Electrical noise generated during the capillary flow of poly(ethylene oxide) solutions. The influence of the solvent power

C. Klason* and J. Kubát†
Department of Polymeric Materials, Chalmers University of Technology, S-412 96 Gothenburg, Sweden

and O. Quadrat
Institute of Macromolecular Chemistry, Czechoslovak Academy of Sciences, Prague, Czechoslovakia
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The electrical noise generated during capillary flow of poly(ethylene oxide) solutions has been studied in detail in mixtures of water and isopropyl alcohol of various solvent powers. The noise level, which increased with flow rate, was found to be an increasing function of the linear dimension of the polymer coils as obtained from intrinsic viscosity data, if the system consists of entangled macromolecules, i.e. if the polymer concentration is higher than the coil overlap concentration.

(Keywords: electrical noise; capillary flow; poly(ethylene oxide) solutions; solvent power influence)

INTRODUCTION

Measurements of electrical fluctuations (noise) associated with Poiseuille flow of various polymer solutions through capillaries have been the subject of a series of papers from our laboratory[1–5]. The bulk of the experiments were carried out with aqueous solutions of poly(ethylene oxide) (PEO). The noise signals were frequency analysed using the Fast Fourier Transform (FFT) technique. The spectra obtained were characterized by a plateau at the low frequency end, the height of the plateau increasing with flow rate, followed by a $1/f^\alpha$ type decrease of noise power at higher frequencies. At the high frequency end the electrical noise generated by the flow approached the thermal[6] level. No noise over the thermal level was recorded with the solutions at rest. The overall power of the noise increased with the flow rate. The value of the exponent[1–3] in the $1/f^\alpha$ spectral distribution was around 3/2. In some cases there appears to be a weak correlation between α and the exponent characterizing the degree of pseudoplasticity (shear thinning) of the solutions used[1,2].

The noise signals obtained in these measurements were generated by the flow process only, no voltage being applied across the capillary. It is therefore interesting to note that similar results, at least with regard to the form of the frequency distribution of the spectrum, have also been reported for current noise measurements on solutions of some simple electrolytes in capillaries with microscopic dimensions[7–9]. Typically, the capillaries used in our experiments had a length of several millimetres and a diameter of 0.3 mm.

With PEO solutions exhibiting sufficient elasticity both periodic and aperiodic flow instabilities were recorded, the former giving rise to a set of harmonic peaks in the noise spectra[1–5]. Such instabilities are known to be a common feature of both elastic solutions and polymer melts[10–12]. The generation of spontaneous noise signals during capillary flow was found to be a useful supplement to existing methods when studying phenomena of this type. Apparently, the harmonic peaks recorded in the noise spectra were related to corresponding fluctuations in the flow rate through the capillary.

Recently[13] we reported on noise generated during capillary flow of two polymer dispersions containing particles of an ethyl acrylate–methacrylic acid copolymer with 15 and 20% of the latter component. After alkalization the particles containing the lower percentage of methacrylic acid exhibited a significant degree of swelling, but retained their spherical shape. In the other case, swelling resulted in a disintegration of the particles into macromolecules or their aggregates. We found that the latter system exhibited no excess noise, while significant noise signals were generated by the more elastic dispersion containing swollen polymer particles.

In general, noise analysis may be a source of valuable information on the motion of a polymer liquid in flow. In spite of the fact that this interesting physical effect has already been studied for many years, its origin remains unexplained. To elucidate this problem we aimed at a more detailed analysis of this phenomenon occurring in PEO solutions in relation to many potentially important factors. In the present paper we show data relating to the role played by the dimensions of the polymer coil, which in turn depend on the solvent power.

