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Advances in Ripplon Surface Laser-Light Scattering Measurement for Highly Viscous Polymer-Solvent System

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Abstract The surface properties of a polymer organic-solvent system was measured using a ripplon surface laser-light scattering (SLLS) technique. The power spectrum (PS) of a ripplon can be obtained by fast Fourier transform (FFT) analysis of the beat signal of scattered light using ripplon SLLS. However, the PS peak shifts to lower frequencies due to the low surface tension of typical organic solvents. This shift means that the PS can be easily affected by external vibrational noise. In addition, higher viscosities broaden the shape of the spectra so that the peak becomes less clear. It is therefore difficult to find a definite peak frequency and to determine its width at half maximum for analyzing surface properties. To address these issues, a new system for SLLS was developed and was used to demonstrate that the available viscosity measurement range can be extended to the higher values needed for organic-solvent systems.

Keywords Coustic-optic modulator · Laser light scattering · Polymer-solvent system · Surface viscoelasticity

1 Introduction

Efficient manufacturing of highly functional films (e.g., optical films) requires precise control of the film's microstructure. Since drying processes determine the final

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qualities of the microstructure, it is of utmost importance to understand the drying behavior and surface properties of coated films. This is particularly true in the case of very sensitive organic-solvent systems. The surface properties of polymer-solvent films at the air–solvent interface can be deduced from the propagation characteristics of high-frequency capillary waves generated by thermal fluctuations of the liquid surface. These waves are called "ripplons." Their characteristics can be studied by ripplon surface laser-light scattering (SLLS) [1]. Ripplons are small-amplitude waves (∼ nm); they are influenced by the viscoelastic properties of molecules adsorbed on the liquid surface. Ripplon SLLS is therefore a suitable and sensitive technique for measuring surface viscoelasticity. In addition, since ripplon SLLS is a non-contact and non-perturbing liquid surface measurement method, it can be effectively used to continually and rapidly monitor the change of surface properties during drying.

In this work, we measure the surface properties at the liquid surface of polymer organic-solvent films using ripplon SLLS. We obtain the ripplon power spectrum (PS) by fast Fourier transform (FFT) analysis of the beat signal of scattered light by using an optical heterodyne technique. However, the shift of the PS peak to lower frequencies poses a problem due to the low surface tension of typical organic solvents. Therefore, the peak is easily affected by external vibrational noise (Fig. 1). In addition, the intensity of the PS is weaker at low frequencies as a result of this noise, which makes it difficult to obtain a definite peak frequency and to determine its width at half maximum for analyzing surface properties.

We developed a new arrangement of the optical system that uses an acoustic-optic modulator (AOM) to extend the available measurement range to higher viscosities. We call this new system the "double-shift method." This system considerably improves the sensitivity and accuracy of the beat signal of ripplon SLLS at low frequencies, as detected by a photomultiplier tube. The surface properties of higher concentrations of polymer solutions mixed with methyl ethyl ketone (MEK) at the air–solvent interface have also been investigated using this new technique.

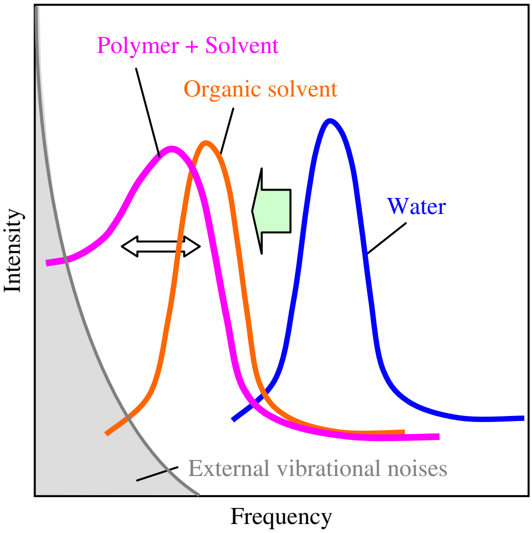

Fig. 1 Expected shift and change of ripplon FFT spectrum for analysis of polymer organic solvent

