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CONDUCTING SYSTEMS WITH CRYSTALLINE CT COMPLEXES

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Abstract The method of reticulate doping previously used to obtain bulk-conducting macromolecular films is modified to yield surface-conducting materials. Morphology and properties of these systems, consisting of a conducting network of CT complex crystallites penetrating the bulk of an inert polymer matrix are briefly described, most of them being supposed to be common for bulk and surface-conducting films. Preparation of surface conducting films is discussed in terms of crystallization of the components of the CT complex initially molecularly dispersed in the matrix due to a controlled increase of the molecular mobility in the surface layer of the film. Possible mechanisms responsible for the unusual effectiveness of the reticulate doping are discussed.

VOLUME CONDUCTING FILMS

Crystallization of highly conducting charge-transfer CT complexes in polymeric matrices during the process of film casting provides an extremely effective method of making commercial polymers conductive^{1,2}. Due to specific conditions under which the crystallization takes place (high supersaturation and high, increasing medium viscosity) non-equilibrium, very fine and branched microcrystals of the "organic metal" are formed. At appropriate cast temperature and solvent evaporation rate the dendrite-like crystals penetrate the volume of the polymer film and form a conducting network. This technique called reticulate doping provides conductive films at surprisingly low additive content - well below 1 wt % - with specific conductivity in the range $10^{-1} - 10^{-3} \text{ ohm}^{-1} \text{ cm}^{-1}$. Depending on the perfection of the conducting network the temperature coefficient

of the conductivity (generally small) can be higher or lower, positive or negative³.

Electrical properties are not significantly deteriorated after prolonged storage (for years) in ambient atmosphere. Morphology of the crystalline network depends qualitatively on the additive concentration and on the solvent used for film casting, as well as on the polymer (amorphous or crystalline, inert or not). In some systems cast at appropriate conditions it is possible to reduce the required amount of additive down to 0.3 wt%, if dendritic structure appears⁴.

The close relationship between morphology of the crystalline network and resulting electrical properties of the conducting films affords possibility of obtaining materials with high anisotropy of the conductivity using zone-solidification technique⁵.

SURFACE CONDUCTING FILMS

Solid solutions of CT complexes in which additives are molecularly dispersed in polymer matrix exhibit conductive properties only in some cases although many of them are photoconductors⁶. Very recently it has been found that when homogeneous solid solutions of conductive CT complexes are treated with vapours of a proper solvent precipitation of the additives occurs and under favourable conditions so-formed conducting network make the film surface-conducting⁷. Precipitation of the conductive complex leads to reticulate crystallization necessary to form a conductive network only when molecular mobility in the surface layer of the polymer film is enhanced to some extent due to swelling with solvent vapours. The change of the viscosity of the layer in which crystallization should occur have to be programmed in such a way that only very fine, not visible under microscope, microcrystals of the CT complex could be formed. The thickness of the conducting layer can be estimated to be lower than $5\mu\text{m}$, thus making it possible to obtain $20\mu\text{m}$ thick

polymer films conducting on both sides independently.

In suitable conditions initial concentration of the molecularly dispersed CT complex can be as low as 0.3 wt %. Surface conductivity of polycarbonate + 0.3 wt % TTT-TCNQ films treated with dioxane vapours is of the order 10^{-4} ohm^{-1} .

Using appropriate masks it is possible to "print" required conducting pattern on the surface of an object made of suitable doped polymer.

Conductive layer on the film surface can be used as a most unusual electrode in investigations of electrical properties of some polymers⁸. It has been found that dark conductivity and especially absorption/resorption currents show different behaviour when such reticulate electrode is used. Observed differences were attributed to field injection of charge carriers (probably electrons) from extremely sharp CT complex crystal spikes into adjacent polymer.

DISCUSSION

The relatively high conductivity observed at so low content of conducting filler can be only partially explained by formation of dendrites. Additional arguments are needed to explain effective charge-carrier transport between individual dendrites. It can be shown that purely statistical contacts between dendrites are not sufficient to yield the observed macroscopic conductivity⁹. One can argue that beside of the dendritic structure visible under microscope which seems to be dominant in bulk-conducting films a fine, sub-microcrystal structure is formed (dominant in surface conducting films). This "second level" structure appears when viscosity of the medium is very high, as it is in the case of producing of surface conducting films, or, for bulk conducting films, such conditions are fulfilled in the last stage of casting, just before film solidification. The polymeric medium is then inhomogeneous and microcrystals of the CT complex grow between polymeric

globules aggregates so the probability to meet another one growing from the opposite direction is relatively high.

Even if the real contact between such microcrystals is not achieved, an effective charge carrier transport between them can be possible by injection of charge carriers from crystal edges or via tunneling (if the distance is short enough). The first possibility seems to be more likely in view of the results the above mentioned experiments on the films provided with reticulate electrodes⁸.

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