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# High-Frequency Dynamical Behavior of Poly(ethylene glycol)+$H_2O$ Mixtures by Brillouin Spectroscopy

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**Summary:** Brillouin spectroscopy has been used to examine high-frequency dynamical behavior of aqueous solutions of poly(ethylene glycol) (Mw $\approx$ 400g/mol) at 298K in the entire concentration region. It was found that a relaxation process takes place in the experimental frequency window that significantly affects the shape of experimentally recorded spectrum of the density fluctuations (dynamical structure factor). The process detected was attributed to segmental motion of the flexible polymeric chain. The full spectrum analysis of Brillouin spectra has been performed taking advantage of the relaxation function previously used in describing a single relaxation process in dielectric examination of water solutions of PEG 400. The proposed data processing procedure permits a qualitative reproduction of concentration dependencies of the hypersonic wave velocity and absorption measured. The shapes of the concentration dependencies of the relaxation times obtained from the Brillouin and the dielectric spectroscopies are in good agreement over a very broad concentration range, although their absolute values are scaled by the factor of 3. This result indicate that the two processes revealed independently by dielectric and Brillouin spectroscopies, apparently separated in time-scale, are just the same relaxation process.

**Keywords:** Brillouin scattering; mechanical properties; polyethylene glycol; relaxation

## Introduction

Polyethylene glycol is a widely used synthetic polymer based on oxyethylene (OE), with the general structure H–(O–$CH_2$–$CH_2$)$_n$–OH, where *n* is the number of monomeric OE units. Many desirable properties of oxyethylene polymers are undoubtedly related to the dynamical properties of polymer chains. This concerns for example their mixtures, characterized by very high ionic conductivity, obtained by dissolving of small amount of salt in POE matrix, where the transport properties of ions through the polymer matrix are correlated with fast localized motions of polymeric chain.[1] To study the dynamics of the polymer occurring in this not easily accessible time-scale of the order of picoseconds, it is necessary to utilize high-frequency methods like dielectric spectroscopy or Brillouin light scattering.

The dielectric spectroscopy method has been applied in investigations of aqueous PEG solutions with different molecular weights (200, 400 and 1450g/mole)[2,3] and in studies of oligo(ethylene glycol)s with a different number of monomeric OE units.[4] The mean value of relaxation time for pure polymer, obtained from the maximum of dielectric loss peak, was of the order of 200ps. Also in earlier Brillouin spectroscopy investigations on PEG200 and PEG400[5–7] a single relaxation process was revealed taking place on a time-scale of the order of 20ps, very close to that observed in

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our recent Brillouin scattering experiments in PEG600 and its solutions in few organic solvents.[8,9]

The time-scale separation between processes revealed by these two high-frequency spectroscopies suggests that dielectric and Brillouin methods analyze two different relaxation processes. This suggestion has been used in interpretation of the dynamical results obtained in our recent Brillouin scattering experiment in PEG600/$H_2O$ mixtures.[10] The fast process revealed by Brillouin scattering has been interpreted as a consequence of the crankshaft motion of C–O–C groups, whereas the slower process, observed in dielectric experiment, has been assigned to the dynamics of the ether oxygens involved as acceptors in hydrogen bonds. In view of those considerations, the absence of the fast process in dielectric spectrum has been interpreted as the result of a quite weak dipole moment fluctuation connected with the crankshaft motion.

However there are two interesting similarities in the results obtained by dielectric and Brillouin spectroscopies: 1) the processes are rather independent on the polymer chain length and 2) the processes are characterized by a distribution of relaxation times. These two occurrences could be taken as a indication that the relaxation observed by means of these two methods concerns just the same process. In this paper we try to answer this question performing the data processing method which takes advantage of the relaxation function previously obtained in dielectric method in order to analyze the Brillouin light scattering spectra.

## Experimental Part

Polyethylene glycol (PEG) of mean molecular mass 400g/mole has been obtained from Fluka Chemie GmbH and was used without any further purification procedure. Solutions of PEG400 in double distilled and deionized water have been prepared as equidistant weight fractions, covering the whole concentration range from pure PEG400 to pure solvent. The concentration scale was then recalculated to monomer molar fraction, $x'$, defined as:

$$x' = \frac{n_{OE}}{n_{OE} + n_{solv.}} \tag{1}$$

$n_{OE}$ being the mean number of oxyethylene units of PEG chains in solution, and $n_{solv}$ the number of the solvent molecules.

