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Shear Induced Vortices in High Molecular Weight Polyethylene Oxide Melt

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SUMMARY

The vortices in laminar flow of high molecular weight polyethylene oxide melt under shear were studied using small angle light scattering technique and applying the statistical and model aproaches.
It was found that vortices are aggregates of large number of molecules with the core of fluctuating density and molecular orientation of surroundings due to this rotation. Perpendicular dimensions of the more dense core is 4.3 µm and for oriented surroundings 7,5 µm.
Longitudinal dimensions are 8 µm and 20 - 35 (depending on shear rate) for the dense and oriented parts, respectively.

INTRODUCTION

It was observed (KULICKE, PORTER 1979) (FAJTELSON, BRIJEDIS 1976) AND (HAN, LAMONTE 1972) that the laminar flow of polymer solutions or melts is disturbed at certain shear rate if molecular weight of the matter is high enough. The disturbances are particularly easy visible in a coneplane rheometers. They possess the character of vortex in a microscale.
There were suggestions that a vortex is formed from a single (or utmost very few) polymer molecules spirally oriented (FAJTELSON, BRIJEDIS 1976). The aim of this work was to determine the dimensions, geometry and orientation of vortices arrising in sheared high molecular weight polyethylene oxide melt by small angle light scattering.

EXPERIMENTAL

Polyethylene oxide of M_w 4000000 (Polysciences product) was purified from solid impurities by solution in CH_2Cl_2, filtration and evaporation of the solvent.

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The viscosity of the polymer melt was characterized by means of Instron Capillary Rheometer. The molten polymer was placed between two quartz plates in an apparatus being a combination of the plane - plane rheometer and the small angle light scattering device as it is shown schematically in Fig. 1.

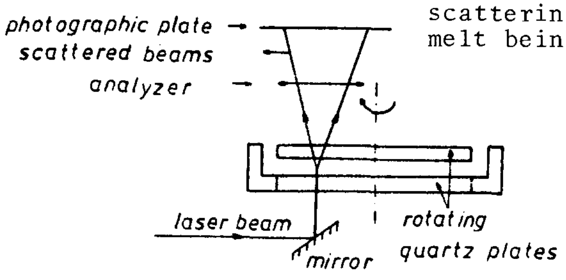

Fig.1. Scheme of apparatus for small angle light scattering from polymer melt being sheared.

The temperature between quartz plates was kept at 90°C. The shear rate in the melt was build up by rotation of the upper plate with a controlled speed. At the distance of 0.2 mm used in the experiments between upper and lower plates the shear rate could be changed from 0.5 - 10.0 s^{-1}. He - Ne laser was used as a light source for small angle light scattering. The V_v and H_v patterns from sheared molten polymer were recorded on photographic plates. For the analysis of the intensity distribution of scattering patterns the statistical (STEIN, WILSON 1962) and model (FRENKEL AT ALL. 1967) approaches were applied. The statistical approach assumes the fluctuations of the density and molecular orientation as the scattering objects. The fluctuations are described by the respective correlation functions. The correlation functions can be deduced from the vertical scattered light intensity distributions of the V_v and H_v patterns by means of the inverse Fourier transform (STEIN, WILSON 1962):

$$\gamma(r) = \frac{C_1}{r}\int_0^\infty (I_{Vr} - \frac{4}{3} I_{Hv})h \sin (hr)dh \qquad (1)$$

and

$$\mu(r)f\ (r) = \frac{C_2}{r}\int_0^\infty I_{Hv}\ h \sin (hr)dh \qquad (2)$$

where $\gamma(r)$ - density fluctuation correlation function, f (r) - orientation fluctuation correlation function, $\mu(r)$ - practically equal 1.0 for the system studied, $h=(4\pi/\lambda)\sin(\Theta/2)$, λ - scattered light wavelength, Θ - vertical angle of the scattering, and C_1 and C_2 - constants depending on the optical properties of the polymer melt.

The model approach is based on the light scattering from the parallelepiped of dimensions L_x, L_y, L_z and polarizabilities a_x, a_y and a_z placed in an isotropic medium of the polarizability a_0. The L_y and L_z dimensions (if the incident light beam goes along x axis) can be calculated from the formulas:

$$L_y = \lambda/\sin\Theta_1 \quad \text{and} \quad L_z = \lambda/\sin\Theta_2 \qquad (3)$$

where Θ_1 and Θ_2 are vertical angles at which I_{Vv} becomes 0.0 for the azimuthal angles equal $\pi/2$ and 0., respectively.

RESULTS AND DISCUSSION

In Fig.2 the dependence of the viscosity on shear rate for polyethylene oxide melt at 90°C is shown after introducing Rabinowitz and Bagley(MIDDLEMAN 1968) corrections. The thick solid line on the shear rate axis shows the limits of shear rates accessible in the experimental setup from Fig.1.

