

Synthesis and Properties of Hydrophilic Gels*

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Three-dimensional hydrophilic gels may principally be considered in terms of the respective linear polymers, modified so as to form a three-dimensional network. The final product possessing the three-dimensional structure is obtained in the two usual ways for preparing cross-linked systems,¹ namely by crosslinking linear macromolecules or by polyreactions of low molecular weight compounds. Formation of three-dimensional networks may occur either by chemical or by physical crosslinking.² Whereas the network structure of hydrophilic gels may be formed in the same manner as in non-hydrophilic gels, the hydrophilic character may be achieved by the introduction of corresponding groups into a pre-formed network. This procedure is e.g. very frequently applied in the case of ion exchangers.

The development of experimental procedures leading to the formation of three-dimensional networks poses minor problems as compared to the difficulties encountered in characterization studies. Reaction mechanisms and properties of networks can only be explained when the real number of crosslinks and their behaviour in the network are known. In particular, it is more difficult to explain the influence of physical than that of chemical cross-links on the properties of a network.

It is also difficult to find a correlation between macroscopic behaviour and relationships valid for molecular dimensions. This problem is overcome only by making certain assumptions. In the present light of knowledge, polymerization of low molecular-weight components is probably the most adequate tool to investigate the structural relationships of strongly polar three-dimensional systems.

To demonstrate these aspects some results of studies of hydrophilic gels will be presented. The conclusions may be considered to a certain extent as more generally valid.

The system studied was diglycol monomethacrylate, cross-linked with a small amount of glycol dimethacrylate in water solution.³ The experimental variables are the change in the concentration of the two monomers and the change of the amount of free vinyl groups attached to the three-dimensional product. Furthermore it is necessary to evaluate the contribution of chain transfer and intramolecular cyclisation reaction, the

result of which is a change in the amount of cross-links compared to the value calculated from the concentration changes of vinyl groups. The advantages of this system are its chemical stability and the possibility of determining the amount of free vinyl groups even in the case of a small amount of crosslinking agent. This system can be defined satisfactorily not only kinetically over the entire range of conversion, but also by relationships describing the behavior of the network formed. The determination of pendant vinyl groups has been effected by UV spectroscopy in the aqueous system making use of the properties of the conjugated system in the monomer molecule against unconjugated carbonyl groups of the polymer substances. UV spectroscopy in this case is only a relative method.

For the initial rate of polymerization R_p in 20–90% water solution the following relationship is valid:

$$R_p = K \cdot M^{0.6} \cdot I^{0.5},$$

where M and I are the concentrations of monomer and initiator, resp. and K a constant.

The low order of monomer concentrations may be explained by inferior solvent properties of water for the polymer. With increasing amounts of water in the monomer mixture the mutual accessibility of the chains decreases. The result of this interaction is the relative decrease of the termination rate in the reaction system.

The amount of intramolecular cyclization has been obtained from the dependence of swelling on the amount of solvent in the initial polymerization mixture. Of the crosslinking agents studied (glycol dimethacrylate, diglycol dimethacrylate, triglycol dimethacrylate), glycol dimethacrylate shows no significant change in intramolecular cyclization up to about 30% water in the monomer mixture. Since glycol dimethacrylate represents a hydrophobic compound, it is possible to assume that this behaviour is due to the formation of association crosslinks. The contribution of this effect to the observed swelling behaviour was studied by replacing a part of the glycol methacrylate by methyl methacrylate at constant amount of glycol dimethacrylate. Glycol dimethacrylate has been considered to correspond approximately to a doubled methyl methacrylate in this respect. It has been shown that the contribution of physical cross-links corresponds to about 5% of the overall value measured.

In this way it was possible to determine the participation of all reactions, which was necessary for evaluation of cross-linker utilization.

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¹ W. FUNKE, *Chimia* 22 (1968) 111.

² H.-G. ELIAS, *Chimia* 22 (1968) 101.

³ J. KOPEČEK, J. JOKL and D. LÍM, Internationales Symposium über Makromolekulare Chemie, Prag 1965, *J. Pol. Sci.*, Part C (in press).

The three-dimensional network has been characterized by combination of deformation behaviour as well as equilibrium swelling. By investigation of these properties during the course of polymerization it was possible to express the formation of cross-links as a function of conversions.

At practically 100% conversion about 10–15% of pendant vinyl groups remain unreacted. The validity of the results obtained has been verified by additional facts. The contents of vinyl groups in the system methyl methacrylate-glycol dimethacrylate determined spectroscopically in the near-infrared region (NIR) and obtained by extrapolation to equal amounts of cross-linker in this system also leads to approximately 10% unreacted pendant vinyl groups.⁴ NIR spectroscopy is an absolute method in contrast to the above mentioned UV spectroscopy.

The procedure suggested is satisfactory as a theoretical background for practical applications of hydrophilic gels of this type. The derivation of more detailed relationships is complicated, since it is difficult to estimate the homogeneity of the three-dimensional network as far as the distribution of cross-links is concerned. There are several facts which may lead to the conclusion that even a homogeneous three-dimensional polymer contains non-randomly distributed cross-links.

It can be shown that the process of three-dimensional polymerization is influenced by the solvent. Three-dimensional polymerization has a homogeneous character in a good solvent, whereas in a bad solvent separation of the polymer phase may result, in analogy to precipitation polymerization of linear macromolecules. Therefore, a state may exist, in which phase separation does not yet occur macroscopically while the network density is non-uniform. For this study the system glycol monomethacrylate glycol dimethacrylate water is suitable.⁵ At normal rates this system is homogeneous up to about 50% water in the initial mixture. From more diluted monomer solution polymer phase separates, leading to a porous polymer product. Even under the conditions for the formation of homogeneous networks, formation of distinct, macroscopic, heterogeneous particles appearing as white spots in the clear gel occurs, if one works with very low polymerization rates.

The very early formation of these particles may be observed under the light microscope using the phase contrast technique. By this method it is possible to observe heterogeneous particles even at so low conversions, where the still thin gel seems to be optically clear. Figures 1 and 2 illustrate the process of growing of such particles. Polymerization has been followed in a Koch's microscopic chamber.

The fact, that this observation has been made with methacrylic acid esters, which generally show a low ten-



Fig. 1 and 2: Heterogeneities in 60% water solution of glycol monomethacrylate cross-linked with 1% glycol dimethacrylate. Initiator 1% diisopropyl percarbonate, 20°C. Situation after 15 (Fig.1) and 100 min (Fig.2). 120 × magnified using phase contrast

dency for popcorn polymerization,⁶ seems to justify the conclusions, that unstatistical distribution of cross-links in a three-dimensional polymer may be a general phenomenon, which is profoundly influenced by the choice of conditions (amount of cross-linker, polymerization, properties of monomer, rate of polymerization, amount and properties of the solvent).

The generation of a very low number of radicals in a non-ideal solvent leads, due to the low rate of termination, to coils of macromolecules which are more compact than random. By fixing the coils in an three-dimensional network conditions favor the decrease of termination and accelerated continuation of the process. One may therefore conclude that, even in the case of a fast and seemingly homogeneous polymerization, irregular distribution of cross-links cannot be excluded. This phenomenon may affect other properties of the system.

⁴ J. JOKL, J. KOPEČEK and D. LÍM, *J. Pol. Sci.*, Part A (in press).

⁵ J. KOPEČEK and D. LÍM, paper submitted to *J. Pol. Sci.*, Part C.

⁶ J. W. BREITENBACH, International Symposium on Macromolecular Chemistry, Paris 1963, *J. Pol. Sci.*, Part C (1960) No 4, P.117.