Summary

A transition has been displayed in a concentrated solution of a linear chain polymer flowing close to a rotating disk. For a critical angular speed of rotation, a discontinuity of the mass transfer rate by diffusion and convection, as well as the existence of flow birefringence are observed. This transition is interpreted as an effect of conformational change (coiled to stretched shape) of the polymer under the local strain in the fluid.

Resumé


Zusammenfassung

In der konzentrierten Lösung eines linearen Polymers wird beim Fließen in der Nähe einer rotierenden Scheibe ein Übergang nachgewiesen: Bei einer kritischen Rotationsgeschwindigkeit tritt eine Unstetigkeit in der Intensität der Stoffübertragung durch Diffusion und Konvektion auf, begleitet von Strömungs- doppelbrechungsscheinungen. Dieser Übergang wird als die Wirkung einer Konformationsänderung interpretiert, bei dem die Polymerketten infolge der lokalen Dehnbeanspruchung aus der verknäuelten in die gestreckte Form überführt werden.

Key words
Polymer solution, rotating disc, flow birefringence, mass transfer, elongational flow

1. Introduction

Most of the non-newtonian or viscoelastic properties of macromolecular solutions close to a rotating disc can be generally well accounted for by classical rheological models (1), but not the loss of flow stability which occurs under definite conditions (2). In previous electrochemical measurements with this flow geometry we indeed observed a sharp and large decrease of the mass transfer rate, for a critical value \( \Omega_c \) of the angular speed of the disc.

This fact implies a discontinuity either of the flow or of the structure of the medium or of both of them. At the transition, characterized by an hysteresis effect, an unstable regime begins.

This stable to unstable transition already observed for other flow geometries (3) and sometimes named structural (4) or early turbulence (5) could, according to recent theories, be induced by a conformational change of the polymers, undergoing a more or less sharp stretching from their initial state of random coil at rest, when local strains appear in the fluid, e.g. (6). In this process, a primary role is devoted to elongational strains, which are always present in the flows leading to such a phenomenon. It is also accredited that, for a dilute solution, this transition occurs if the elongational strain rate \( S \) in the fluid and the terminal relaxation time of the polymer \( \tau_R \) are connected by \( S \tau_R > 1 \) (6, 7).

The analysis of the tridimensional velocity field close to a rotating disc shows that the
overall strain is the result of a shear and an elongation. By taking into account the only elongation, one finds a maximum value of the strain rate in the boundary layer, which is around $\Omega$ and independent of the radial coordinate (8). The general relation as given in (7), may then be written for the rotating disc $\Omega_C \tau_R > 1$. The agreement between the Zimm relaxation time $\tau_R$ and $\Omega_C^{-1}$, as well as the lack of effect of the disc radius on $\Omega_C$, have been corroborated, so long as the flow is laminar (8).

As the suggested explanation of the observed phenomena was bound to the intrinsic limitations of the electrochemical methods, it was necessary to look for a method providing independent informations, especially on the anisotropy of the medium structure which has to occur at the transition. The flow birefringence (F.B.) appeared as the most relevant to this need, as it was moreover able to complete the data we already got on mass transfer by the electrochemical method.

In the following section we describe the F.B. experimental set up and present the results we obtained by both methods in parallel experiments i.e. for identical electrodes and macro-molecular solutions prepared from the same powder samples and with the same dissolution procedures.

2. Experimental conditions

2.1. The cell and the optical arrangement

The rotating disc cell is schematized in figure 1. It consists of a 1 liter vessel approximately, bounded on two opposite sides by two parallel windows $l$ of low residual birefringence, through which a white light beam of high intensity is going.

The electrode is a cylindrical rod rotating at a constant angular speed of rotation $\Omega$ by means of a motor (M in figure 1). The flow under investigation is only generated by the cross section, the one caused by the lateral surface is not considered in this study. Therefore, the base of the cylinder is placed at the level of the optical axis of the system so that we can observe the phenomena taking place in its direct vicinity under a grazing angle thanks to a lens focused on the rotation axis of the cylinder. The cell is placed between the polarizer P and the analyser A crossed at 90°, the polarization planes of both at 45° as regards to the rotation axis of the disc.

Discs of different diameters (1, 2, 3 cm) have been elaborated in opaque plastic so as to cancel the polarization phenomena possibly induced by the reflexion on the disc plane observed under a grazing incidence.

2.2. Electrochemical measurements – Solutions

Electrochemical measurements are performed with electrodes of the same geometry but the cross section is made of smooth platinum. The principle of the method (9) is based on the measurement of the limiting diffusion current of a fast redox reaction taking place at the electrode interface. This current is proportional to the mass transfer rate flowing towards the interface by convective diffusion. The electrochemical reaction is the reduction of potassium ferricyanide ($10^{-3}$ M) with an excess of KCl (M) as supporting electrolyte. The F.B. measurements have been performed in the same electrolyte.

The investigated polymers were industrial polyethyleneoxides (PEO) of high molecular

![Fig. 1. Flow birefringence measuring system](image)