During the Brillouin scattering experiment the samples were contained in a quartz cell (Hellma, Germany) placed in a thermostatic holder, whose temperature was set to 298K and controlled to the accuracy of $\pm 0.1$ K. The linearly polarized line ($\lambda = 532$nm) of a Coherent DPSS 532 laser, with a mean power of about 100 mW, was used as the probe. In each measurement the VV component of scattered light ($I_{\|}$) has been collected in a backscattering geometry ($\theta = 180°$) and analyzed by a Sandercock-type (3+3)-pass Tandem Fabry-Perot interferometer with a finesse, estimated by the line-width of the elastic line, of about 90. For each concentration three spectra has been collected with different free spectral ranges (FSR) of 7.5, 20 and 100GHz. These three spectra were then jointed together in order to obtain one high resolution spectrum with sufficient frequency extension. The spectrum of the density fluctuations ($I_{\rho\rho}$), proportional to dynamic structure factor $S(q,\omega)$, can be obtained according to the equation:[11]

$$I_{\rho\rho}(\omega) = I_{\|}(\omega) - r^{-1} I_{\perp}(\omega) \tag{2}$$

where $I_{\perp}$ is a depolarized spectrum and $r$ is the depolarization ratio. Isotropic spectra for each concentration has been obtained according to Equation (2) using standard procedure[12,13] where for $I_{\perp}$ we took spectrum recorded for pure PEG400. Obtained $I_{\rho\rho}$ spectra for PEG400 aqueous solutions are presented in Figure 1.

## Results and Discussion

The shape of the dynamic structure factor can be derived within the framework of the generalized hydrodynamics[14,15] using the

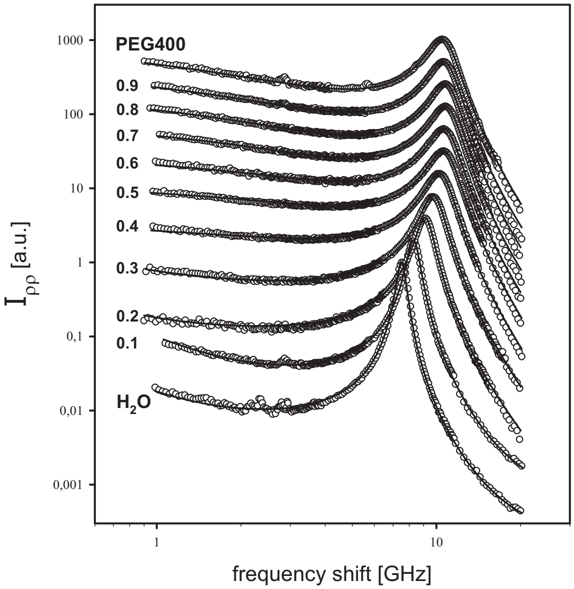

***Figure 1.***
Normalized $I_{\rho\rho}$ spectra for PEG400 aqueous solutions. The solid lines represent the fits to the data using Equation (3) as explained in text. Half of the overall data points are shown for clarity.

frequency dependent complex longitudinal acoustic (LA) modulus $M(i\omega)$

$$I_{\rho\rho}(\omega) = \frac{I_0}{\omega}\frac{M''(\omega)+\omega\eta_\infty}{[\omega^2\rho/q^2 - M'(\omega)]^2 + [M''(\omega)+\omega\eta_\infty]^2}, \quad (3)$$

where $q = (4\pi n/\lambda_0)\sin(\theta/2)$is the amplitude of the exchanged wave-vector, $\lambda_0$ is the incident wave-length, $\theta$ is the scattering angle, $\rho$ is the mass density, and $n$ is the refractive index of the medium. The longitudinal modulus $M(\omega) = M'(\omega) - iM''(\omega)$ describes the response of a medium to a propagating longitudinal wave. The term $\omega\eta_\infty$ is often introduced into $M''$ and describes additional contributions to the damping including processes occurring at frequencies higher then those covered by experimental method (instantaneous processes). The value of longitudinal modulus changes with the frequency and for two limiting cases of very low frequencies (high temperatures) and very high frequencies (low temperatures) takes the values of $M_0$ and $M_\infty$, respectively. In these cases the $M''$ is zero and the acoustic damping is characterized only by the limiting value of longitudinal viscosity $\eta_\infty$. Between those limiting cases the frequency dependence of both real and imaginary parts of the longitudinal modulus have to be considered in order to take into account the relaxation process.