2 Experimental Setup

A schematic diagram of the ripplon SLLS experimental apparatus is shown in Fig. 2. The light source is an Nd:YAG laser with a wavelength of 532 nm and an output power of 20 mW. The output of the laser is divided into incident and reference light by a beam splitter (PBS) and then superimposed onto the sample surface at crossing angle θ, which determines the scattering wave number. The frequency of the scattered light is modulated based on the Doppler effect through interaction with the moving wave. However, the intensity of the scattered light is very weak and its frequency shift is very small; therefore, by mixing the scattered light and reference light, a weak signal can be detected in the form of a beat signal. This process is called heterodyne detection. We can obtain the ripplon PS by FFT analysis of the beat signals. The propagation of a ripplon is described as a decay oscillation in the form of $A \exp\{i(kx - \omega_0 t) - \Gamma t\}$. The angular frequency ω_0 and the damping constant Γ are approximated by Eqs. 1 and 2 [2], respectively, as follows:

$$\omega_0^2 = \frac{\sigma}{\rho} k^3, \tag{1}$$

$$\Gamma = 2\frac{\eta}{\rho} k^2, \tag{2}$$

where σ is the surface tension, η is the kinematic viscosity, ρ is the density, and k is the wave number of ripplons.

The basic idea of the experimental setup is the same as that used in our previous study [3]. However, two AOMs are added as frequency shifters to enable shifting of the ripplon PS by any arbitrary frequency (Fig. 3).

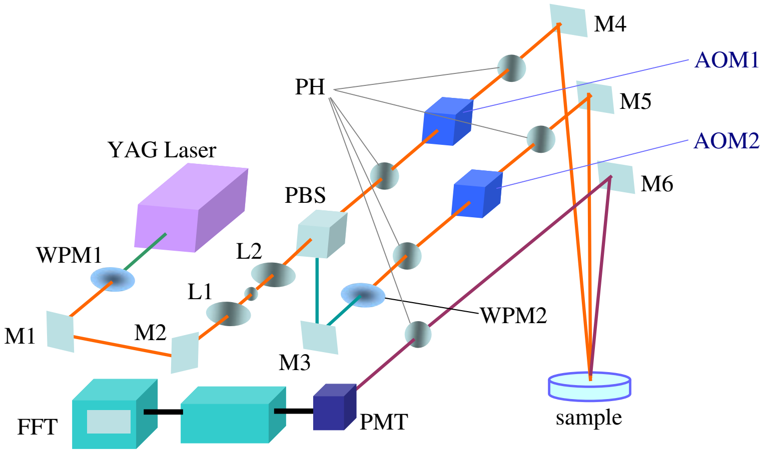

Fig. 2 Schematic diagram of experimental apparatus: waveplate (WPM), mirror (M), lens (L), polarizing beamsplitter (PBS), pin hole (PH), acoustic-optic modulator (AOM), photomultiplier (PMT), fast Fourier transform (FFT)

