

REMOVAL OF A LOW MOLECULAR WEIGHT, CRYSTALLIZABLE POLYMER FRACTION FROM SOLUTIONS OF POLY[OXY-1,4- PHENYLENESULPHONYL-1,4-PHENYLENEOXY- 1,4-PHENYLENE(1-METHYLETHYLIDENE)- 1,4-PHENYLENE] (POLYSULPHONE®)*

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Abstract—The oligomer fraction of poly[oxy-1,4-phenylenesulphonyl-1,4-phenyleneoxy-1,4-phenylene(1-methylethylidene)-1,4-phenylene] (Polysulphone®) with molecular weight between 450 and 900 daltons is responsible for the precipitation in concentrated solutions of polysulphone in *N,N*-dimethylformamide and other solvents. The precipitate is of a crystalline nature and consists mainly of the oligomers. These oligomers differ from the higher molecular weight molecules not only in crystallization properties. In a liquid-liquid phase separated system consisting of polysulphone, *N,N*-dimethylacetamide and water, the oligomers accumulate exclusively in the polysulphone-poor, dilute phase. The solubility parameter concept is used to illustrate the origin of this difference in behaviour. The removal of the oligomers from the dissolved polysulphone can be achieved by a crystallization process.

INTRODUCTION

Concentrated solutions of polysulphone (PSf) in various solvents tend to become turbid and produce a white solid mass upon sedimentation. The deposit is believed to be of a crystalline nature [1-3] and also the existence of crystalline entities in PSf films has been reported; the only evidence presented is that of microscopic observation.

In our laboratory, research on the mechanism of formation of synthetic membranes is carried out and therefore we are interested in the properties of casting solutions in relation to membrane structure and performance. PSf asymmetric ultrafiltration membranes, prepared from identical solutions, may show a wide variation of flux and rejection properties [4]; this effect could be connected with the fact that the casting solution itself is thermodynamically unstable. Therefore an investigation into the precipitation phenomenon has been made and a method to eliminate it has been sought.

EXPERIMENTAL

Polysulphone: P3500, Union Carbide, characterized by $\bar{M}_n = 14,000$, $\bar{M}_w = 46,000$ and $\bar{M}_z = 75,000$ (determined with HPLC). Referred to as PSf a.r. (as received).

The polysulphone precipitate (PSf precipitate) was kindly supplied by Dr H. C. W. M. Buys (TNO Research Institute, Utrecht, The Netherlands) and was prepared in the following way. A 15% solution by weight of polysulphone P3500 in *N,N*-dimethylformamide (DMF) was allowed to stand for 3 months. The solution became turbid and slowly separated into two phases, *viz.* a clear solution above a white solid deposit. The deposit was filtered off and washed with

DMF and petroleum ether 60/80 successively, and was dried at room temperature. The yield was about 1 g of precipitate from 150 g of PSf.

***N,N*-dimethylformamide (DMF):** p.a., ex. Fluka AG.

***N,N*-dimethylacetamide (DMAc):** "analyzed reagent", ex. J. T. Baker.

Water: demineralized and ultrafiltered.

Molecular weight distributions (MWD) were determined by means of a Waters High Performance Liquid Chromatograph. The eluent was tetrahydrofuran (THF).

Crystallinity was examined with a Philips 1310 Röntgen Diffractometer. For the diffraction experiment, where a powder was needed, the PSf a.r. granules were treated as follows. A solution of 3 g PSf a.r. in 100 g DMAc was added to a well stirred ethanol bath of 1.5 l. The precipitated PSf was filtered off and washed three times with isomeric hexane. The residue was dried *in vacuo* at 110°. The MWD of this PSf powder showed that the low molecular weight fraction up to 900 daltons had disappeared during this procedure.

Infrared spectra were obtained with a Perkin-Elmer 257 apparatus. The spectrum of the PSf precipitate was taken from a KBr platelet containing the precipitate. The spectrum of the PSf a.r. was obtained from a thin PSf film, which was made by casting a solution of PSf a.r. in DMAc on a glass plate and evaporation of the DMAc in a N_2 atmosphere.

Differential Scanning Calorimetry was performed with a Perkin-Elmer DSC 2B apparatus.

Mass spectrometry was performed with a Varian Mat 311A apparatus.

RESULTS AND DISCUSSION

The nature of the precipitate

The molecular weight distribution (MWD) of the polysulphone (PSf) as received from Union Carbide shows that a certain amount of low molecular weight material is present (Fig. 1). According to Allison [1]

*Polysulphone is a registered trademark of Union Carbide.

