高分子濃厚溶液の定常流動の粘弾性*

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Dynamic Viscoelasticity of Concentrated Polymer Solutions in Steady Shear

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Dynamic viscoelasticity of concentrated polymer solutions in steady shear is studied by means of a coaxial cylinder type rheometer, of which outer cylinder can be given three types of motion, namely sinusoidal (rotational) oscillation, stationary rotation and oscillatory rotation. Oscillatory and stationary parts of inner cylinder motion are separately recorded by electric devices. It was found experimentally that synthesis of inner- and outer-cylinder oscillations gave an ideal Lissajous pattern irrespective of magnitude of steady shear superimposed, and that the dynamic modulus $G_{\dot{\gamma}}^*$ under a constant rate of shear $\dot{\gamma}$ can be determined as function of angular frequency ω by using the Markovitz equation for the motion of linear viscoelastic materials in an annular space.

Eight samples of polystyrene, ranging in viscosity average molecular weight from 2.4×10^4 to 3.0×10^6 , were prepared by thermal polymerization, and all measurements were performed in toluene for 15 weight % polymer at 30°C . Typical results are shown in Fig. 1 where the real and imaginary parts of dynamic modulus, $G_{\dot{\gamma}}'$ and $G_{\dot{\gamma}}''$, for the sample with molecular weight 3.0×10^6 are plotted against the angular frequency. Fig. 2 shows the corresponding viscosity data in steady shear. It can be concluded from these results that:

Fig. 1 Log-log plots of the dynamic modulus $G_{\dot{\gamma}}'$ and the loss modulus $G_{\dot{\gamma}}''$ at various rates of shear against the angular frequency ω

Fig. 2 Log-log plot of the steady shear viscosity at various rates of shear $\dot{\gamma}$ against the viscosity average molecular weight M_v

* 原稿受付 昭和 38 年 3 月 18 日

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(1) The famous 3.4th power law in the viscosity-molecular weight relationship is well conformed in the region of molecular weight M higher than about $M_c=3 \times 10^5$;

(2) The rate of shear at which non-Newtonian behavior in viscosity becomes observable depends on the molecular weight of polymers, decreasing with M . Thus, when $\dot{\gamma}=0.482\text{sec}^{-1}$, the polymers having M less than about 10^6 are practically regarded as Newtonian, while the sample with $M=3 \times 10^6$ displays an appreciable non-Newtonian effect;

(3) In the region of Newtonian flow, no effect of $\dot{\gamma}$ on $G_{\dot{\gamma}}^*$ is observed. In the region of higher rate of shear, the values of $G_{\dot{\gamma}}^*$ are decreased as $\dot{\gamma}$ is increased, and the effect becomes more marked for the lower frequency. Similar effect is also observed in $G_{\dot{\gamma}}''$. This type of effect is qualitatively analogous to that of lowering of molecular weight, suggesting that the effect of rate of shear is caused by destruction of chain entanglements in solution.

In order to obtain more quantitative picture of the effect, analysis of the data is tried on the basis of a modified ladder model of Marvin which consists of three sections of different frictional coefficients, instead of two in the original model,²⁾ and gives:

$$G_{\dot{\gamma}}^*(i\omega) = (\Gamma_1/c_2)[\tanh\Gamma_1 + \rho_2 \tanh(l_2-1)\Gamma_2 + \rho_2 \rho_3 \tanh(l-l_2)\Gamma_3 + \rho_3 \tanh\Gamma_1 \cdot \tanh(l_2-1)\Gamma_2 \cdot \tanh(l-l_2)\Gamma_3] / [1 + \rho_2 \tanh\Gamma_1 \cdot \tanh(l_2-1)\Gamma_2 + \rho_2 \rho_3 \tanh\Gamma_1 \cdot \tanh(l-l_2)\Gamma_3 + \rho_3 \tanh(l_2-1)\Gamma_2 \cdot \tanh(l-l_2)\Gamma_3] \quad (1)$$

and

$$\eta = r_1 + (l_2-1)r_2 + (l-l_2)r_3 \quad (2)$$

with

$$l = M/M_c, l_2 = M_{\dot{\gamma}}/M_c, c_2 = M_c/2nRT, \Gamma_j = (i\omega c_2 r_j)^{1/2}, \rho_2 = \Gamma_2/\Gamma_1 \text{ and } \rho_3 = \Gamma_3/\Gamma_2. \quad (3)$$

Here r_j is the friction constant of the j -th section, n is the number of chains per unit volume, $M_{\dot{\gamma}}$ is the molecular weight corresponding to the boundary between the second and third sections, and RT has its usual meaning. Since the first section does not include entanglement effects, r_1 can be defined as the viscosity of a sample of molecular weight equal to M_c , and three quantities, r_2 , r_3 and l_2 , are treated as adjustable parameters representing shear rate effect. Comparison of our dynamic and steady state data with Eqs. (1) and (2) leads to conclusions that the observed effect of shear rate is compatible only with choice of a very small value for r_3 , *i.e.* $r_1 \approx r_3 \ll r_2$, and that $M_{\dot{\gamma}}$ is approximately equal to the second break observed in $\log \eta$ vs. $\log M$ plot for a given $\dot{\gamma}$. The calculated values of $G_{\dot{\gamma}}^*$ and $G_{\dot{\gamma}}''$ in the region of low ω and $M_{\dot{\gamma}}$ at $\dot{\gamma}=0.482\text{sec}^{-1}$ are shown by the broken lines in Fig. 1 and by a filled square in Fig. 2. The agreement obtained indicates that the same mechanisms of destruction of entanglement are responsible for the in $G_{\dot{\gamma}}^*$ depression and η .

References

- 1) H. Markovitz, J. Appl. Phys. **13**, 1070 (1952)
- 2) R.S. Marvin and H. Oser, J. Research Natl. Bur. Standards, **66B**, 171 (1962)
- 3) R.S. Marvin, K. Osaki, M. Kurata and M. Tamura, to be published elsewhere

(Received Mar. 18, 1963)