

Turbulent flow with polymer additives

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FOR A BETTER understanding of the Toms-phenomenon it is necessary to correlate molecular characteristics with the turbulent drag reduction effect. In this paper experimental results concerned with the effect of molecular weight on drag reduction and mechanical degradation in turbulent fully-developed pipe flow are presented. The polymeric material investigated was very clean laboratory synthesized polyacrylamide.

Dla lepszego zrozumienia zjawiska Tomsa należy skojarzyć ze sobą charakterystyki molekularne z efektem redukcji oporu turbulencji. W pracy przedstawiono wyniki doświadczalne dotyczące wpływu ciężaru cząsteczkowego na zmniejszenie oporu i degradację mechaniczną przy w pełni rozwiniętym przepływie burzliwym w rurze. Badanym polimerem był laboratoryjnie czysty poliakrylamid.

Для лучшего понимания явления Томса следует сочетать с собой молекулярные характеристики с эффектом редукации сопротивления турбулентности. В работе представлены экспериментальные результаты, касающиеся влияния молекулярного веса на уменьшение сопротивления и механическую деградацию при вполне развернутом турбулентном течении в трубе. Исследуемым полимером являлся лабораторно чистый полиакрилоамид.

1. Introduction

THE ADDITION of very small amounts of certain high molecular weight polymers to turbulent pipe flow can dramatically reduce the frictional drag and the associated pressure loss along the pipe at a given flow rate. TOMS [1] gave the first clear description of this phenomenon in his study of the turbulent flow of polymethyl methacrylate in monochlorobenzene. The drag reduction by polymer additives therefore is often called the Toms phenomenon.

Toms reported drag reductions of up to 50% compared with the pure solvent with a 0.25% weight addition of polymer. Many investigators since then have confirmed this effect. For water as the solvent the additives polyethyleneoxide (PEO) and polyacrylamide (PAA) are mainly used. Solutions of PEO or PAA with concentrations of about 50 ppm give drag reductions of up to 80%.

In spite of the extensive research activity in the past there is still no uniform interpretation of the mechanism of drag reduction which explains all aspects of the effect. It is generally accepted, however, that the presence of the polymer in a homogeneous solution may alter the turbulence production near the boundary [2]. Thus the Toms phenomenon generally is regarded as being essentially a wall phenomenon.

BEWERSDORFF and STRAUSS [3] presented results obtained when a viscoelastic liquid is injected into a Newtonian liquid flowing under turbulent conditions in a straight pipe.

If the concentration of the injected liquid was higher, the solution remained as a "liquid-thread" and was conveyed in the centre region of the pipe. Under these conditions a remarkable drag reduction was also observed, though the polymer had not migrated noticeably into the layers near the wall. The question is still open how this experimental result can be explained.

If polymer molecules are subjected to high shear forces, breakage of the molecular chain can take place. The shorter molecules produced obviously are less effective as the increase of the drag coefficient in the case of chain scission shows. This effect of mechanical degradation is a severe obstacle for the broad technical application of the Toms effect in closed circuit systems.

Polymer molecules are composed of n identical structural units X and can be described by the chemical formula X_n . As n can differ widely, the masses of the individual polymer molecules can be distributed over a large range of values.

The flow properties of the polymers strongly depend on the molecular mass spectrum. From the effect of degradation it already can be seen that the ability of a polymeric material to reduce the drag of a turbulently flowing liquid is markedly influenced by the molecular mass or, consequently, the molecular size of the polymer additive.

Experiments concerning the Toms effect generally are characterized by the mean molecular mass of the polymer used. But, especially, commercial samples of polymers contain a large spectrum of molecules of varying molecular mass not only due to the kind of polymerization process applied but in addition because of further blending of batches by the manufacturer. Thus the molecular mass spectrum can be expected to vary amongst samples with the same average molecular mass. In these cases the mean molecular mass is not a significant parameter and quantitative comparison of different drag reduction tests is impossible. This among other facts explains why experimental results presented in the literature often differ widely.

As the Toms phenomenon is strongly influenced by molecular parameters of the dissolved polymer, we started a series of experiments in order to correlate the molecular mass with the turbulent drag reduction and the degradation effect. In this paper some of the results obtained for the polymer PAA are presented.

For various reasons so far there are no systematic investigations presented in the literature concerning the influence of the molecular mass of water soluble polymers like PEO and PAA.

