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# Physical Corrosion of Semi-crystalline Polymers

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SUMMARY: Polymer-solvent compounds can be formed from homogeneous solutions obtained at high temperature but also by solvent diffusion at the solid interface of a bulk polymer at room temperature. This phenomenon we call "physical" corrosion as it modifies the surface structure without chemical change. Here we report preliminary experiments indicating that the thermodynamics seems to be little dependent upon the path used while the morphology is.

## Introduction

Many stereoregular polymers form polymer-solvent compounds[1-4]. These compounds can be prepared either from a quench of homogeneous solutions prepared at high temperature or by exposure to solvent (liquid or vapour). The latter case, often designated as solvent-induced crystallization5), has been little studied in details although promising materials are engineered through this method 6). Also, these compound-forming polymers are therefore liable to be altered when placed, from sheer necessity, in a hostile environment (for instance cable insulators near car engines, etc.), or exposed to liquid solvents when receiving coatings such as paints. We shall designate this phenomenon as *Physical corrosion.* This concept can be defined as follows: *Physical Corrosion of polymers occurs when damages are inflicted on a smooth polymer surface through the growth of polymer-solvent compounds after exposure to liquid solvent or vapour.* It differs from chemical corrosion in the sense that no chemical modification is involved in this phenomenon although the net result (surface alteration) is the same. This concept is best illustrated by considering the aspect of a polymer surface where spherulites have grown: the resulting surface is quite reminiscent of a corrosion process. Another way of approaching this concept is to consider the fractal dimension $D_s$ of the surface: for a flat surface $D_s = 2$ and therefore corrosion occurs when $D_s > 2$. Several questions arise when comparison is made with the way compounds are prepared from homogeneous solutions. For instance: i) compound formation occurs at a solid interface so that the polymer concentration is not necessarily a constant quantity throughout the sample. How does this concentration gradient affect the final state; ii) chains are highly-entangled in the polymer bulk state unlike in

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solutions, does this influence the structure and morphology? All these questions are obviously not answered in this short paper but a few clues are given. In particular, preliminary experiments suggest that, unlike the morphology, the thermodynamics is not significantly dependent upon the path followed to reach a given concentration.

## Thermodynamic aspect: temperature-concentration phase diagrams

We have focused our investigations on *syndiotactic polystyrene* (sPS). This polymer easily forms compounds with a large variety of solvents7), and also gives rise to various morphologies. Two types of sample have been used for establishing the temperature-concentration phase diagrams: shapeless samples and flat-cylindrical samples. Both have been obtained in the amorphous state by heating above 270°C followed by a rapid quench into liquid nitrogen. The amorphous samples have been immersed in an excess of liquid solvent and aged for a minimum of one week prior to DSC scanning. Several ageing temperatures have been used. For a given temperature the concentration reached after ageing is virtually the same. As a rule the higher the temperature the lower the polymer concentration. So far concentrations have been determined by weighing the sample before and after vacuum drying. This procedure proved to be reproducible within a few percent. Two solvents have been considered because of the availability of the T-C phase diagram previously established for samples prepared from homogeneous solutions8,9): *benzene* and *toluene*.

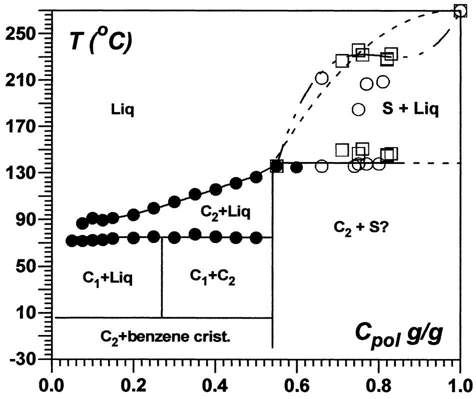


Fig. 1: Temperature-concentration phase diagram *sPS/benzene*. The full circles stand for data points obtained by quenching homogeneous solutions while the open symbols are for solvent-induced samples. The open circles stand for the shapeless samples while the open squares stand for the disc-shaped samples. The dotted lines outline possible transition lines.

