From Solvent to Solid - The Rheological Characterisation of Polystyrene

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ABSTRACT

This work reveals the various rheological properties a single polymer has under different conditions, i.e. as a dilute solution, as a melt or as a solid. In order to establish a relationship between the different concentrations a wide range of mechanical and even optical tests were employed on the polymer itself, on solutions and on polymerisation processes.

INTRODUCTION

The applications of polymers cover an extremely wide range of concentrations. For drag reduction polymer solutions with concentrations of only a few ppm are needed, while plastic materials for everyday use ideally consist of the pure polymer itself. Other applications like coating or food additives require concentrated or semidilute polymer solutions. Due to these different applications a wide range of concentrations has to be characterised. Different structures of dilute, semidilute and concentrated solutions, melts and solids lead to different interactions between the molecules and their segments. On the one side these interactions depend on parameters like concentration, temperature, or solvent quality. On the other side the structure of the polymer itself, i.e. its molecular mass, branching, or molecular mass distribution, influences the application properties strongly. Moreover every different application needs a different rheological test to characterise its necessities which lead to different methods, like step strain, yield stress, steady shear, creep, transient or oscillation experiments to cover all applications. By using polystyrene as an example we investigated how strong different applications are linked to the properties of the polymer itself.

EXPERIMENTAL PART

Due to the wide range of concentrations, viscosities, and experiments normally a wide range of equipment is necessary. To test the viscosity of solvents and very low viscous solutions customarily capillary viscometers

are used. Step strain and relaxation experiments can be done only with rheometers which can control shear rate and strain. For the determination of yield stress points and for the observation of curing processes shear stress controlled rheometers are commonly used.

To avoid this wide range of instrumentation the unique shear rate, shear stress and strain controlled rheometer PHYSICA UDS 200 was employed to perform all the measurements. Due to its EC measuring drive it can control stress or strain or shear rate and using all the benefits a measuring drive gives, i.e. the wide torque range (0,5μNm to 150mNm) and the wide range of environmental systems for temperature control.

RESULTS AND DISCUSSION

The state of solution of a polymer depends on the concentration and the molecular mass. Figure 1 shows this dependence for the chosen example polystyrene in toluene.
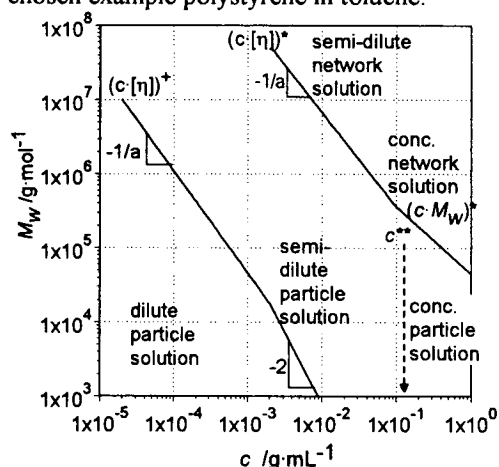

Figure 1. The different states of solutions of narrowly distributed polystyrene in toluene as a function of the molecular mass and the polymer concentration [1].

The viscosity and the viscoelastic properties of the solution are therefore a result of the different interactions in the different regimes.

The lowest concentration of polymer is found in the solvent. Naturally, as figure 2 shows, it exhibits only Newtonian properties. But with an rotational instrument it is possible to observe much lower shear rates as it is possible in a capillary or rolling ball instrument [2]. The accuracy better than 1 % enables the proper determination of the intrinsic viscosity, i.e. the extrapolation of concentration and shear rate.
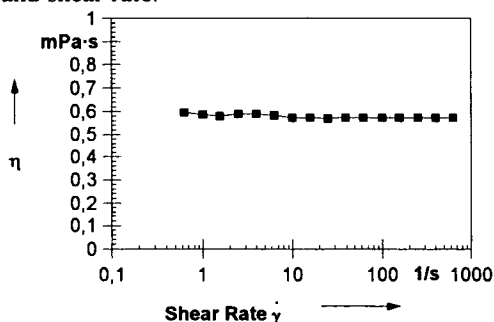
Figure 2. The viscosity of toluene as a function of shear rate at 293 K. This diagram shows the capabilities of measuring low viscous samples.

By increasing the concentration the interactions between the molecules will increase as well. On the one hand the viscosity and the viscoelastic properties will increase. On the other hand it would be interesting to observe these interactions directly which is possible via rheooptical techniques like flow birefringence.
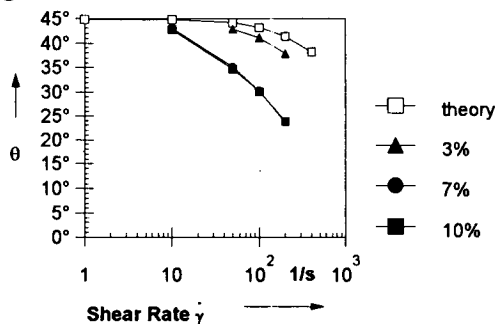
Figure 3. Orientation angle of polystyrene in toluene, detected by flow birefringence[3]. M = 1,86 Mg/mol, T = 298 K.

Three concentrations of polystyrene were chosen to detect the transition between a semidilute particle solution (3%) and a concentrated network solution (7%, 10%). By calculating the rotational diffusion coefficient[4] and therefore the orientation angle[5] it became possible to predict the orientation of an individual molecule.

