Networks and crystallinity

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Three different aspects of the relation between networks and crystals are presented and discussed. (1) Crystallization of networks; (2) network formation through crystallization; (3) influence of crystallinity on network formation as induced by radiation.

CRYSTALLIZATION OF NETWORKS

This part of the paper will discuss this from the point of view of stress-induced crystallization, where the network nature of the polymer, permanent or temporary, serves to transmit the stress, hence facilitate the extension of the chains, and so induce crystallization conditions. The crystallization is of a fibrous nature with transverse lamellar overgrowth (e.g. ref 1). The lamellae themselves can have a range of orientations in different polymers, and in a given polymer crystallized under different circumstances. Thus the lamellae can all be straight and parallel with lamellar planes perpendicular to the central fibre direction or can twist to varying extents, the extreme case being complete randomization around a direction perpendicular to the central fibre axis. The former case is the counterpart of solution-grown shish-kebabs, the latter corresponds to two-dimensional spherulites piled one on the other ('row structure')[2,3].

The factor determining the lamellar orientation was originally held to be the external stress imposed, high stress providing parallel, and low stress randomized (twisting) lamellae. More recently two additional factors influencing the orientation of the overgrowth have been recognized: (i) the nucleation density along the central fibre which, in a given polymer, can be influenced by crystallization conditions[4] (higher nucleation density gives rise to straighter lamellae); (ii) the mutual separation (hence number) of central fibres, more closely packed fibres preventing the development of full twisting which accordingly results in a more uniform overall lamellar orientation[5,6]. The origin of all this complex fibre platelet morphology rests on the fact that the most highly stressed chains give rise to the central fibre while those chain elements which are less stressed or even unstressed produce the platelets. In a crosslinked system the former are necessarily load-bearing elements, while the latter are non (or less) load bearing network portions, or may even be chains which are not parts of the network[7].

The main emphasis in this part of the paper is on the following points: (a) the stress distribution in a network is uneven; this has a profound influence on the resulting crystallization; (b) as a consequence of (a), complex multicomponent morphology results. It follows that the crystallization of stretched networks cannot be profitably discussed using traditional schemes without a knowledge of the intricacies of the resulting composite fibre–platelet morphology, including the relative amounts, mutual arrangements and internal fine structure of the components.

NETWORK FORMATION THROUGH CRYSTALLIZATION

While deeply rooted in past concepts of fringed micellar crystallization, this survey will essentially be concerned with recent results on gel-forming crystallization from solutions. The examples will be polyolefins but reference will also be made to some biopolymers[11]. The essential point here is the fact that through the phenomenon of thermoreversible gelation, the network-forming ability of crystallization is clearly manifest (e.g. ref 8). The network-forming connections are the crystals themselves which arise through the confluence of different chains along limited portions of their lengths (as opposed to the chains folding upon themselves in conventional chain-folded crystallization). The crystals thus formed are necessarily of fringed micellar character[9]. This mode of crystallization arises at very high supercoolings in place of the usual chain folded lamellae, presumably because here the critical nucleus such as may arise by the 'sticking-together' of a few chains is sufficiently small to remain a stable crystal entity[9]. Further, it is found that chains which are chemically inhomogeneous are particularly prone to the formation of such crystalline gels where the irregularities can be different isomers of the same chemical species or chemically different entities (copolymers), e.g. refs 10–13. Here it is the limited defect free runs which associate and thus form the micellar crystal entity, while the defects create natural stops for crystal growth, thus leaving sizeable lengths of flexible links between the junctions. Whether such inhomogeneities are necessary for gel crystallization or are merely factors which promote it is one of the open questions at present[9,10,12,13].

The gels themselves can be highly elastic just as the usual covalently-linked networks which enable X-ray diffraction studies on these systems in the stretched state; this in turn can provide the new information on which much of the current work in our laboratory is based[9,13–16]. Perhaps the most conspicuous novel X-ray diffraction effect is that arising in isotactic polystyrene which indicates a new nearly-extended closely all-trans chain conformation[9,13,16] as has been considered to be incompatible with the isotactic chain in the past. In the case that the chain is fully isotactic, as opposed to containing blocks of different isomers, this requires the re-examination of the conformational possibilities of polyolefins – an activity in which we are currently involved. It appears at present that a much wider range of regular chain conformations are possible than traditionally envisaged[16]. This has wider implications for conformational analysis in general[16,17] in addition to the central question of why should gel crystallization, and *only* gel crystallization, be inducive to such novel chain conformations.