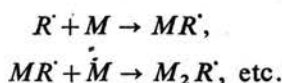
Some experiments of preliminary character were published by BERMAN [4]. This author analysed the molecular mass distribution of Polyox WSR-205 and N-80. Fractions of both substances were separated by gel chromatography (GPC) and their drag reducing efficiency was studied. Actually, the separation of fractions of polymers soluble in water in the high molecular weight region ($M > 2 \cdot 10^6$) by GPC is still the subject of chemical research and till now is not possible to conduct with sufficient reliability. The unsystematic variation of the parameters concentration and molecular mass in Berman's paper might have been brought about by the experimental difficulties he had.

Thus we applied a different concept. The average molecular mass actually is a significant parameter characterising the molecules of a polymer sample if the mass distribution is sufficiently narrow. Therefore we synthesized PAA in the laboratory by radical

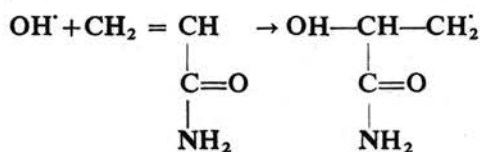
chain polymerization. By appropriate control of the process we were able to obtain comparatively narrow molecular mass fractions. This paper reports on measurements of drag reduction and degradation for three molecular mass fractions with the viscosity average molecular weights $\bar{M}_\eta = 3.24 \cdot 10^6$, $\bar{M}_\eta = 4.6 \cdot 10^6$, $\bar{M}_\eta = 5.03 \cdot 10^6$ g/mol. As the PAA samples synthesized were very clean and did not contain ionic groups, it was possible to determine the change of the mean molecular mass of the polymer after degradation runs with great accuracy.

2. Experimental procedure

Polyacrylamide (PAA) was synthesized in the laboratory by radical chain polymerization. During the polymerization reaction the monomer molecules acrylamide are joined together to form the polymer chain. In order to start the polymerization mechanism, an initiator R_2 is required which decomposes to form free radicals R' . The chain reaction begins with the introduction of a free radical R' into an unsaturated monomer molecule M . The radical adds to the unsaturate to give a larger radical MR' which in turn adds to another unsaturated molecule, etc.



The initiator we applied was H_2O_2 which decomposed into $2OH'$. The addition of the first acrylamide molecule to the radical is described by the reaction



Finally the growing radical may encounter a second radical and the polymerization chain is broken by recombination. Such a chain mechanism leads to polymer molecules having a distribution of molecular weights since not all chains will break exactly at the same stage. It is possible to obtain samples with a rather narrow molecular weight spectrum by an appropriate control of the polymerization process.

The data we applied for the polymerization of polyacrylamide are presented in Table 1.

Table 1.

AAm [g]	H ₂ O [ml]	H ₂ O ₂ [ml]	Methanol [ml]	T [°C]	\bar{M}_η [10 ⁶ g/mol]
151	1500	4.5	0	34	5.03
152	1500	5	0	34	4.6
154,3	1500	6	0	67	3.24
153,2	900	6	600	50	0.9
152,5	900	6	600	67	0.5

In Table 1 at the left hand side the amount of monomer acrylamide (AAM) and solvent water are given. The data show that the mean molecular mass of the polymer \bar{M}_n becomes larger if less H_2O_2 was used because then fewer molecular chains were started, each one thus becoming longer. As the polymerization reaction is exothermic, larger temperature values result in shorter and less effective molecules. On the other hand, the temperature has to be large enough in order to have the energy available which is necessary to start the polymerization reaction. Thus our temperature values were between 34°C and 70°C. Methanol is a substance which stops the chain reaction. It was used when the intention was to obtain very short molecules.

Five rather narrow molecular weight fractions were synthesized. The PAA obtained was very clean, linear and did not contain ionic groups. In this paper we only present results for the first three of the five molecular mass fractions of Table 1. The mean molecular masses of these samples were determined first by measuring the intrinsic viscosity with the use of a Zimm-Crothers viscosimeter and second by applying the Staudinger-Mark-Houwink relationship between intrinsic viscosity and mean molecular weight for PAA afterwards.

The drag reduction measurements were performed with a pipe flow system. The air pressure above the liquid in a container drove the test liquid through a 0.0061 m diameter horizontal pipe. To prevent degradation caused by pumping a single pass rather than a recirculating system was employed.