Obviously the dynamic behaviour of polystyrene in a semidilute solution (3%) is not strongly affected by interactions between the molecules. By increasing the concentration to the regime of a concentrated network solution (7%, 10%) the interactions increase and a stronger orientation in the direction of shear can be found (figure 3).

More important than the behaviour in toluene are the melt properties of polystyrene. During the polymer processing (extrusion, fibre spinning, etc.) the flow properties of the polymer influence directly the quality of the end product. Due to the sensitivity of the C-C-bond against longer heat treatment oscillation test at very low frequencies are somehow restricted.

Figure 4. shows the step strain test performed with polystyrene at 483 K using the UDS 200. The relaxation was observed for 100 s and the linear relaxation modulus was directly obtained.
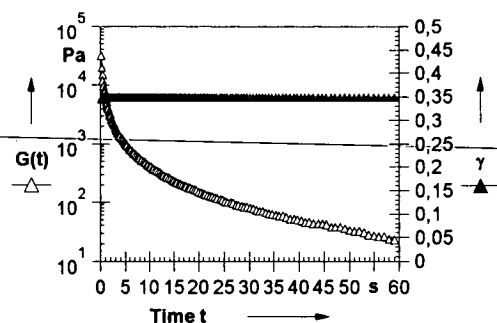
Figure 4. Step strain test of polystyrene at T = 483 K, which displays the relaxation modulus versus time.

By measuring the relaxation directly without an oscillation test all relaxation times can be detected within the shortest possible period. Afterwards the data can be used to recalculate the storage and the loss modules via the continuous relaxation time spectrum.

Normally it can be expected that the results of a step strain test and an oscillation test are similar. Figure 5 displays the experimental date obtained with the polystyrene. Both curves are quite similar except for the fact that the oscillation test is more suitable for the higher frequencies up to 100 Hz. On the other side, the step strain test covers the frequency range at the lower end. Therefore it is possible to detect even longer the relaxation times within a reasonable time.
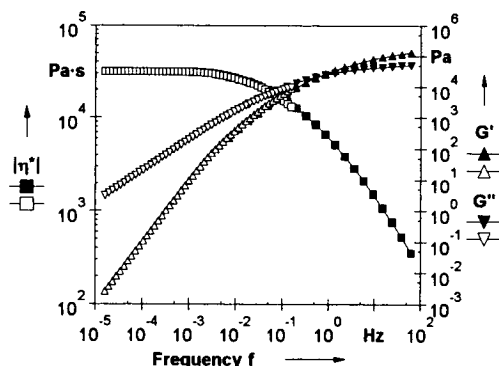

Figure 5. The open symbols represent the recalculated data from the step strain test, while the filled symbols were obtained directly by an oscillation test at T = 483 K.

But even during the process of polymerisation one can observe the transition between the states of solution. Besides the significance for the transition itself the viscoelastic data yield information about the kinetic of the polymerisation[6]. Normally the polymerisation of styrene takes place in an exothermic reaction within a very short period. Normally the frequency dependence of the viscoelastic properties can not be observed due to the very fast reaction. But nevertheless the viscoelastic properties during this transition from a monomer to a polymer, i.e. from a dilute particle solution to a concentrated network are quite important to characterise the polymer and its quality in application. Hence it will be demonstrated how these properties can be detected.

Further information can be obtained by characterising the solid itself. This is especially important for processes like moulding as transitions from the solid to the melt or glass transitions of commonly used mixtures of polymers may interfere with the application of the end products. By using the same rheometer as for the characterisation of the solvent the temperature dependence of the dynamic behaviour of solid bars was tested.

SUMMARY

The viscous and viscoelastic properties of polystyrene show a wide variety over the concentration range which was investigated. Nevertheless it was possible to clarify the relationship between the different concentration by using a simple phase diagram and observing the transitions between different regimes.

REFERENCES

1. Kulicke, W.-M., Griebel, Th. and Bouldin, M. (1991), „Description and Forecast of Rheological Characteristics of Semi-Dilute Polymer Solutions as a Function of the Molecular Weight, Concentration and Solvent Quality", *Polymer News*, **16**, 39-48.

2. Gruber, E., Sezen, M.C., and Schurz, J. (1972), „Ein Fallviskosimeter mit geneigtem Rohr für sehr kleine Probenmengen, *Angew. Makrom. Chem.*", **28**, 57-73.

3. Reinhardt, U.T. (1995), „Rheomechanische und rheo-optische Charakterisierung wäßriger Biopolymerlösungen", Shaker, Aachen, pp.61-63.

4. Perrin, F. (1934), „Mouvement Brownien d'un Ellipsoide (I). Dispersions diélectrique pour des Molécules ellipsoidales", *J.Phys.Rad.*, **5**, 497-511.

5. Scheraga, H.A., Edsall, J.T., and Gadd, J.O. (1951), „Double Refraction of Flow: Numerical Evaluation of Extinction Angle and Birefringence as a Function of Velocity Gradient", *J.Chem.Phys.*, **19**, 1101-1108.

6. Malkin, A.Y., and Kulichikhin, (1996), „Rheokinetics", Hüthig & Wepf, Basel, pp. 60-68.