

## Effect of Molecular Weight and Molecular Weight Distribution on the Rheological Properties of Aqueous Poly(Ethylene Oxide) Solution

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*Dedicated to Prof. Dr. H.-J. Cantow on the occasion of his 60th birthday*

### Abstract

The effect of the molecular weight and the molecular weight distribution on the rheological properties of aqueous poly(ethylene oxide) (PEO) solutions has been investigated with four PEO samples differing in their  $M_w$ ,  $M_w/M_n$  and purity. The main result of this study is that the steady shear viscosity as well as the complex dynamic viscosity of the samples with broad molecular weight distribution greatly differed from the viscosities of the samples having a narrow molecular weight distribution. Furthermore, the samples with broad molecular weight distribution showed a distinct molecular weight dependent non-Newtonian behavior at increasing shear rates and frequencies. This behavior was not observed for the sample with a narrow molecular weight distribution. Both effects are mainly attributed to the influence of the high molecular weight fraction in the PEO samples of broad molecular weight distribution. The often reported degradation of PEO solutions was not observed within the time scale of our experiment.

### Introduction

Poly(ethylene oxide) (PEO) is one of the few polymers which are soluble in water as well as in organic solvents. Poly(ethylene oxide) is also a polymer having a linear chain structure without side groups. The advantage of dual solubility along with the simple chain structure makes this polymer a simple model for the study of the rheological behavior of aqueous polymer solutions.

The aim of this paper is to reveal some features of the rheological properties (steady shear flow and dynamic rheology) of aqueous PEO solutions and to try to explain how these properties depend on the molecular weight, the molecular weight distribution and impurities present in the polymer sample. An attempt was also made to explain how all these parameters influence the shear stability of PEO.

The samples investigated were commercially available PEO's with a broad molecular weight distribution. For comparison, a PEO sample having a relatively narrow molecular weight distribution was prepared by anionic living polymerization. Except for the specially prepared PEO sample, all commercial polymer samples contained inorganic catalyst impurities<sup>1)</sup>.

### Experimental

Three commercial PEO samples with molecular weights of 210 000, 460 000, and 1 100 000 g/mol were obtained from H. G. Zachmann, University of Hamburg; the values of  $[\eta]$  and  $M_w$ , respectively, were taken from<sup>2)</sup>. A fourth sample ( $M_w = 220 000$ ) was prepared in our laboratory by anionic polymerization of ethylene oxide (EO) with N-carbazolylpotassium as initiator in the presence of a crown ether (Kryptofix 222, Merck, Darmstadt, F.R.G.) in THF as solvent (cf.<sup>3,4)</sup>). The experimental details of the preparation of the

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initiator system and of the polymerization will be published in a later paper 5,6).

The characterization of the different PEO-samples with regard to the molecular weight and molecular weight distribution was done by gel permeation chromatography (HPCL/GPC) in *N,N*-dimethylacetamide using modified silica columns 7). The characteristic data are compiled in Table 1 and the GPC-traces are depicted in Fig. 1.

Tab. 1: Molecular weight  $M$  (in g/mol) and polydispersity  $U$  of poly(ethylene oxide) (PEO) samples

Sample No.	$M\eta$ in ml/g		$M_{max}^e$	$M_{GPC}$		$U_{GPC}^g$
	c)	d)		$M_w$	$M_n$	
1 <sup>a)</sup>	-	220.000 (183)	197.000	222.000	140.000	0,58
2 <sup>b)</sup>	210.000 (340)	542.000 (300)	303.000	284.000	70.000	3,09
3 <sup>b)</sup>	460.000 (660)	575.000 (310)	450.000	520.000	59.000	8,80
4 <sup>b)</sup>	1.100.000 (1.280)	809.000 (375)	457.000 <sup>g)</sup>	-	-	-