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* Present address: Polymer Centre, University of Lund, Sweden
† To whom correspondence should be addressed

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EXPERIMENTAL

Polymer solutions. A series of PEO solutions (WSR-301, Polyox, $M_w = 4 \times 10^6$) was prepared with polymer concentrations of 0.5, 0.75 and $1\ \mathrm{g\,dl^{-1}}$ in redistilled water (solvent). Also, samples were prepared with a polymer concentration of $0.5\ \mathrm{g\,dl^{-1}}$ using redistilled water mixed with 20, 40, 70 and 85 wt% isopropyl alcohol (non-solvent). As some polymer degradation by flow could be expected, especially at higher shear stresses due to the high molecular weight of the polymer used, all measurements were carried out with fresh solutions. For the same reason, filtration of the solutions (glass filter G 2) was performed at a very slow rate. To reach the optimum resistance ($\simeq 5$ Mohm) between the electrodes, which secured a good matching with the input impedance of the preamplifier used, 30 ppm of KCl was added to each sample.

Noise measurements. The experimental set-up (*Figure 1*) consisted of two glass reservoirs (~ 150 ml) connected by a glass tube, in which a capillary (length 3 mm, diameter 0.3 mm) was fixed with an epoxy resin. The electrodes in the form of spiral platinum wires (0.6 mm in diameter) were placed at the bottom of the reservoirs at the capillary axis. It has been shown that the shape, size and position of the electrodes does not influence the noise signal. The same intensities and the shapes of the spectra were obtained with another electrode material (Pt) and another electrode type (Ag/AgCl).

The electrodes were connected to a low noise preamplifier (Princeton Applied Research Co., model PAR 113) followed by a frequency analyser (Princeton Applied Research Co., model PAR 4513) and Philips x-y recorder. The frequency range used was 0.2–200 Hz, the resolution being 0.2 Hz. The flow through the capillary was produced by applying a defined constant pressure (maximum 6×10^4 Pa) of nitrogen to one of the reservoirs. Compared to the previous work where a 0.2 mm capillary was used, the larger diameter (0.3 mm) employed in the present study caused such a change of the flow character that flow instabilities which might affect the estimation of the total noise power from the frequency spectra practically disappeared.

Flow rate measurements and viscometry. The volumetric flow rate of the solutions through the capillary under the conditions used in the noise measurements was determined. In order to determine the solvent power and to estimate the thermodynamic expansion of the polymer coils intrinsic viscosity was measured in Ubbelodhe-type capillary viscometers (capillary length 10 cm, diameter 0.47 and 0.6 mm). Due to the long measuring times, kinetic energy corrections and end effects were negligible. The intrinsic viscosity values were computed by the least square method using measurements performed at five concentrations, according to Heller's relation[14], from $(c/\eta_{sp} + c/\ln \eta_r)/2$ *versus* c, where η_r and η_{sp} are the relative and specific viscosity and c is the polymer concentration. All measurements were carried out at 19°C.

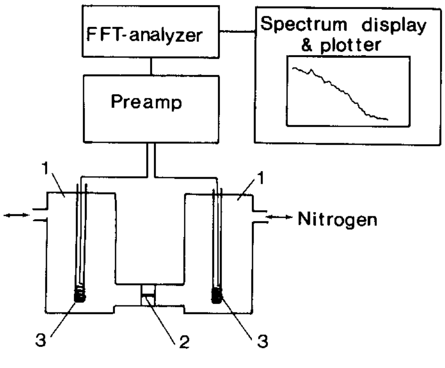

Figure 1 Schematic diagram of the experimental set-up: 1, reservoir; 2, capillary; 3, electrodes

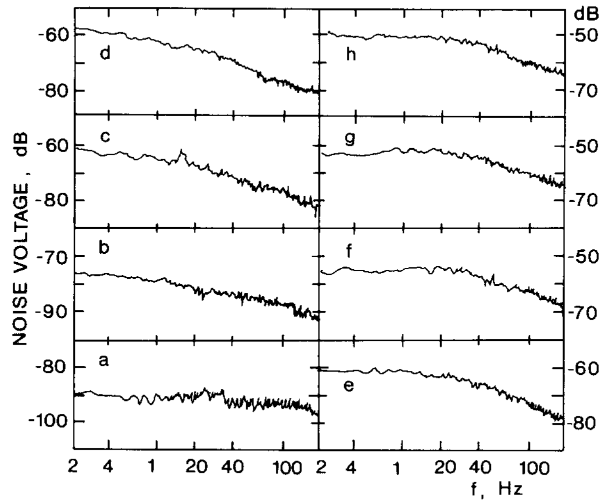

Figure 2 Spectral distribution of the noise generated during capillary flow for PEO solutions. Concentration = $0.5\ \mathrm{g\,dl^{-1}}$ in water. Applied pressure: ($\times 10^{-4}$ Pa): (a) 0 (at rest); (b) 0.26; (c) 0.51; (d) 1.12; (e) 1.99; (f) 3.31; (g) 4.64; (h) 5.97