The liquid flow rate was monitored by weighing the quantity collected in a second container over a measured interval of time. Two pressure taps were placed at approximately 1.5 m and 2.0 m from the upstream end of the pipe. Measurements of viscosity for solutions of the samples of PAA were made in a Ubbelohde viscosimeter. The mean flow velocity and the wall shear stress were then calculated by using the calibrated constants of the apparatus. Runs were at Re numbers for turbulent flow.

3. Results and discussion

In Fig. 1 the drag coefficient λ is shown as a function of the Reynolds number Re for PAA concentrations between 5 ppm and 50 ppm. The drag coefficient λ and Reynolds number Re are defined by the formulae

$$(3.1) \quad \Delta p = \lambda \frac{\rho}{2} \bar{u}_m^2 L/d,$$

$$(3.2) \quad Re = \bar{u}_m d/\nu,$$

Δp being the pressure loss along the distance L in the region of fully-developed flow, d being the pipe diameter, \bar{u}_m the mean velocity, ρ and ν being density and kinematic viscosity of the polymer solution, respectively.

For all concentrations and low Re numbers the drag coefficient follows the curve representing the drag formula for fully-developed laminar pipe flow of pure water. But for Re numbers larger than about 1000 there is a deviation of the λ -values measured for the PAA solution from the λ -values as given by the formula for laminar pipe flow of

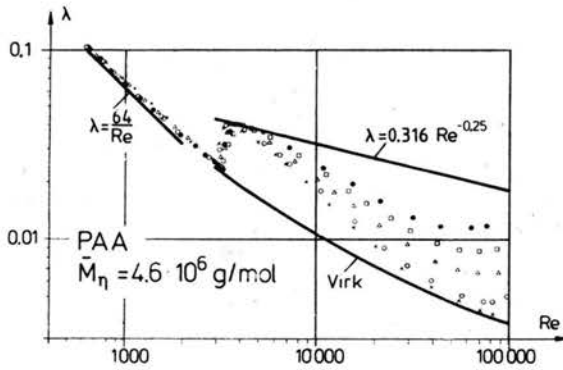


FIG. 1. Drag coefficient λ as a function of the Re number for various PAA concentrations. (●—5ppm, □—10 ppm, △—20 ppm, ○—30 ppm, ×—50 ppm). The mean molecular weight of all PAA samples is $\bar{M}_\eta = 4.6 \cdot 10^6$ g/mol.

pure water. This discrepancy which first is very small but then is heightened for increasing Re numbers was found by other authors, too and can be explained by the effect of early turbulence [5]. The transition from laminar to turbulent flow appears for Re numbers between about $Re = 2800$ and $Re = 3500$, the Re number being lower for larger polymer concentrations. The drag coefficient then first is about the same as for fully-developed turbulent pipe flow of pure water given by the relationship $\lambda = 0.316 \cdot Re^{-0.25}$.

Stretching of the polymer molecules is combined with the molecules becoming drag reducing effective. Drag reduction only appears for shear stress values larger than a critical value necessary in order to produce sufficient molecular stretching. From Fig. 1 it can be concluded that for a given pipe diameter and a given mean molecular weight of

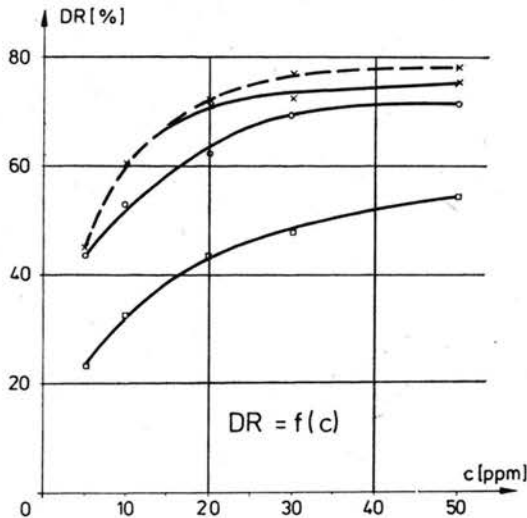


FIG. 2. Drag reduction DR as a function of the PAA concentration for three different PAA samples with the mean molecular weights, □— $\bar{M}_\eta = 3.24 \cdot 10^6$ g/mol, ○— $\bar{M}_\eta = 4.6 \cdot 10^6$ g/mol, ×— $\bar{M}_\eta = 5.03 \cdot 10^6$ g/mol and two different Re numbers — $Re = 30000$, — — — $Re = 60000$.

the polymer the Reynolds number for the drag reduction becoming apparent is smaller for larger polymer concentrations.