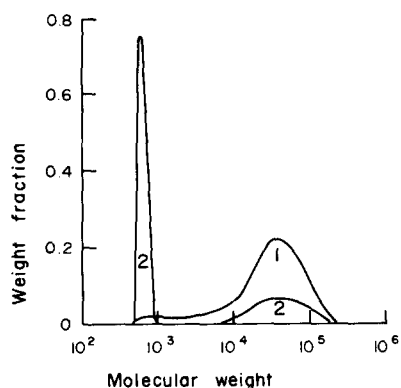


Fig. 1. Molecular weight distributions of polysulphone: 1. The polymer as received; 2. The PSf precipitate.

these oligomers are responsible for the PSf precipitate, but no experimental evidence was given.

The PSf precipitate is insoluble at room temperature in the liquids that are good solvents for the PSf a.r., but it can partly be dissolved at elevated temperatures. A solution of the precipitate in THF was made in an autoclave. The MWD of the dissolved fraction of the precipitate is bimodal (see Fig. 1); this MWD shows that most of the material has a molecular weight between 450 and 900 daltons. In Fig. 2 the linear oligomers with molecular weights in that range are given. The insoluble part of the PSf precipitate was isolated by filtration and was dried *in vacuo* at 110°. The yield was about 10 mg from 2 g PSf precipitate. From this insoluble fraction, a mass spectrum has been obtained and the spectrum shows a parent peak at 884 daltons. This value corresponds with the molecular weight of a cyclic PSf oligomer, i.e. the oligomer D of which the end-groups have joined, leading to a cyclic structure. Since this insoluble component is not present in the PSf a.r., we conclude that this cyclic PSf oligomer has been formed during the precipitation and sedimentation step which produced the PSf precipitate.

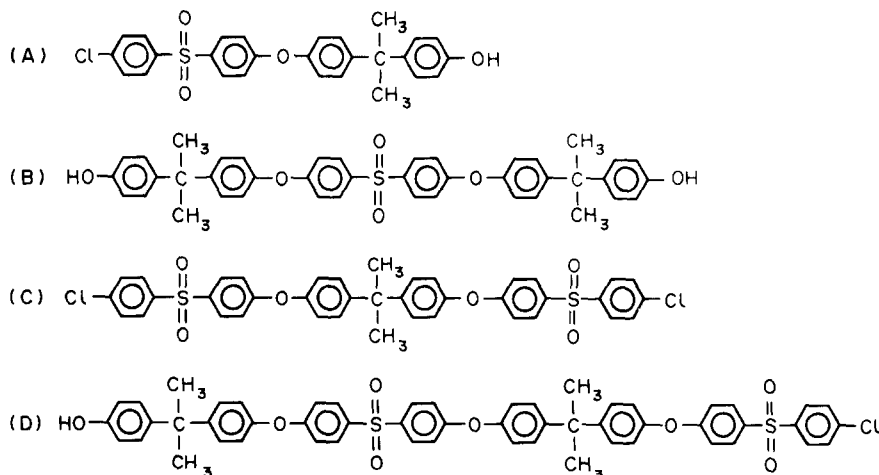


Fig. 2. Oligomers of polysulphone. Polysulphone is the polycondensation product of 2,2-bis(4-hydroxyphenyl)propane and 4,4-dichlorodiphenylsulphoxide. The molecular weights are 478.5 (A), 670.0 (B), 729.0 (C) and 920.5 daltons (D).

The X-ray diffraction pattern of the PSf precipitate demonstrates the presence of crystalline material (see Fig. 3, graph II). Since it was impossible to perform diffraction experiments on the PSf a.r. granules, the granules were converted into powder as described in the Experimental Section. The diffraction pattern of this powder shows amorphous scattering only (see Fig. 3, graph I). It should be noted that the oligomer fraction up to 900 daltons has disappeared during the coagulation. We tried several ways to grind or pulverize the granules and thus preserve the oligomers in the powder, but we were not successful. The PSf granules have too high elastic-mechanical strength, even if cooled to liquid N₂ temperature.

An i.r.-spectrum was taken to prove that the precipitate is indeed a polysulphone fraction. From Fig. 4 it can be seen that the precipitate has an additional absorption at 6 μ compared to the spectrum of the PSf a.r. Upon heating the precipitate for 2 hr at 110° *in vacuo*, this particular absorption disappears, whereas the crystallinity of the sample is not affected (see Fig. 3). Since DMF, in which solvent the precipitation has taken place, has a C=O stretch absorption at 6 μ , we conclude that DMF was present in the precipitate and that the precipitate itself is a fraction of the polysulphone sample.

The precipitate was heated from 60 to 430° in a Differential Scanning Calorimeter (DSC) in order to determine the melting temperature. Surprisingly, no endotherm was observed but there was an exotherm between 280 and 340°. The heat effect amounts to about 20 J/g. After cooling to 60°, no heat effects are observed upon reheating to 430°. Inspection of the sample showed that the precipitate changed from a powder into a hard platelet with some mechanical strength. According to the i.r.-spectrum, no structural changes occurred during the DSC run. It seems that the exotherm is the result of a sintering process, i.e. a decrease of the total crystalline surface. Recrystallization, another phenomenon producing an exotherm, is not considered here since in that case an endotherm should be expected shortly after the exotherm.