- a) PEO prepared in our laboratory by living anionic polymerization technique:  $M_w$  (Light Scattering) = 250.000;  $M_n$  (Osmosis) = 170.000;  $U=0,47$ .
- b) PEO from EGA Chemie, Steinheim (cf. 2)).
- c) Determined in  $CHCl_3$  at 25°C by using the  $[\eta]/M$ -relation  $[\eta] \cdot M = c_1 + c_2(M^{0,5} - 0,00027 M)$ , cf. 2)).
- d) Determined in wafer at 25°C and calculated from  $[\eta]=19,2 \cdot 10^{-2} M^{0,557}$  (cf. 8)) (sample 1) and  $[\eta] = 1,25 \cdot 10^{-2} M^{0,78}$  (cf. 1)).
- e) Based on the elution volume of the peak maximum in the GPC trace.
- f) Incorrect figure since the nominal molecular weight of this sample exceeds the exclusion limit of the column system.
- g)  $U_{GPC} = (M_w/M_n) - 1$ .

For the rheological investigations, PEO solutions were prepared by gentle rotation of the polymer-water mixture for a period of a week. The aqueous solutions of the commercial samples showed slight turbidity which increased with increasing polymer concentration. The turbidity also increased with increasing storage time. The solutions of the PEO sample prepared by ionic polymerization was clear in the entire concentration range used and no change was observed even after a long storage time.

The Mechanical Spectrometer (Rheometrics Inc., U.S.A. Model: System Four) was used to determine the material functions in steady shear flow as well as in dynamic rheology. Both measurements were performed on a cone-and-plate device with a diameter of 5 cm and a cone angle of 0.04 radians. The maximum accessible shear rate range was between  $10^{-2}$  and  $10^3 \text{ sec}^{-1}$ . The shear stability tests at  $\dot{\gamma} = 5140$  and  $700 \text{ sec}^{-1}$  with the sample  $M = 1\ 100\ 000 \text{ g/mol}$  were performed on a rheometer from the Fa. Haake, F.R.G. (Model Rotovisco RV 3, System NV). Dynamic rheology material functions were measured in an oscillatory experiment. The maximum accessible frequency range was between  $10^{-2}$  and  $500 \text{ sec}^{-1}$ .

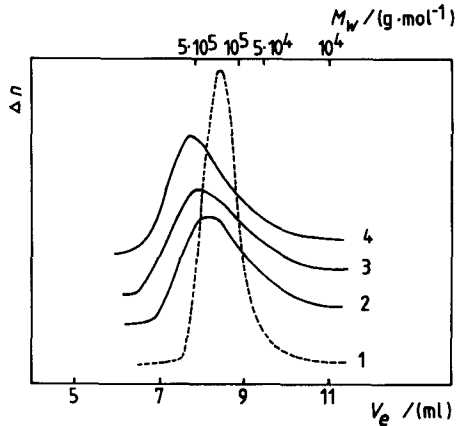


Fig. 1: GPC-traces of the PEO samples 1-4 (see Tab.1); the molecular weight of sample 4 is higher than the exclusion limit of the columns used.

### Results and Discussion

The rheological properties of polymer solutions are significantly connected with their internal structure and depend strongly on the molecular weight and molecular weight distribution. In order to investigate these relationships, the material functions in steady shear flow ( $\eta$ , shear viscosity;  $\dot{\sigma}$ , shear rate;  $\sigma_{11} - \sigma_{22}$ , first normal stress difference) have been measured:

$$\begin{aligned} \eta &= f(\dot{\gamma}) \text{ (viscous behavior)} \\ \sigma_{11} - \sigma_{22} &= f(\dot{\gamma}) \text{ (elastic behavior)}. \end{aligned}$$

Also the complex dynamic viscosity,  $|\eta^*|$ , as a function of frequency,  $\omega$ , in oscillatory experiments was measured.

$$|\eta^*| = f(\omega)$$

The results are shown in Fig. 2. The arrows above the two curves indicate the experimental limit of measurements. The dynamic measurements sometimes can be extended to higher frequencies than the rate of shear in steady shear measurements can (see Fig. 2).