For PAA molecules with ionic groups it was found that the λ -values do not reach the curve for fully-developed turbulent pipe flow because molecular stretching due to electric charges interferes with Re number influence.

For increasing polymer concentration the drag coefficient is diminished, finally approaching Virk's asymptote which gives the maximum drag reduction obtainable for a given Re number [6].

The drag reduction depends on the Re number being supported by increasing Re numbers as larger Re numbers are combined with larger stress values and stronger stretching of the polymer molecules. Finally, for Re numbers becoming larger and larger, stretching becomes too intensive and breakage of the molecules takes place. The shorter molecules produced by this effect of mechanical degradation are less effective and the drag coefficient increases, see Fig. 1.

In Fig. 2 the drag reduction DR is shown as a function of the concentration for PAA-solutions obtained from three different molecular weight fractions of PAA. The drag reduction DR is defined by the expression

$$(3.3) \quad DR[\%] = \frac{\lambda_w - \lambda}{\lambda} \cdot 100$$

with λ_w and λ being the drag coefficient for pipe flow of pure water and of polymer solutions respectively. In Eq. (3.3) $\dot{V}(\lambda_w) = \dot{V}(\lambda)$ is assumed. As we have $\eta \cong \eta_w$, it follows that $Re(\lambda_w) \approx Re(\lambda)$. It can be seen that drag reducing additives are more effective when they are of high molecular weight.

With increasing polymer concentration the drag reduction is first enhanced, then an upper value is reached, which cannot be surpassed by further increasing the concentra-

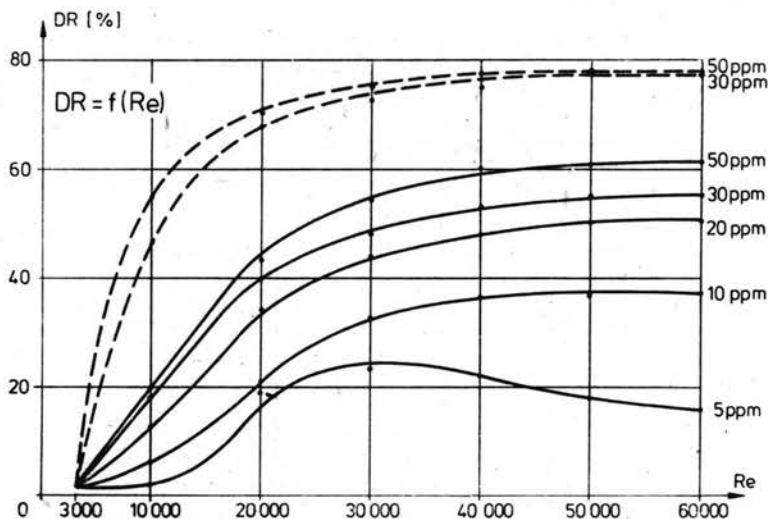


FIG. 3. Drag reduction as a function of Re number for various PAA concentrations and two different molecular weight fractions of PAA (--- $\bar{M}_\eta = 5.03 \cdot 10^6$ g/mol, — $\bar{M}_\eta = 3.24 \cdot 10^6$ g/mol).

tion. The maximum drag reduction obtainable for a given Re number depends on the \bar{M}_η -value of the PAA sample. Thus Virk's asymptote can be reached only for molecules sufficiently large. An explanation could be that larger polymer molecules are able to suppress a larger part of the spectrum of turbulence. This obviously cannot be compensated by a larger number of shorter molecules.

Increasing the Re number from 30 000 to 60 000 makes the PAA molecules ($\bar{M}_\eta = 5.03 \cdot 10^6$ g/mol) more effective.

In Fig. 3 the Reynolds number influence on drag reduction is presented for various PAA concentrations. The viscosity average molecular weights \bar{M}_η are $3.24 \cdot 10^6$ and $5.03 \cdot 10^6$ g/mol.

For larger Re numbers the effectiveness of the molecules is raised. Because of stronger molecular stretching, shorter and shorter molecules contribute to the drag reduction. Thus for all concentrations the drag reduction first increases with an increasing Re number. While the curve for $c = 5$ ppm shows a decrease of drag reduction for Re numbers larger than about 30 000, a broad maximum is reached for larger concentrations as in this case molecules destroyed in the region of high shear stress values at the wall can be replaced by molecules from the inner part of the pipe.