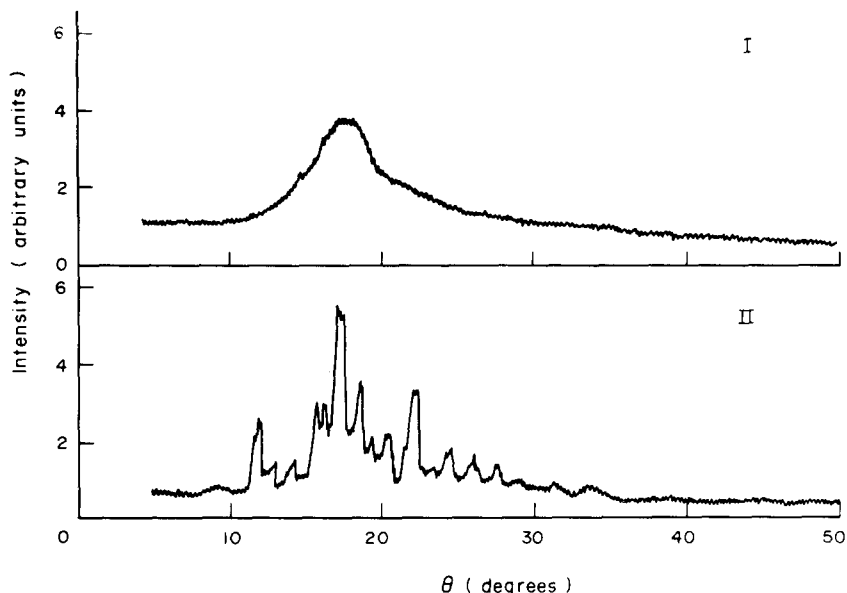


Fig. 3. Diffraction patterns of polysulphone. I. PSf; II. PSf precipitate, fresh and after heating *in vacuo* at 110°.

It is concluded that the phase separation found in concentrated solutions of PSf in DMF is a crystallization process, in which mainly the oligomers of the PSf take part. The same explanation is expected to hold for the precipitation phenomena in solutions of PSf in other solvents, such as *N,N*-dimethylacetamide (DMAc) and dichloromethane. It should be noted here that the precipitation process shows a different time-scale in different solvents.

Solubility properties of the precipitate

The reason why the oligomers have a specific tendency to crystallize is not clear. From the standpoint of equilibrium thermodynamics, crystallization is more favourable for larger molecules in a homologous series. On the other hand, crystallization will be faster for smaller molecules.

There is evidence that the oligomers of PSf do not have the same thermodynamic properties as the

higher molecular weight molecules. Figure 5 shows the MWD of PSf in the two phases of a liquid-liquid phase separated system consisting of PSf, DMAc and water. The oligomers have accumulated in the phase with the high water and low polymer content. Although fractionation during liquid-liquid phase separation is not uncommon, the complete disappearance of the oligomers from the concentrated phase is remarkable and in our opinion this reflects a higher affinity of the oligomers for water in comparison with the high molecular weight molecules.

The hydroxy and the chloride end-groups influence the solubility properties of PSf and this influence will be larger for the oligomers than for the higher molecular weight molecules. Table 1 gives the solu-

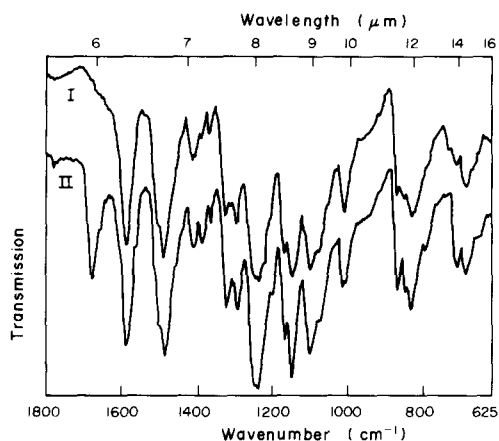


Fig. 4. i.r. Spectra of polysulphone. I. PSf a.r. and PSf precipitate after heating *in vacuo* at 100° for 2 hr. II. PSf precipitate, fresh.