RESULTS

The spectral distribution of the noise generated by the capillary flow showed a $1/f^{\alpha}$ type behaviour for all samples, with a plateau at the low frequency end of the spectrum (*Figure 2*). In general, the level of the spectrum increased with flow rate (applied pressure).

The ratio of the total noise power obtained by the integration of the square of the noise voltage over the frequency range available (0.2–200 Hz) and the corresponding noise power for solutions at rest ($U = U^2_{\mathrm{flow}}/U^2_{\mathrm{rest}}$) increased with the pressure P applied across the capillary. In the following, U will be used as a measure of the flow induced noise intensity. It was found that the increase of the noise ratio with P depends strongly on the composition of the solvent (*Figure 3*). At the same P and constant c ($0.5\ \mathrm{g\,dl^{-1}}$) the higher the content of isopropyl alcohol in the solvent, the lower was the noise power generated.

It has been reported[1–5] that due to the high elasticity of high molecular weight PEO solutions substantial P losses at the capillary entrance may be expected. To avoid problematic shear stress or shear rate calculations, the volumetric flow rate Q obtained by direct measurement under the same P conditions as in the noise experiments was used to characterize the flow field in the capillary. Since all experiments were performed with the same capillary, Q is a measure of the average transport speed of the liquid and represents a suitable basis for comparing noise characteristics and intensities under different flow conditions. *Figure 4* shows that the rate of increase of the Q–P curves passes through a minimum when the water content in the solvent decreases.

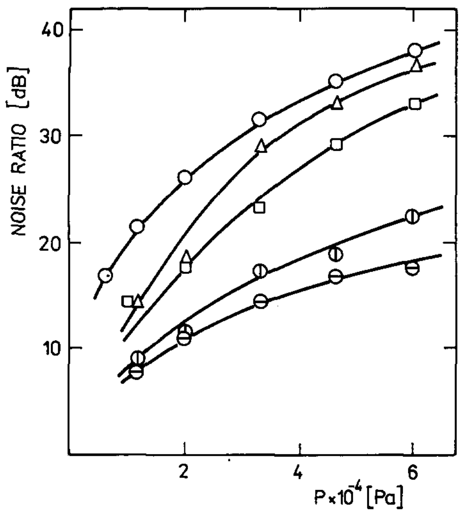

Figure 3 Dependence of noise ratio on the applied pressure P of PEO solutions at a polymer concentration of 0.5 g dl^{-1} in water and mixtures of water with isopropyl alcohol. Weight fraction of water in the mixture: (○) 1; (△) 0.8; (□) 0.6; (⦶) 0.3; (⊖) 0.15

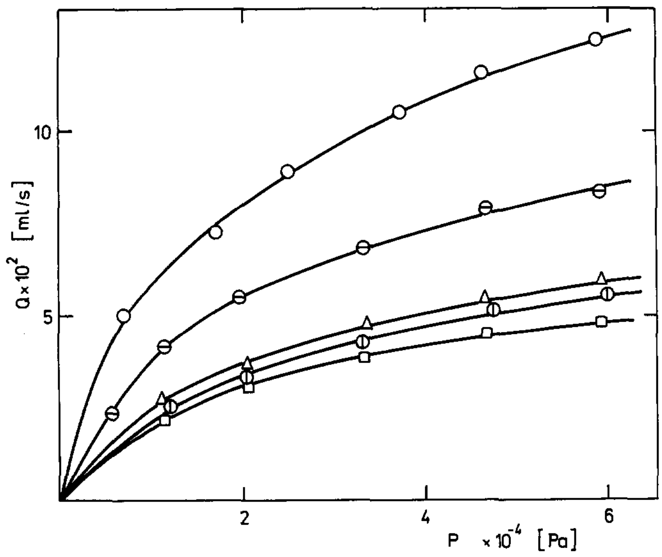

Figure 4 Dependence of the volumetric flow rate Q during noise measurement on the applied pressure P. Symbols as in *Figure 3*

Combining the U–P and Q–P plots shown in *Figures 3* and *4*, we obtain the dependence of U on Q for the various solutions at constant c (*Figure 5*). Surprisingly and significantly, the U–Q diagram consists of a family of straight lines going through the origin. The slopes of these lines depend on the composition of the solvent, although not in a monotonic manner.