For larger \bar{M}_η -values the DR-values are higher and the DR-maximum is reached for smaller Re numbers since these long molecules are subject to more intensive stretching in a given flow field as compared to shorter molecules.

The few experimental data on the mechanical degradation of PAA presented in the literature are confined to highly concentrated aqueous solutions. The degradation effect in these publications is studied by recording the change of the drag reduction as a function of the number of degradation runs or the time during which the PAA molecules were exposed to the shear fields.

There are two difficulties which arise following the primary degradation process, that is the change of molecular mass during the process of degradation. First, it is not possible to monitor changes of molecular weight by determining \bar{M}_η directly from a very dilute aqueous solutions of PAA (or PEO). The second problem is that, in general commercial polymers especially contain impurities, particularly ionic groups.

The determination of the viscosity average molecular weight then only is possible if the ionic groups are compensated by other ions. Actually this procedure does not give very reliable results. As our clean laboratory PAA products did not contain ionic groups, we were able to determine \bar{M}_η with great accuracy.

The first problem could be overcome by increasing the polymer concentration by vaporization of the solvent. This was done under low pressure so that vaporization appeared for 35°C already and thermal degradation could be avoided as was confirmed control measurements.

In Fig. 4 the drag coefficient λ is presented as a function of the Re number for $c = 50$ ppm and the viscosity average molecular weight $\bar{M}_\eta = 4.6 \cdot 10^6$ g/mol. The results presented were measured after n degradation runs during which the pressure gradient in the pipe was $\Delta p/L = 0.45$ bar/m for all samples. Degradation of the polymer molecules changes the Re number for transition from laminar to turbulent flow to higher values. The drag coefficient rises with the number of degradation runs.

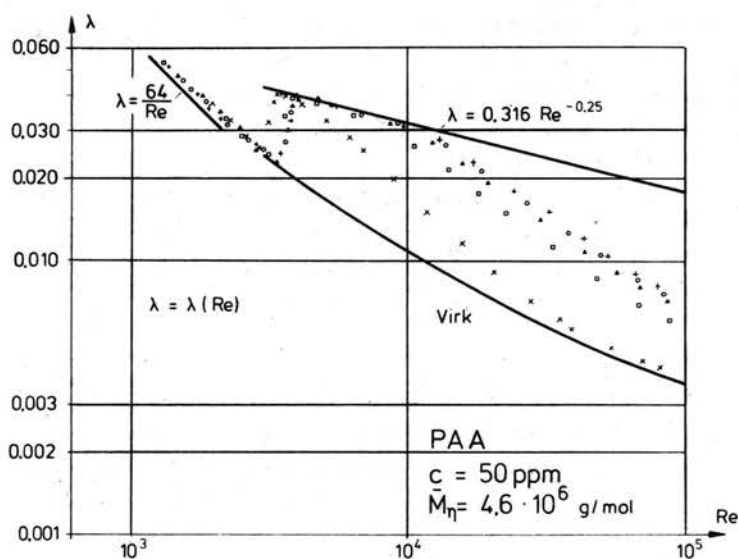


FIG. 4. Influence of the number of degradation runs on the drag coefficient λ as a function of the Re number (\times —fresh PAA solution, $\bar{M}_\eta = 4.6 \cdot 10^6$ g/mol, $c = 50$ ppm; λ —values after \square 2 degradation runs, \triangle 6 degradation runs, \circ 10 degradation runs, $+$ 15 degradation runs).

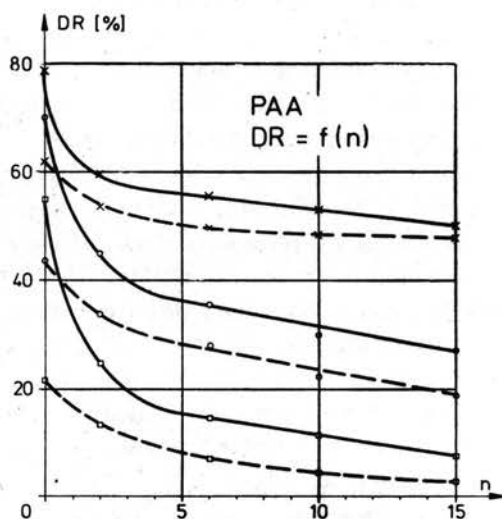


FIG. 5. Drag reduction DR for two PAA solutions (--- $\bar{M}_\eta = 5.03 \cdot 10^6$ g/mol, --- $\bar{M}_\eta = 3.24 \cdot 10^6$ g/mol; $c = 50$ ppm) measured for three different Re numbers (\times Re = 60000, \circ Re = 20000, Re = 10000) after n degradation runs ($\Delta p/L = 0.45$ bar/m).