The spectrum described by the Equation (3) shows a maximum near the frequency of longitudinal acoustic modes (LA) corresponding to the peak at about 10GHz in Figure 1. For frequencies close to the LA peak, spectrum given by Equation (3) can be approximated by the spectrum of a damped harmonic oscillator (DHO):

$$I_{LA}(\omega) = I_0\frac{2\Gamma_{LA}\omega_{LA}^2}{[\omega_{LA}^2 - \omega^2]^2 + [\omega 2\Gamma_{LA}]^2} \quad (4)$$

where $\omega_{LA}$ and $\Gamma_{LA}$ correspond to the frequency position and half width at half maximum (HWHM) of the LA peak. The values of Brillouin shift and linewidth are usually used to estimate the values of hypersonic longitudinal velocity, $c_B$, and the normalized sound absorption coefficient,

$\alpha/f^2$ through the formulas

$$c_B = \omega_{LA}/q;$$
$$\alpha/f^2 = 2\pi\Gamma_{LA}/(c_B\omega_{LA}^2) \quad (5)$$

Monomer molar fraction dependencies of the quantities calculated from Equation (5) has been plotted on Figure 2.

Comparison of the Brillouin and the ultrasonic velocity data[16] presented on Figure 2 (open circles) shows that at low concentrations, low and high frequency velocities turn out to be coincident, suggesting that in both cases we are measuring the same low frequency limit sound velocity, $c_0$. At high concentrations the values of the hypersonic velocity are definitely higher than those measured by the ultrasonic probe confirming a viscoelastic behavior already observed in similar compounds.[10,17] The concentration characteristic of normalized absorption (presented in Figure 2) shows a quite complicated non-monotonic behavior, suggesting the existence of concentration dependent relaxation process.

The choice of the proper model for longitudinal modulus for liquid PEG solutions could be difficult because of the complex dynamics of pure PEG. Dynamical behavior of PEG and its aqueous solutions have been investigated by the dielectric relaxation method.[2–4] It was observed that pure PEG as well as its solutions are characterized by single asymmetric relaxation peak and the mean value of relaxation time for pure polymer, obtained from the maximum of dielectric loss peak, was of the order of 200ps. Brillouin spectroscopy investigations on pure PEG200 and PEG

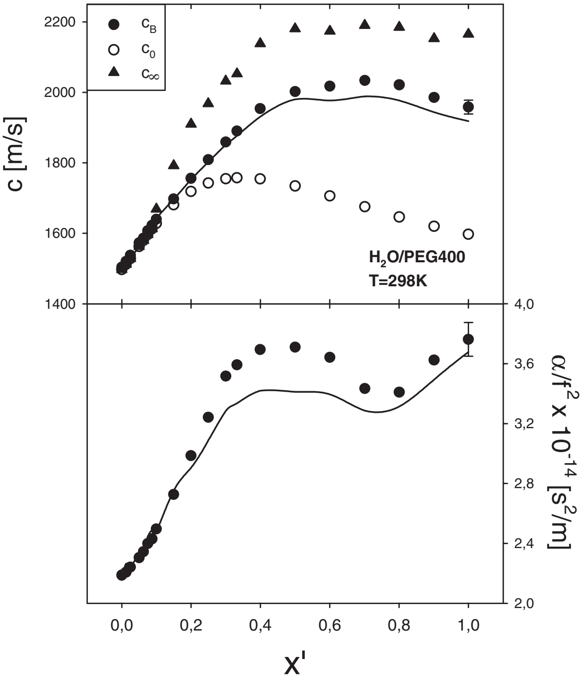

***Figure 2.***

Concentration dependence of the longitudinal velocity $c_B$ and normalized absorption coefficient $\alpha/f^2$. Full circles represent values calculated from frequency position and linewidth of Brillouin peaks (Equation (5)). Open circles are the values of the relaxed sound velocity $c_0$ taken from ref.16; triangles are the values of unrelaxed sound velocities $c_\infty$ obtained from the fit. Solid lines are the values of $c_{LA}(\omega_{LA})$ and $\alpha/f^2(\omega_{LA})$ calculated at each concentration from Equation (8) (using Equation (6) and (7) to calculate values of modulus $M$) using the relaxation parameters obtained by the full spectrum analysis.