It is worth emphasizing that not only the surface but also the bulk of the samples investigated have been totally transformed into compounds. This is necessary for performing the DSC experiments. We, however, believ that the conclusions drawn from these investigations have a direct bearing upon the changes occurring at the very surface of the solid polymer.

The phase diagram obtained in benzene is shown in fig. 1. As is apparent from this diagram, the data for the solvent-induced samples are essentially located on the left-hand side of the diagram, i.e. at high concentrations. It is also clear that the wel-defined shaped samples show less experimental scatter than the shapeless samples. The main outcome is that the data obtained from solvent-induced samples seem to complete the phase diagram established for homogeneous solutions. There is no discontinuity. This suggest that a compound displaying singular melting is formed whose stoichiometry is about *1 solvent molecule/monomer*. Unlike toluene, there is no evidence for a less solvated compound.

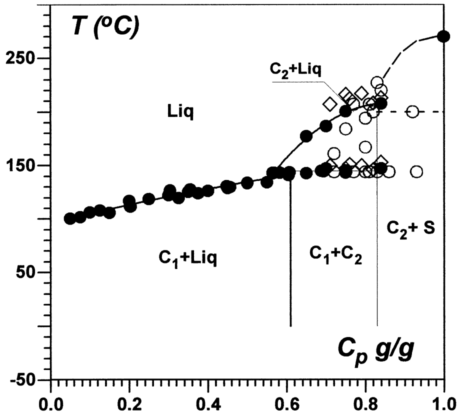
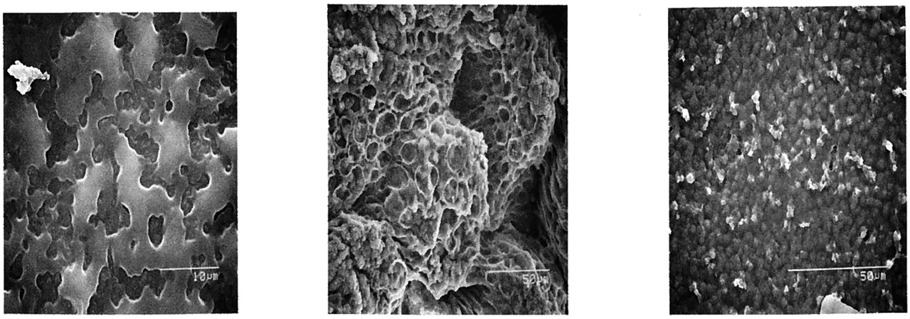


Fig. 2: Temperature-concentration phase diagram *sPS/toluene*. The full circles stand for data points obtained by quenching homogeneous solutions while the open symbols are for solvent-induced samples. The open circles stand for the shapeless samples while the open diamonds stand for the disc-shaped samples. The dotted lines outline possible transition lines.

In the case of *sPS/toluene*, the scatter is again far less important with disc-shaped samples than with the shapeless ones. Also, the data points fall on the phase diagram established for homogeneous solutions. Clearly, the path used for producing a given concentration has no consequence on the thermal behaviour.

After one week ageing, the same range of polymer concentrations, namely between 0.7 and 0.8 are obtained in benzene and in toluene.



(a) (b) (c)

Fig. 3: Scanning electron microscopy pictures of sPS surfaces exposed to liquid solvents: (a) sPS/benzene 40°C; (b) sPS/benzene 90°C: (c) sPS/Toluene 40°C.

## Morphology

The morphology has been observed by scanning electron microscopy on the samples after solvent extraction under vacuum. The sample have been gold-coated as usual. Typical electron micrographs can be seen in fig. 3.

As is apparent from these micrographs, the morphology is strongly dependent upon the path followed, and, as expected on the solvent type. Benzene tends to produce honeycomb structures whereas toluene favours a spheroidal morphology(10).

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