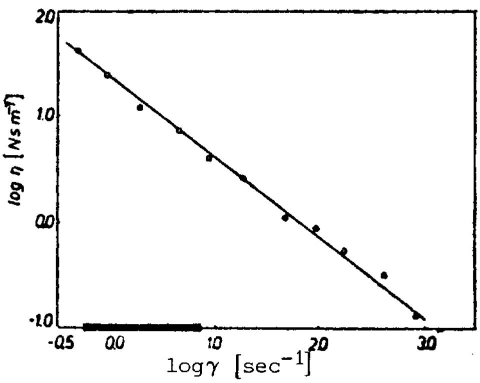

Fig.2. Viscosity vs. shear rate for polyethylene oxide $M_w=4\times10^6$ at 90°C.

Those limits are on the beginning of the shear rate range within which the uniform structure of the melt undergoes destruction and the clusters of molecules are formed.

At all used shear rates in plane - plane rheometer from Fig.1. the turbidity of the polymer melt appears giving rise to a strong light scattering. The objects responsible for the turbidity were recognized as vortices since they were limited in sizes and moved slower than the rotation applied as it is seen through the magnification lense. The V_V as well as H_V (less intensive) patterns were rhombic in shape with axes oriented to the rotation direction as it is shown schematically in Fig. 3.

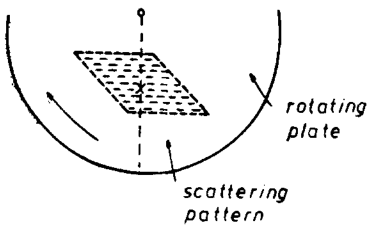

Fig.3. Small angle scattering pattern orientation with respect to the rotation of the upper quartz plate.

The statistical approach applied to the longer and shorter axes of the rhombic scattering pattern leads to the density and orientation fluctuation correlation functions shown in Fig. 4.

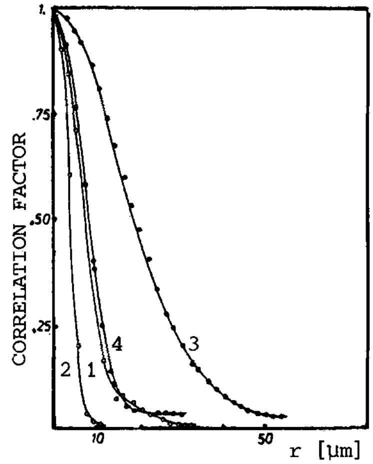

Fig.4. The density fluctuation correlation functions for shorter and longer axes of the scattering pattern (curvers 1 and 3 respectively), the orientation fluctuation correlation functions for shorter and longer axes of the scattering pattern (curves 2 and 4 respectively). Shear rate 0.76 s^{-1}.

o - $\gamma(r)$ ● - $f(r)\mu(r)$

The correlation functions calculated from scattering patterns for other shear rates do not show any significant differences i.e. the strong decrease of both types of correlation functions occur at the same distances independently of the shear rate applied.
All orientation fluctuation correlation functions decrease at larger distances than the respective density

fluctuation correlation functions. It follows then that the scattering objects are fluctuations of the density surrounded by a layer of oriented polymer melt. Both fluctuations are anisotropic in shape as it is shown in Fig. 5.

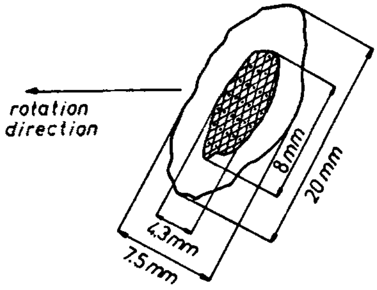

Fig.5. Hypothetical shape and sizes of a vortex with respect to the experimental setup.
The doted area is the density fluctuation.

The model approach leads to the conclusion that the vortex in a scattering object has longitudinal dimension from 20.0 to 34.8 µm dependent on increasing shear rate and perpendicular direction of 6.8 µm independent of shear rate.
The number of randomly coiled molecules possibly placed in the central core is 10^5 while in the whole aggregate 10^6 as they follow from volume of the vortex. Therefore the hypothesis that vortex is formed from a single or few molecules is not supported.
Since vortex are rather longitudinal object it should orient itself under shearing forces radially with regard to the rotation. It happens in fact, however, with little deviationdue to Coriolis force.
The vortex seen from the radial direction side resemble a rotating cylinder. The rotation of the density fluctuation in center of the aggregate causes orientation of molecules around. It is reflected in orientation fluctuation correlation function.
The large size of vortices suggests that they are just disturbances in a laminar flow and a certain conformation of molecular chains should not be attributed to them.

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