The composition dependence of U at an arbitrary flow rate was easily obtained from *Figure 5*. The result, presented in *Figure 6* related to a particular value of Q (4.8×10^{-2} ml s^{-1}), shows a curve exhibiting a maximum for solutions containing ~55 wt% isopropyl alcohol. This method is of general validity (independent of Q) since the U–Q data on which this diagram is based consists of straight lines through the origin. Choosing other Q values would just scale the curve of *Figure 6* in a linear fashion.

Figure 6b is a plot showing the dependence of the intrinsic viscosity [η] on the solvent composition. Due to the preferential sorption[15,16] of one component of the solvent on the polymer molecules, [η] shows a maximum.

There is an obvious similarity in the overall appearance of *Figures 6a* and *b*. *Figure 7* shows that a plot of U obtained with different solvents when plotted *versus* [η] at a given flow rate and polymer concentration exhibits

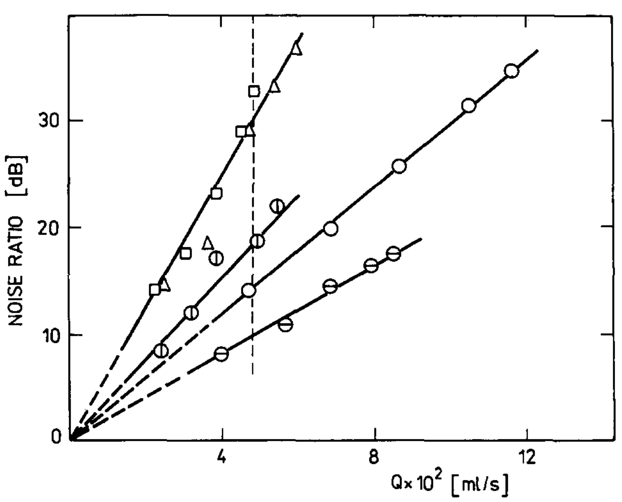

Figure 5 Noise ratio as a function of the volumetric flow rate Q. Broken vertical line at $Q = 4.8 \times 10^{-2}$ ml s^{-1}. Symbols as in *Figure 3*

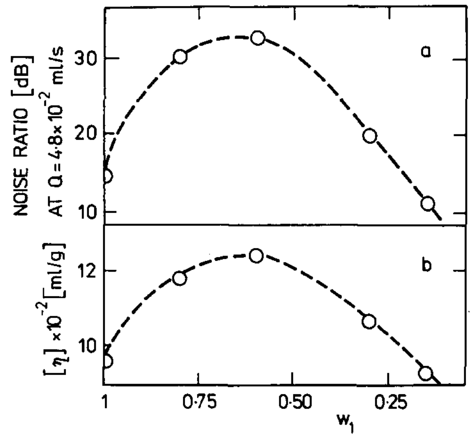

Figure 6 Dependence of the noise ratio (a) and intrinsic viscosity [η] (b) of PEO solutions on the solvent composition (w_1 is the weight fraction of water in the mixture with isopropyl alcohol). Flow rate 4.8×10^{-2} ml s^{-1}

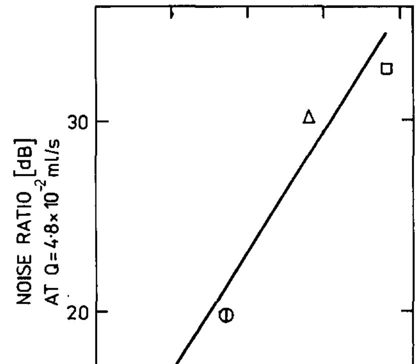

Figure 7 Noise ratio as a function of the intrinsic viscosity [η] of the solutions. Flow rate 4.8×10^{-2} ml s^{-1}. Symbols as in *Figure 3*

a high degree of linearity. This indicates that an important factor influencing the noise generation in these systems is the dimension of the polymer coils and that the noise intensity increases with the thermodynamic expansion of macromolecules caused by improving solvent power.