400 indicated a relaxation time of about 20ps.[5–7]. A very close value was obtained in our recent Brillouin scattering experiments in PEG600 and its solutions in few organic solvents.[8,9] In this study, the characteristic temperature dependencies of hypersound velocity and absorption, being the manifestation of the relaxation process taking place within GHz frequency range, have been analyzed in terms of the single Debye process. The observation that temperature dependence of relaxation time described by VFT behavior gives better fits than a simple Arrhenius dependence, suggested for a distribution of relaxation times or for the occurrence of additional processes taking place at almost the same time scale.

It is interesting that in dielectric as well as in Brillouin scattering study, only one asymmetric relaxation peak was revealed and that the frequency position of this peak was apparently independent of polymer chain length. This observation could be taken as an indication that, in spite of the difference in obtained values of relaxation times, both methods measures in fact the same process. On the other hand, the mentioned differences could be also attributed to the different quantities measured be those techniques. The dielectric spectroscopy method measures the dipole moment fluctuation, whereas the Brillouin scattering is sensitive to the density fluctuations. One could then imagine a situation where molecular motions induce fluctuations in density without much influence on dipole moment fluctuations. In such condition the process which affect the light scattering spectrum could be undetected in dielectric spectrum and, as a consequence, the relaxation functions for both methods would be different.

To answer this question the full spectrum analysis of Brillouin spectra has been performed preserving the shape of the relaxation function deduced from earlier dielectric spectroscopy experiment.[2] It is known that the shape and the frequency position of the relaxation function assumes different values if the modulus or compliance formalism is used to describe the same relaxation process.[13] For this reason, for a direct comparison with dielectric measurements, the spectra at different concentrations have been fitted by Equation (3) where the modulus $M(\omega)$ was written in terms of the compliance $J(\omega)$ as $M(\omega) = 1/J(\omega)$. The longitudinal compliance was expressed as a Havriliak-Negami function

$$J(\omega) = J_\infty + \frac{J_0 - J_\infty}{[1 + (i\omega\tau)^\beta]^\alpha}, \tag{6}$$

where $J_0$ and $J_\infty$ are related to the relaxed ($c_0$) and unrelaxed ($c_\infty$) sound velocities, respectively, through the relation $J = 1/\rho c^2$, $\tau$ is the relaxation time, $\alpha$ and $\beta$ are shape parameters of the relaxation function. In order to reduce number of free parameters, the shape parameters $\alpha$ and $\beta$ for each concentration has been taken from dielectric experiment,[2] whereas the values of $c_0$ were taken from earlier ultrasonic experiment[16] (the latter are presented in Figure 2). The relaxation parameters determined during procedure of fitting whole Brillouin spectrum are therefore $c_\infty$, $\tau$, $\eta_L$.

For concentrations $x' < 0.1$ the process proceeds at frequencies much higher then those accassible to Brillouin spectroscopy In this case we are dealing with the relaxed case and the spectra were fitted assuming that longitudinal compliance can be written as

$$J(\omega) = J_0 + i\omega\eta_\infty, \tag{7}$$

where $\eta_\infty$ takes into account all dissipative processes occurring at frequencies higher then experimentally covered (shear and bulk viscosities).

The results of the described fitting procedure are presented on Figure 1 as solid lines. It can be observed that the quality of the fit is very good in the whole frequency and concentration range, which proofs the consistency of the adopted procedure. To further test the reliability of this procedure we have calculated the values of hypersonic velocity and absorption using the relaxation parameters obtained by the fit and compared them with the values previously obtained from the frequency position and linewidth of Brillouin peaks. For that purpose we have firstly estimated the values of $M'$ and $M''$ at frequency $\omega_{LA}$ from Equation 6 or 7 (depending on the concentration of mixture) and then calculated the values of $c_{LA}(\omega_{LA})$ and $\alpha/f^2(\omega_{LA})$ through relations

$$c_B = \sqrt{M'(\omega_{LA})/\rho};$$
$$\alpha/f^2 = \frac{2\pi^2}{\rho c_B^3}\frac{M''(\omega_{LA}) + \omega_{LA}\eta_\infty}{\omega_{LA}} \tag{8}$$

The results of this procedure are presented in Figure 2 as a solid lines. It can be seen that the adopted procedure, making use of dielectric relaxation function for description of dynamical structure factor, enable to reproduce the concentration dependencies of acoustic parameters, at least at qualitative level, which confirms the correctness of data processing procedure applied. The proper quantitative reproduction of the experimental acoustic parameters presented on Figure 2 probably needs to consider additional high frequency relaxation process whose existence is indicated by non-zero value of $\eta_\infty$ viscosity.