As can be seen from the plots in Fig. 2, the dynamic and steady state viscosities are very close to each other, even at high shear rates and frequencies. According to this behavior, the system satisfies the Cox and Merz rule<sup>9)</sup>. The same observation was also reported by Powell and Schwarz<sup>10)</sup>. The commercial samples showed non-Newtonian behavior, i. e., the  $\eta$  and  $|\eta^*|$  values decreased with increasing shear rate and frequency (see Fig. 2a, c, d). The deviation from the non-Newtonian behavior increases with both increasing concentration at fixed molecular weight (Fig. 2a, c) and increasing molecular weight at concentration (Fig. 2d). The viscosity increases steeply for polymer solutions above a molecular weight of about  $1 \cdot 10^6$ . A strong difference in the initial viscosity of the solutions of PEO 210.000 and 460.000 compared to the viscosity of the solution of PEO 1.100.000 was observed (Fig. 2d).

This observation is in agreement with the findings reported by Chmutin et al.<sup>11)</sup> that the viscosity of aqueous PEO solutions sharply increases when the molecular weight exceeds  $2 \cdot 10^6$ . However, our results indicate that the required minimum molecular weight is somewhat lower, i. e. below  $10^6$ . This overproportional increase in the zero shear viscosity corresponds to the sharp increase in the reduced viscosities, i. e., the intrinsic viscosity, when going from PEO 460.000 to PEO 1.100.000 (Fig. 3).

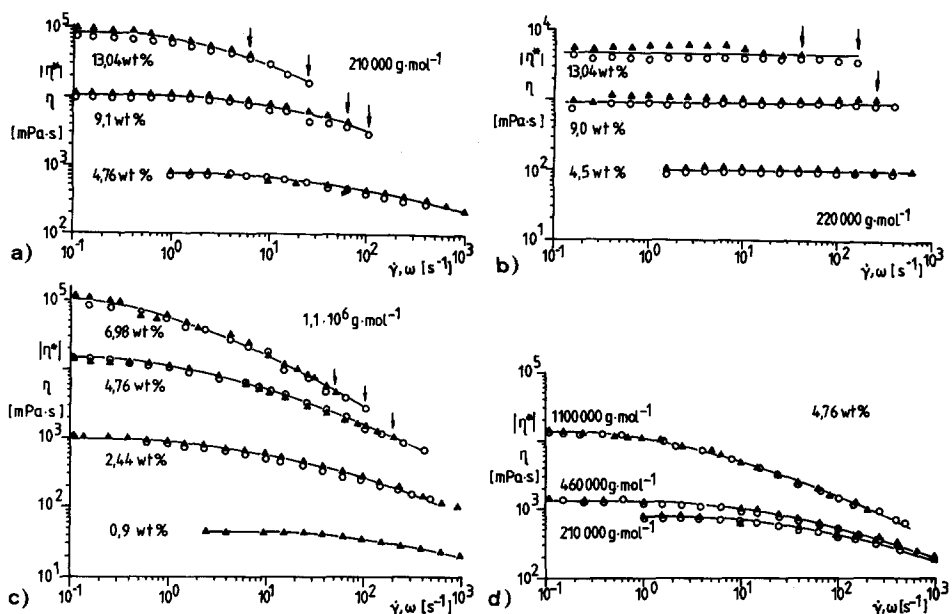


Fig. 2: Dependence of the complex dynamic viscosity  $|\eta^*|$  (○) and the steady shear viscosity  $\eta$  (▲) on the frequency and shear rate for aqueous solutions of poly(ethylene oxide) (PEO) samples of different molecular weight and molecular weight distribution (MWD) at 25°C: a) PEO 210.000 (EGA, broad MWD); b) PEO 220.000 (narrow MWD); c) PEO 1.100.000 (EGA, broad MWD); d) PEO 210.000, PEO 460.000 and PEO 1.100.000 (all broad MWD).

This phenomenon is attributed to the increasing importance of the high molecular weight fraction in the samples with broad molecular weight distribution.