As we found earlier, this effect does not always occur. At low polymer concentrations ($\gtrsim 0.1$ g dl^{-1}) the noise intensity does not depend on solvent character. This implies that the behaviour of 0.5 g dl^{-1} solutions results from their entangled structure.

The coil overlap critical concentration c^* at which the space occupied by the solution is filled up by swollen polymer coils may be expressed by[17]:

$$c^* = (3/4\pi N)(M/R_h^3) \qquad (1)$$

where N denotes Avogadro's number, R_h^3 is the hydrodynamic radius of polymer coils and M is the molecular weight. If we suppose that R_h can be replaced by the root-mean-square radius of gyration of the macromolecules $\langle s^2 \rangle^{1/2}$ for infinitely diluted solutions using the Flory equation[18]:

$$\langle s^2 \rangle^{1/2} = (1/6^{1/2})([\eta]M/\phi)^{1/3} \qquad (2)$$

(neglecting a slight suppression of coil expansion due to particle interaction at higher c values), we obtain:

$$c^* = (3/4\pi N)6^{3/2}\phi/[\eta] \qquad (3)$$

where the Flory constant ϕ equals 2.87×10^{23} mol^{-1}. At $c > c^*$, the domains of coils overlap and the chains entangle. In the case of our polymer solutions in water–isopropyl alcohol mixtures, $[\eta]$ ranges from 9.32 to 12.83 dl g^{-1} corresponding to $c^* = 0.179$–0.130 g dl^{-1}. Thus, at $c \lesssim 0.1$ g dl^{-1}, when the system consists of isolated polymer coils, no solvent power effect appears.

The increasing U in the 0.5 g dl^{-1} solutions resulting from greater expansion of polymer coils causing a higher degree of overlapping c/c^* is illustrated in *Figure 8*. With regard to the role played by c, we also show the U values in water solutions at different c values.

Results of similar character as in *Figure 8* were obtained by plotting U *versus* correlation length ξ (defined as the mean distance between the two points of entanglement)[17,19]:

$$\xi = 6^{1/2}\langle s^2 \rangle^{1/2}(c/c^*)^{-3/4} \qquad (4)$$

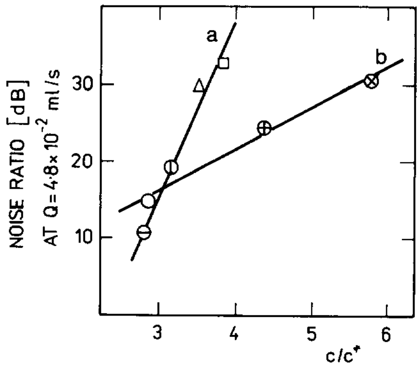

Figure 8 Noise ratio as a function of c/c^* at a constant flow rate of 4.8×10^{-2} ml s^{-1}. (a) Constant polymer concentration (0.5 g dl^{-1}) in different solvent compositions. Weight fraction of water in the mixtures: (○) 1; (△) 0.8; (□) 0.6; (⦶) 0.3; (⊖) 0.15. (b) Different polymer concentrations (g dl^{-1}) in one solvent (water): (○) 0.5; (⊕) 0.75; (⊗) 1.0

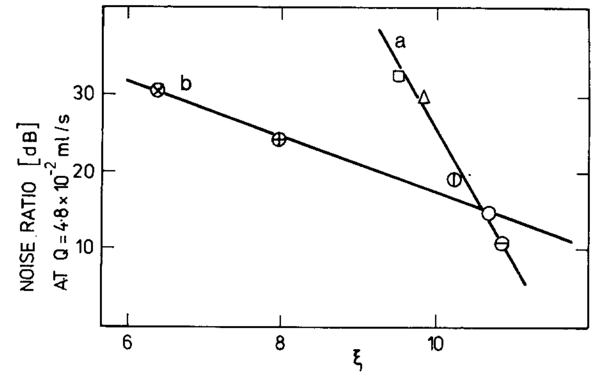

Figure 9 Noise ratio as a function of the correlation length ξ at a constant flow rate of 4.8×10^{-2} ml s^{-1}. For (a) and (b) see *Figure 8*

The slope of the U–ξ plots (*Figure 9*) is negative, because the correlation length decreases with increasing c/c^*.

