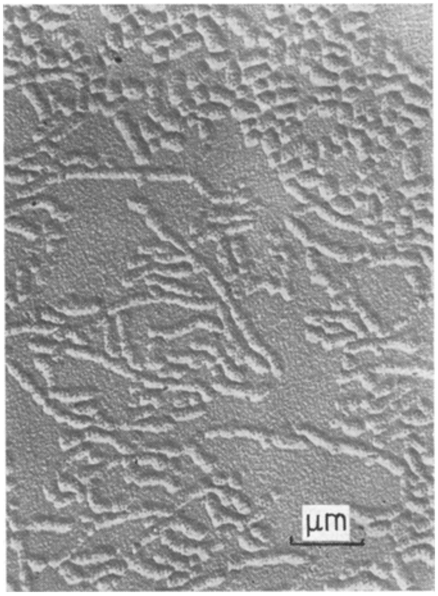


Figure 1 Electron micrograph of supermolecular structure obtained from 1×10^{-2} mole/l chloroform solution of polyphenyl methacrylate (× 10000).

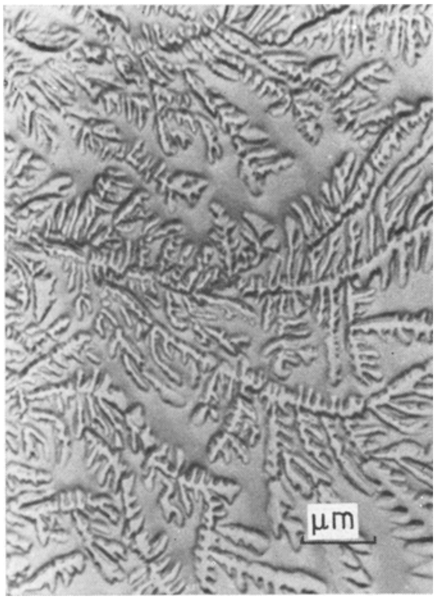


Figure 2 Electron micrograph of supermolecular structure obtained from 1×10^{-2} mole/l chloroform solution of tetracyanoethylene complex of polyphenyl methacrylate (× 10000).

The electron microscopic picture of PPM as shown in figs. 1 and 2 presents the picture of the complex of TCE with the same polymer.

That PPM builds a supermolecular structure of globules or more complicated globule aggregates is quite evident. The complex of the polymer with TCE forms structures not much differing from the structures which are typical of crystalline polymers. A similar tendency of building morphologically perfect structures was observed in the TCE complexes of poly-2-naphthyl methacrylate and polyvinyl carbazole.

It is well known that decrease of flexibility of the macromolecular chain improved its ability to adopt an ordered structure. Presumably, the great difference in the nature of supermolecular structures of PPM and its TCE complex should be ascribed to a change of flexibility of the polymer chain provoked by complex formation.

Further studies will be directed to investigation of the inner arrangement of the polymers and their complexes and to finding out whether the building of such a morphologically perfect structure is to be associated with crystal lattice formation.

References

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Transparent Sc_2O_3 by Hot-Pressing

The development of transparent ceramic materials has been the object of several investigations in attempting to fabricate material for I-R windows, windows for high temperature application, etc.

Previous studies, primarily concerned with the fabrication of transparent rare earth oxides, have been reported for Y_2O_3 by several investigators [1-4]. A variety of techniques were used in these studies including press forging with and without the use of lithium fluoride as a sintering aid [1, 2], sintering of a 90% Y_2O_3-10% ThO_2 composition [3], and hot-pressing of Y_2O_3 [4].

In this work, Sc_2O_3 was hot-pressed to determine whether a transparent product could be produced by hot-pressing techniques which had already been used successfully for other ceramic oxides in previous investigations [4, 5].

A commercially available Sc_2O_3 powder* of 99.0 to 99.9% purity was used as a starting material. The powder was analysed by semi-quantitative spectrographic analysis. Trace impurities detected are shown in table I. The "as-received" powder was dispersed in distilled water and subjected to ultrasonic treatment for 3 to 4 h in a Sonogen Automatic Cleaner†. The dispersion was subsequently filtered through successively finer filter papers to remove the larger agglomerates. The finest filter used was Whatman No. 42 paper.

TABLE I

Element	Amount (ppm)
Ag	10-100
Al	1000
B	10-100
Bi	10-100
Ca	1000
Cd	1000
Cu	100
Fe	100
Mg	100
Mn	10-100
Ni	10
Pb	10-100
Si	100-1000
Sn	10-100
Y	1000

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*Semi-Elements, Inc. Saxonburg, Pa.
†Cole-Parmer Instrument & Equipment Co, Chicago, Ill.