To investigate the effect of molecular weight distribution (see Tab. 1) on the rheological behavior, the PEO samples prepared in our laboratory were investigated and their rheological data were compared with a commercial sample of almost the same molecular weight (see Fig. 2a and 2b). The narrow distributed PEO sample showed almost a Newtonian behavior in the concentration range investigated (Fig. 2b) while the commercial sample with wider distribution in molecular weight showed a non-Newtonian behavior (Fig. 2a). The values of  $\eta$  and  $|\eta^*|$  in the narrow molecular weight distributed samples are lower by almost one order of magnitude than the corresponding commercial samples. This marked difference and also the deviation from the non-Newtonian behavior in the commercial samples can be attributed to the high molecular weight fraction in these latter polymers. This high molecular weight fraction is evident from the tail in their molecular weight distribution curve as seen in Fig. 1.

In this context, it is also interesting to note that there is a large difference in the reduced viscosities of the aqueous solutions of PEO 220.000 and PEO 210.000 (Fig. 3) due to the high molecular weight fraction in the latter sample (see Fig. 1).

The normal stress difference material functions of the commercial samples are shown in Fig. 4. The initial slope of the  $\sigma_{11} - \sigma_{22}$  shear rate plots had a slope of about 2 as expected<sup>12)</sup>. However, the normal stress difference

for the narrow distributed sample was much lower and below the sensitivity range of the available transducer.

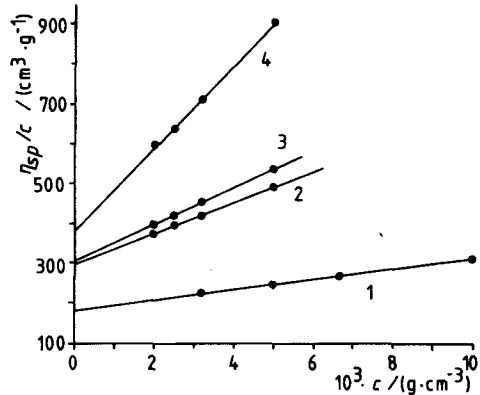


Fig. 3: Reduced Viscosity of PEO samples 1-4 (see Tab. 1) in water at 25°C.

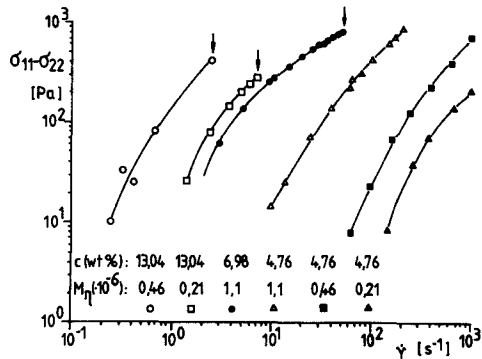


Fig. 4: First normal stress difference  $\sigma_{11} - \sigma_{22}$  of aqueous solutions of PEO with broad molecular weight distribution.

At sufficiently low shear rates, the viscosity of polymer solutions is constant. If a constant shear rate in this range is imposed, the shear stress should grow monotonically to its steady state value. At higher shear rates, the steady-state viscosity begins to depend on  $\dot{\gamma}$ . If a constant shear rate in this range is imposed, the shear stress rises beyond its steady state value and passes through a maximum before approaching the steady state <sup>13</sup>). The normal stress displays a similar overshoot behavior, although the total shear at the stress maximum appears to be greater for the normal stress than for  $\sigma_{12}$ . A noticeable overshoot phenomenon was observed in the commercial samples. The time needed to reach the maximum stress was found to be inversely proportional to the rate of shear: For an aqueous solution of PEO 460.000 ( $c = 13.04$  wt-%), times of 5 sec., 4,5 sec., 2,5 sec., and 1,5 sec. were found for shear rates of 0,2, 0,3, 0,44 and 0,65 s<sup>-1</sup> respectively. The maximum overshoot was found also to increase when increasing the shear rate until it reached a certain upper limit. The overshoot was found to occur at lower shear rates when the molecular weight and the concentration were increased.