In Fig. 5 the change of the DR-value defined by Eq. (3.3) due to mechanical degradation is shown for three different Re numbers and two PAA solutions with different viscosity average molecular weights ($\bar{M}_\eta = 3.24$ and $5.03 \cdot 10^6$ g/mol) but identical concentrations of PAA ($c = 50$ ppm). By n the number of degradation runs ($\Delta p/L = 0.45$ bar/m) is given to which the PAA solutions had been exposed before the drag reduction was measured.

According to the results presented in Fig. 5, the strongest decrease of drag reduction appears during the first degradation runs, becoming much smaller afterwards. For a given degradation the decrease in drag reduction is largest for the smallest Re numbers.

Comparison of the curves for two PAA solutions obtained from different fractions with viscosity average molecular weights of $\bar{M}_\eta = 5.03$ and $\bar{M}_\eta = 3.24 \cdot 10^6$ g/mol shows that for a given number of degradation runs the decrease of drag reductions is stronger for the solution containing larger PAA molecules. The difference in drag reduction for the two molecular weight fractions diminishes with an increasing number of runs. The DR-value for Re = 60 000 and 15 runs is about 50%.

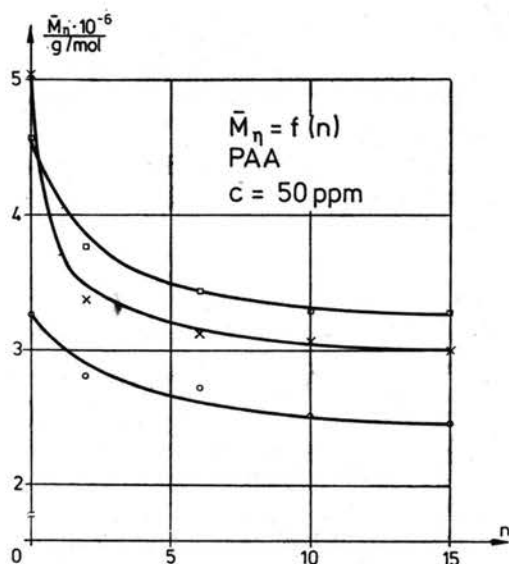


FIG. 6. Viscosity average molecular weight of PAA as a function of the number of degradation runs for aqueous solutions of PAA samples with $\times \bar{M}_\eta = 5.03 \cdot 10^6$ g/mol, $\square 4.6 \cdot 10^6$ g/mol, $\circ 3.24 \cdot 10^6$ g/mol (pressure gradient during degradation $\Delta p/L = 0.45$ bar/m).

In Fig. 6 \bar{M}_η is presented as a function of the number of degradation runs for three solutions equal as far as the concentration is concerned but obtained from three different molecular mass fractions of PAA. The curve marked by \square was obtained by using a different pipe and a different degradation pressure gradient, thus we exclude it from the discussion.

It can be seen from Figs. 5 and 6 that the DR changes actually are connected with distinct alterations of \bar{M}_η . Thus the results of this paper support those explanations which combine the Toms effect with the properties of the single polymer molecule but are in contrast to the aggregation hypothesis presented in [7].

In Fig. 5 it is shown that \bar{M}_η changes are largest for the first degradation runs and become much smaller afterwards. Comparison of Figs. 5 and 6 shows that the reduction of \bar{M}_η results in a related decrease of DR. Further it emerges from Fig. 6 that high molecular weight favours mechanical degradation. Thus our measurements confirm that the

decrease of drag reduction results mainly from the scission of the molecular chain of the largest molecules.

Further the results of our degradation experiments are in accordance with our hypothesis that the increase of drag reducing efficiency with an increasing Re-number at least partially is due to the fact that for larger Re numbers shorter and shorter molecules become effective. If Re is large, DR is less diminished by degradation because short molecules only become effective for sufficiently high Re numbers, see Fig. 5.

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