CHAIN STRUCTURE AND SOLVENT QUALITY: KEY FACTORS IN THE THERMOREVERSIBLE GELATION OF SOLUTIONS OF VINYL POLYMERS

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ABSTRACT

The influence of chain structure and solvent quality on the thermoreversible gelation of stereoisomers of polymethylmethacrylate is discussed. In n-butanol, amorphous gels are obtained with the different isomers. Under the correct annealing conditions, the isotactic isomer will also form crystalline gels. In o-xylene and toluene, the syndiotactic PMMA forms gels by a conformational change, followed by an intermolecular association. In the same solvents, the isotactic polymer seems to form gels by crystallization. In solvents like MEK and DMF, the last polymer behaves in the same way as the syndiotactic in the aromatic solvents.

The data are discussed in the more general framework of the different possibilities of physical network formation in relation to the chain structure of vinyl polymers.

INTRODUCTION.

Moderately concentrated solutions of many synthetic and biological polymers solidify on cooling. This phenomenon, known as thermoreversible gelation, results from the formation of some kind of interconnectivity throughout the solution. It is fully reversible as heating restores the original solution\(^{(1)-(3)}\). The term gel originates from polymer chemistry, where these structures are obtained by chemical cross-linking of the molecules to form a permanent, molecular network that can be swollen by a solvent. These gels however are not reversible and the solution can only be restored by decomposing the network.

Another basic difference between chemical and thermoreversible gels is their mechanical behaviour. Chemical gels do not flow and have very characteristic elastic properties, generally not encountered with the thermoreversible ones. These last ones also show an absence of flow when e.g. the test tube in which they are prepared is turned upside down. They
nevertheless show these solid-like characteristics only between well
determined limits of applied strain, time, etc. These characteristics
differ furthermore from one case to the other, making it very difficult to
formulate a precise definition.

For that reason, thermoreversible gels must be considered as
solutions of moderate concentration, solidified by cooling, with some
elastic characteristics within well determined limits. Starting from this
general definition, they can be classified according to their formation
mechanism resulting from thermal transitions. The most frequently
encountered is a liquid-solid (L-S) demixing or crystallization. (2)-(5)
Because one is working with solutions, a liquid-liquid (L-L) demixing has
not to be excluded as it can interfere with a L-S demixing. (5) Interference
with a glass-transition – concentration curve can also be at the origin of
a solidification of a solution. (6) On cooling a polymer solution containing
chains with a regular structure, a change from a random coil to a helical
conformation can also occur. (7) This regular conformation can then be
stabilized by intramolecular interactions and by interaction with the
solvent.

It is obvious then that many factors have to be well controlled in
order to obtain an exact picture of a mechanism of formation and the
structure of a thermoreversible gel. This will be illustrated in this paper
for the different stereoisomers of poly(methylmethacrylate). Isotactic,
atactic and different types of syndiotactic isomers are available and an
accurate analysis of their tacticity can be obtained from NMR data. These
isomers also have rather different properties and consequently are good
candidates to illustrate the influence of the experimental factors on their
solution behaviour and gelation. The non crystallizable, atactic chain has
a glass transition temperature, \( T_g \), in the vicinity of 105°C. The
crystallization from the melt of the isotactic isomer was reported to be
very slow, resulting in the formation of a crystalline lattice in which the
chains adopt a double helix conformation. (8). A \( T_g \) around 45°C was
reported. This transition was found around 120°C in the case of the
syndiotactic isomer. Its crystallization from the melt is very difficult.
Crystallization on the other hand, induced by solvent vapour, seems to
proceed rather easily. It was further shown that the tacticity influences
their \( \theta \)-temperature.