For the PEO-sample with narrow molecular weight distribution, no overshoot phenomenon could be observed. Either the phenomena does not occur in this sample or it is negligibly small in the concentration range investigated and also over the entire range of shear rate. The high molecular weight polymer fraction is believed to cause the observed overshoot phenomena. These fractions present in the commercial samples can conceivably cause more entanglement of the polymer molecules. The narrow molecular weight distributed polymer does not contain these high fractions. It is planned to further investigate this phenomenon with PEO samples of varying polydispersity, e. g., with mixtures of PEO's of narrow and broad molecular weight distributions.

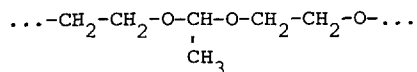
A comparison of PEO in aqueous solution with other water soluble polymers like polyacrylamide <sup>14)</sup> shows the pronounced differences in the viscoelastic behavior. For example, comparing the onset of pseudoplastic behavior  $\dot{\gamma}_{crit}$  (where  $\eta$  starts to depend on  $\dot{\gamma}$ ), it was found that  $\dot{\gamma}_{crit}$  for the PEO samples is observed at much lower  $\dot{\gamma}$ -values (see Tab. 2).

Tab. 2: Comparison of the onset of the pseudoplastic behavior of aqueous polyacrylamide (PAAm) and poly(ethylene oxide) (PEA) solutions

Polymer/H <sub>2</sub> O	M in g/mol	c in wt-%	$\dot{\gamma}_{crit}$
PAAm/H <sub>2</sub> O	0,51 · 10 <sup>6</sup>	5	150
PEO/H <sub>2</sub> O	0,46 · 10 <sup>6</sup>	4,76	2
PEO/H <sub>2</sub> O	0,21 · 10 <sup>6</sup>	4,76	8
PAAm/H <sub>2</sub> O	1 · 10 <sup>6</sup>	5	10
PEO/H <sub>2</sub> O	1,1 · 10 <sup>6</sup>	4,76	0,2

The overshoot behavior was observed to be more pronounced in PEO-solution than in aqueous PAAm-solutions <sup>13)</sup>. As already stated, a deviation from the Cox-Merz-rule could not be observed for PEO-solution, but deviations from this empirical relationship were observed in the case of PAAm/H<sub>2</sub>O-solutions <sup>9)</sup>.

The degradation behavior of the different PEO-samples in aqueous solution (see Tab. 3) was also investigated by GPC-analysis of the polymers before and after the shear experiments. As can be seen from the figures given in Tab. 4, there is no evidence for degradation of the highly pure sample with narrow molecular weight distribution or for the contaminated commercial sample of a corresponding nominal molecular weight. The latter finding is surprising, since it is well known that PEO has a strong tendency to degrade either by oxydation or mechanical stress <sup>1)</sup>. This degradation can be attributed to both the contamination of the commercial high molecular weight polymers with inorganic catalyst-residues and to the chemically unstable acetal links in these polymers <sup>5,6)</sup>:



These acetal links are due to the fact that acetaldehyde, an impurity in not specially purified EO (cf. <sup>5)</sup>), is incorporated into the polymer as comonomer during the polymerization process. Both impurities were not present in our sample, and therefore degradation effects were not be expected for this highly pure PEO. However, for the commercial samples, it may well be the case that those samples were already degraded when we started the investigations. This possible pre-aging will be investigated in further experiments with PEO samples freshly prepared by using earth alkali salt ca-

Tab. 3: Degradation experiments in steady shear flow experiment on poly-(ethylene oxide) samples of different molecular weights dissolved in water.

Sample No.	a) M in g/mol	C in wt-%	shearing time in sec.	$\dot{\gamma}$ in $s^{-1}$	$\eta$ -change	CPG-change <sup>b)</sup>
1	220.000	13	78	100	no	no
		13	354	100	no	no
		9	54	100	no	no
2	210.000	9	54	100	no	no
		9	358	100	no	no
4	1.100.000	6,98	60	10	no	-
		6,98	354	10	no	-
		2,44	60	100	no	-
		2,44	342	100	no	-
		2	660	5140	no	-
		5	780	700	no	-

a) See Tab. 1

b) See Tab. 4; the sample 4 could not be investigated by HPLC/GPC because the molecular weight exceeds the exclusion limit of the column system used.