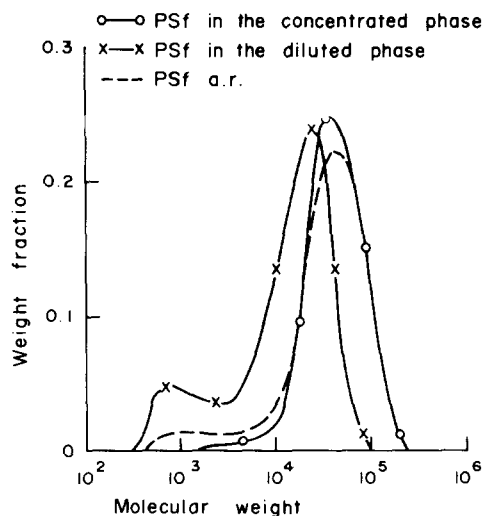


Fig. 5. Molecular weight distributions of polysulphone, a liquid-liquid phase separated system, consisting of PSf, DMAc and H₂O. The PSf was isolated from the phases by a rapid distillation method described by Patat [5]. The volume ratio of the two equilibrium phases was about 1.

Table 1. Solubility parameters of components in the system PSf-DMAc-water or ethanol

| | δ_d (cal/cm ³) ^{1/2} | δ_p (cal/cm ³) ^{1/2} | $\delta_h = \delta_{chem}$ (cal/cm ³) ^{1/2} | δ_{phys} (cal/cm ³) ^{1/2} |
|-----------------|---|---|---|--|
| 1. Polysulphone | 9.0 | 2.3 | 2.7 | 9.3 |
| 2. Oligomer A* | 9.0 | 2.1 | 4.2 | 9.2 |
| 3. Oligomer B* | 9.3 | 1.8 | 4.7 | 9.5 |
| 4. Oligomer C* | 8.7 | 2.5 | 2.7 | 9.1 |
| 5. Oligomer D* | 9.0 | 2.1 | 3.5 | 9.2 |
| 6. DMac† | 8.2 | 5.6 | 5.0 | 9.9 |
| 7. Ethanol† | 7.3 | 4.3 | 9.5 | 8.5 |
| 8. Water† | 6.0 | 15.3 | 16.7 | 16.4 |
| Water‡ | 7.6 | 7.8 | 20.7 | 10.9 |

*See Fig. 2. †Taken from Ref. [8]. ‡Taken from Ref. [10].

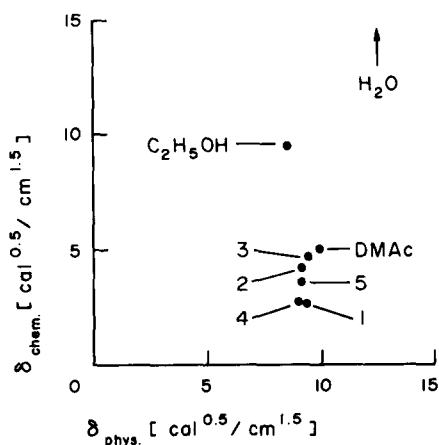


Fig. 6. Solubility parameters for PSf (polymer and oligomers), DMac, ethanol and H₂O. The numbers indicated correlate with those in Table 1.

bility parameters of the PSf molecules with different molecular weights. The parameters have been calculated with the aid of the molar attraction constants of characteristic groups as listed by van Krevelen [6]. The molar attraction constants of the sulphone group, which are not included by van Krevelen, are calculated from the solubility parameters of dimethylsulphone [7]. In Fig. 6 the solubility parameters of PSf, DMac, ethanol and water are represented, using a two dimensional solubility parameter plot following Bagley [8]:

$$\begin{aligned}\delta_{phys} &= (\delta_d^2 + \delta_p^2)^{1/2} \\ \delta_{chem} &= \delta_h\end{aligned}\quad (1)$$

where δ_d = solubility parameter due to dispersion forces, δ_p = solubility parameter due to dipole forces, δ_h = solubility parameter due to hydrogen bonding, δ_{phys} = solubility parameter due to physical forces and δ_{chem} = solubility parameter due to chemical interactions.

From Fig. 6 it can be concluded that the oligomers A, B and D differ from the PSf polymer mainly in their capability to form hydrogen bonds (i.e. the sulphone and hydroxy groups). This indicates indeed

a higher affinity of the oligomers for water and ethanol compared to the PSf polymer.

Removal of the oligomer fraction

In order to prevent precipitation in solutions of polysulphone, Allison [1] proposed a process, involving two coagulation steps, to remove the oligomers. This method is laborious and consumes large quantities of chemicals if carried out on a scale larger than laboratory experiments. A better procedure to obtain an oligomer free solution is the following.

As has been stated above, a concentrated PSf solution produces after a sufficiently long sedimentation period a clear solution above a white precipitate. The resulting solution remains homogeneous for months if the precipitate is removed. The same observations have been made by Buys [10]. The concentration of the solution is scarcely affected by the precipitation.

We did not elaborate on an optimization of the process by studying the crystallization kinetics. Once the kinetics are known, one could investigate the feasibility of an improved sedimentation step (e.g. by centrifugation) after a certain crystallization period and thus accelerate the process.

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