The contributions to the overall acoustical damping are presented in Figure 3. It is clearly seen that for concentrations lower then $x' = 0.1$, because of the absence of the relaxation process in examined frequency range, the longitudinal viscosity ($\eta_\infty$) completely account for the elastic loss and its value increases with the polymer content. The shear viscosity data measured for diluted $H_2O$/PEG400 solutions[18] has been used to present the contribution of this process to the elastic loss. It is seen that for concentration $x' < 0.2$ the longitudinal viscosity is higher then the shear viscosity. In this concentration range our mixture behave like ordinary liquid and the relation $\eta_\infty = \eta_V + 4/3\eta_S$ holds, where $\eta_V$ is the bulk or volume viscosity (related to structural, chemical, conformational or other processes).[19] At higher concentrations, however, the observation that the contribution from shear viscosity is higher then that of longitudinal viscosity can be assumed as the direct evidence of viscoelastic effects taking place in our mixtures even in the semi-dilute region.

In Figure 4 we present the semi-log plot of monomer mole fraction dependencies of relaxation times obtained from the dielectric spectroscopy and from Brillouin spectroscopy. It can be observed that shapes of the concentration dependencies of $\log\tau$ obtained from both experimental methods are nearly the same. This result proves that the two processes revealed by dielectric spectroscopy and Brillouin light scattering methods and being apparent separated in time-scale are just the same relaxation process. The difference concerns just the absolute value of the relaxation time, that

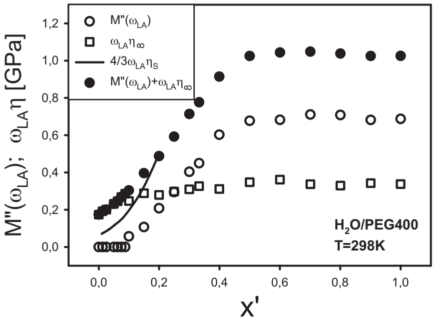

***Figure 3.***
The overall acoustic damping (solid circles) and its components: Imaginary part of the longitudinal acoustic modulus M″ (open circles) and the longitudinal viscosity $\omega_{LA}\ \eta_\infty$ (open squares). Solid line is the contribution to elastic loss from the shear viscosity $\eta_S$.[18]

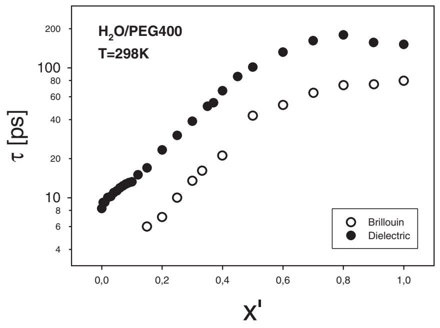

***Figure 4.***
Concentration dependence of relaxation times. Full circles represent the dielectric relaxation times taken from ref.2. Open circles are the values obtained in this work from full spectrum analysis.

in case of dielectric method is about 3 times higher then the appropriate Brillouin data, in very broad concentration range.

Similar observation was made in earlier Brillouin scattering experiment performed in temperature study of glass-forming epoxy resin where analogous fitting procedure has been adopted.[13] The fact that the utilization of dielectric relaxation function to reproduce the isotropic light scattering spectrum furnishes the same value of reduction factor (namely 3) between relaxation times in two dissimilar compounds in different thermodynamic conditions, can be taken as a general result indicating that one should approach with care when comparing the absolute values of the relaxation time obtained from these two spectroscopic techniques.

## Conclusion

The Brillouin spectroscopy has been used to obtain isotropic spectra for aqueous solutions of PEG400 at different concentrations ranging from neat solvent to pure polymer. It was found that the characteristic change in the shape of experimentally recorded spectrum of the density fluctuations is due to the segmental relaxation process that takes place in the GHz frequency range. The full spectrum analysis of Brillouin spectra has been performed taking advantage of the relaxation function previously used in describing a single relaxation process in dielectric examination of the same system. It has been shown that such elaboration procedure provide qualitative reproduction of concentration dependencies of measured velocity and absorption of hypersonic wave. The lack of the full quantitative consistence between the experimental data and the model dependencies suggests different shapes of the relaxation functions for acoustic and dielectric susceptibilities. The result of the data processing procedure applied indicates that that the two methods, i.e. dielectric and light scattering, detect the same relaxation process but the frequency ranges covered by the two methods seem to be shifted by a certain constant value. However, in order to reach a definite conclusion, the temperature dependence of the relaxation time from both the techniques should be obtained.

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