Tab. 4: Molecular weight M and polydispersity U of poly(ethylene oxide) (PEO) of different purity and molecular weight distribution (see Tab. 1 and Fig. 1) after shear experiments ( $\dot{\gamma} = 100 s^{-1}$ ) of aqueous PEO solutions as determined by GPC analysis.

M and U of sample No. 1 and 2 (PEO EGA 210.000) before the shear experiments: No. 1(2):  $M_{max} = 197.000$  (303.000);  $M_w = 222.000$  (284.000);  $M_n = 140.000$  (70.000); U = 0,58 (3,09).

Sample No.	a) PEO in wt-%	time in s	M <sub>max</sub> <sup>b)</sup>	M <sub>w</sub> <sup>c)</sup>	M <sub>n</sub> <sup>c)</sup>	U <sup>d)</sup>
1	9	54	181.000	192.000	112.000	0,71
	13	78	222.000	218.000	125.000	0,74
	13	354	196.000	200.000	119.000	0,68
2	9	54	320.000	293.000	73.000	3,01
	9	348	332.000	296.000	75.000	2,95

a) See Tab. 1

b) Based on the elution volume of the peak maximum in the GPC traces.

c) Calculated from the traces.

d)  $U = (M_w/M_n) - 1$ .

talysts. It should be mentioned here, that other water soluble polymers, such as polyacrylamide<sup>14)</sup>, polyacrylamide-co-sodium acrylate<sup>15)</sup> and sulfonated polystyrene<sup>16)</sup> show a time dependent viscosity decrease. The molecular origin may be different, but one has to be aware of a time dependent phenomenon.

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#### References:

- 1) BAILEY, F. E., KOLESKE, J. V.: "Poly(ethylene oxide)", Academic Press, N. Y. (1976)
- 2) MÜLLER, R., ZACHMANN, G. G.: Collöid + Polym. Sci. 258 753 (1980)
- 3) LASALLE, D., BOILEAN, S., SIGWALT, P.: Europ. Pol. J. 13 591 (1977)
- 4) EISENBACH, C. D., PEUSCHER, M.: Makromol. Chem., Rapid Commun. 1 105 (1980)
- 5) PEUSCHER, M., EISENBACH, C. D., WEGNER, G.: Makromol. Chem. (in preparation)
- 6) EISENBACH, C. D., PEUSCHER, M.: Makromol. Chem. (in preparation)
- 7) PEUSCHER, M., EISENBACH, C. D.: J. Polym. Sci. (in preparation)
- 8) EISENBACH, C. D., PEUSCHER, M.: Macromolecules (in preparation)
- 9) KULICKE, W. M., PORTER, R. S.: Rheol. Acta 19 601 (1980)
- 10) POWELL, R. L., SCHWARZ, W. H.: Journal of Rheology 23/3 323 (1979)
- 11) CHMUTIN, G. I., KIRIYANENKO, A. A.: Isslect. Teplofiz. Svoisto Rastovod Rasplavov 80-9 (1974). Edited by Kutateladze, S. S. Akad. Nank SSSR, Sib. oce. Inst. Teplofiz. Novosibirsk, USSR
- 12) FERRY, J. D.: Viscoelastic properties of Polymers J. Wiley, N.Y. (1980)
- 13) KULICKE, W. M., KLEIN, J., PORTER, R. S.: Angew. Makromol. Chemie 76/77 191 (1979)
- 14) KULICKE, W. M., KNIEWSKE, R., KLEIN, J.: Progress in Polymer Sciences 8 373 (1982)
- 15) KULICKE, W. M., KNIEWSKE, R.: Makromol. Chem. 182 2277 (1981)
- 16) KULICKE, W. M., HÖRL, H. H.: Angew. Makromol. Chemie (submitted)

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