A second family of novel X-ray effects, observed to date with poly(vinyl chloride)[14,15] [standard commercial (surprisingly!) and more highly syndiotactic] and with polypropylene[18], indicate unusual crystal orientations associated with such gel crystallization. It appears that the gels contain two kinds of crystal which are morphologically distinct; one set aligns with the chains parallel and the other with the chains perpendicular to the stretch direction. This effect is currently under examination.

Whatever the final answer to the many questions raised by network-crystallization, it is evident that gel crystallization produces important technological materials (e.g. commercial PVC with appreciable crystallinity!) in physical states not obtainable by other processes.

INFLUENCE OF CRYSTALLINITY ON NETWORK FORMATION AS INDUCED BY RADIATION

This last and apparently separate topic is relevant to attempts at creating networks from crystalline polymers by irradiation, whether these are to be used for technological purposes or as model networks, in addition to being central to the study and understanding of the physical effects of ionizing radiation. It will be illustrated using selected examples taken from extensive work on the radiation-induced crosslinking of polyethylene that the initial crystallinity and crystal morphology can decisively influence the effect a given radiation dose has on the physical properties of the resulting networks.

Thus it can be shown on solution-grown single crystals of polyethylene by solubility (gel content) tests that the crosslinks which are effective in network formation are those which arise between overlying layers and thus necessarily occur at the fold surfaces. Accordingly, network development is greatly influenced by the intimacy or otherwise of the contact between consecutive layers in addition to the nature of the fold surface itself (e.g. refs 19–23). It is further demonstrated that at least at low or moderate doses (up to a few hundred Mrads) crosslinking within the crystal lattice is negligible (e.g. ref 22–23). This, amongst other effects, raises the issue of whether the different degree of network development in samples which have received the same radiation dose but possess different morphologies or physical consistencies (degree of lamellar contact) are due to differences in the absolute number of crosslinks produced, or whether they are due to the different effectiveness of the otherwise identical number of crosslinks. This issue is fundamental and so far unresolved.

Corresponding differences are also being observed in melt-crystallized material which have been given different physical treatment but have received identical doses[7,24]. Such differences can become striking. Thus of two different polyethylenes, both given a dose of, say, 30 Mrad (a technologically applied level of irradiation), one may become a true rubber while the other may remain a viscous liquid when tested in its molten state. This and the previously mentioned examples, together with many others, demonstrate the fallibility of testing which relies on network formation (gelation or modulus measurements) for the assessment of the absolute number of junction points when this is not directly available from chemical evidence. In addition it demonstrates that crosslinks, such as are forming, cannot be distributed at random, where the departures from randomness must be at least on the scale of the crystal thickness.

Most recent work on polyethylenes and paraffins employing high doses (many hundred Mrads and beyond) such as affect the perfection of the crystal lattice and lead to its destruction, reveals even greater departures from random crosslinking than may be inferred from the previous low dose studies. It has emerged[25,26] that the crosslinks can become segregated into separate domains in certain paraffins; these are recognizeable even in the images of crystals seen under the electron microscope. According to the sample type and circumstances of irradiation such segregation can result either from long range migration of the intermediate products of the energy deposition (excitation, ionization, free radicals) or by the bodily migration of the crosslinked species already formed. In either event the product is a grossly clustered distribution of network junctions; this conclusion has been arrived at independently in these laboratories by statistical analysis of the cluster size distribution below the gel point where this can be directly determined by g.p.c.[27].

We judge that all the above points in this section are of the utmost relevance to the radiation chemistry of paraffinoid substances and for application of radiation to form crosslinked products. In the context of the subject matter of the present meeting it purports to demonstrate the problem of obtaining well-characterized random networks even by a method such as radiation which (absorption effects apart – negligible in the above experiments) is normally believed to act homogeneously throughout the full sample volume.

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