DISCUSSION AND CONCLUSIONS

The origin of the noise generation is not yet clear. Obviously, this behaviour depends strongly on the viscoelastic properties of the flowing material. The published data[1–5] show that the effect occurs only if the elasticity of the solution is sufficiently high.

We believe that viscoelastic properties also play a central role in the problem investigated in this study. Clearly, with higher overlap of polymer coils and increasing entanglement density the elasticity of the polymer solutions rises and the intensity of the noise generated during flow increases. *Figures 8* and *9* show that there is a difference in the noise behaviour of the solutions if overlapping of polymer coils is caused by thermodynamic expansion or by increasing c. This suggests that in the former case a stiffer entangled structure from expanded polymer coils arises. Hence the U–c/c^* dependence is steeper than if overlapping of macromolecules results from increasing c with the dimensions and stiffness of the polymer coils remaining practically unchanged.

A full elucidation of the mechanism of noise generation in flowing polymer solutions from the rheological and physical point of view will require further experiments. Polymer samples having various concentrations and molecular weights should be investigated, and the noise behaviour of these systems correlated with the results of measurement of streaming potential as a possible source of the electrical signal induced by flow. This will be the subject of a future study.

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REFERENCES

1 Hedman, K., Klason, C. and Kubát, J. *J. Appl. Phys.* 1979, **50**, 8102
2 Hedman, K., Klason, C. and Poupetová, D. *Rheol. Acta* 1983, **22**, 449
3 Hedman, K. and Kubát, J. *Rheol. Acta* 1984, **23**, 417
4 Klason, C. and Kubát, J. *J. Appl. Phys.* 1985, **58**, 2060
5 Hedman, K. and Kubát, J. *Rheol. Acta* 1986, **25**, 36

6 Nyquist, H. *Phys. Rev.* 1928, **32**, 110

7 van der Berg, R. J., de Vos, A. and de Goede, J. *Phys. Lett. A* 1981, **87**, 98

8 van der Berg, R. J., de Vos, A. and de Goede, J. *Phys. Lett. A* 1989, **139**, 249

9 Muska, T., Sugita, K. and Kaneko, M. in 'Noise in Physical Systems and 1/*f* Noise' (Eds M. Savelli, G. Lecoy and J. P. Nougier), Elsevier, New York, 1983, p. 389

10 Adashi, K. and Yoshioka, N. in 'Rheology Vol. 2' (Eds G. Astarita, G. Marruchi and L. Nicolais), Plenum Press, New York, 1980, p. 47

11 Boger, D. V. and Nguyen, H. *J. Non. Newt. Fluid Mech.* 1979, **5**, 353

12 Oyanagi, Y. *Appl. Polym. Symp.* 1973, **20**, 123

13 Klason, C., Kubát, J. and Quadrat, O. *Rheol. Acta* 1991, **30**, 180

14 Heller, W. *J. Colloid Sci.* 1954, **9**, 541

15 Dondos, A., Viras, K. and Aroni, F. *Eur. Polym. J.* 1973, **9**, 1051

16 Carton, B., Bottiglione, V., Morcelet, M. and Loucheux, C. *Makromol. Chem.* 1978, **179**, 2931

17 Coviello, T., Burchard, W., Dentini, M. and Crescenzi, V. *Macromolecules* 1987, **20**, 1102

18 Flory, P. J. 'Principles of Polymer Chemistry', Cornell University Press, New York, 1969, p. 611

19 de Gennes, P. G. 'Scaling Concepts in Polymer Physics', Cornell University Press, New York, 1979, p. 92