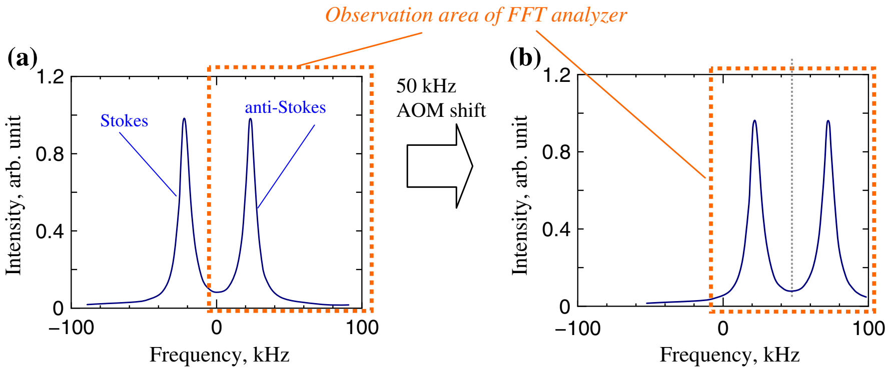

Fig. 3 Image of PS (**a**) with no AOM shift and (**b**) with 50 kHz AOM shift

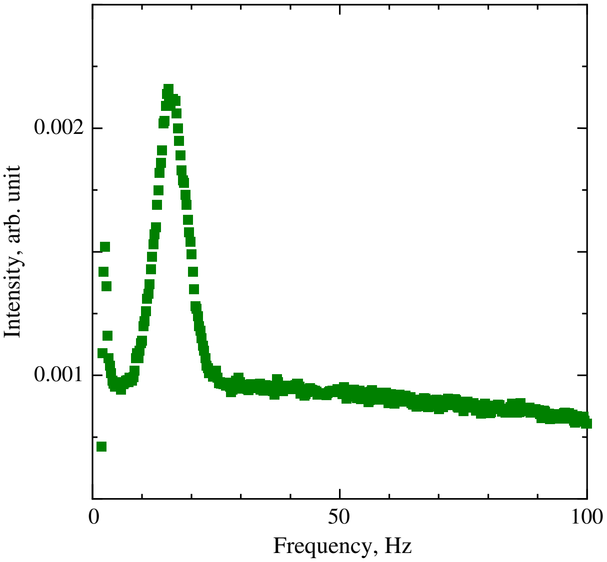

Fig. 4 Typical PS observed by ripplon SLLS for MEK

We introduced the double-shift method for our new system by using two AOMs; the first frequency shift (AOM shift) is only used for choosing the shift position to avoid external vibrational noise. The second frequency shift (Doppler shift) on the sample surface through the interaction with the moving ripplon determines the surface properties of the ripplon. The advantage of this double-shift method is that the shifts can be independently controlled, making it easy to control the observed frequency position while ensuring the accuracy of the surface property measurements.

Another feature of the double-shift method is that the Stokes (left peak) and anti-Stokes (right peak) components can be separately observed at the same time and they appear symmetric with respect to the AOM-shift frequency. Both of these components

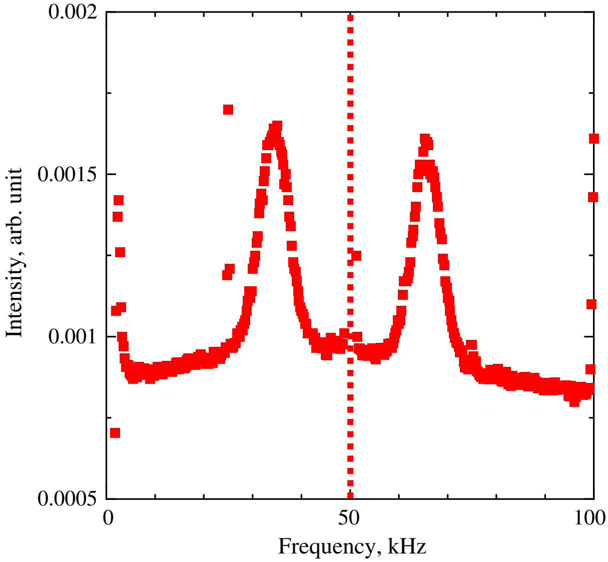

Fig. 5 PS shift of 50 kHz observed by ripplon SLLS for MEK

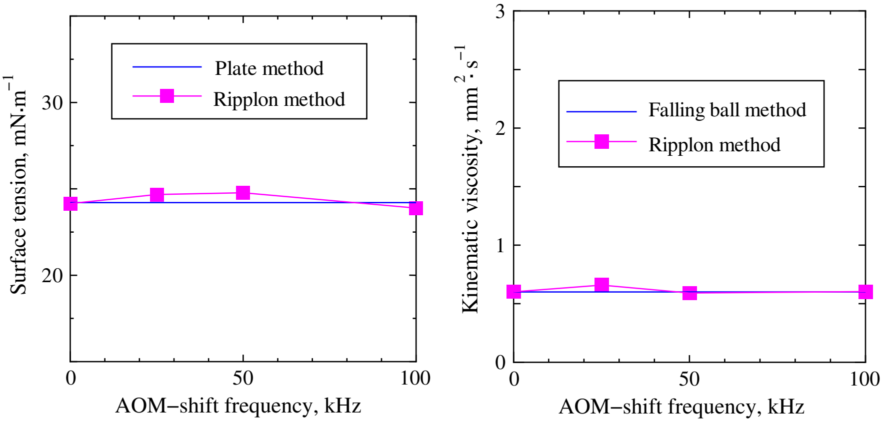

Fig. 6 Variation of measured surface properties for AOM-shift frequency for methyl ethyl ketone

may be used to analyze the surface properties, because both have the same shape and appear symmetrical.

3 Results and Discussions

The typical PS observed by ripplon SLLS for MEK is shown in Fig. 4. Figure 5 shows the shift spectrum obtained by our new system, using two AOMs. Since the PS is shifted upward by the AOMs (shift frequencies are 80 MHz and 80.05 MHz) the

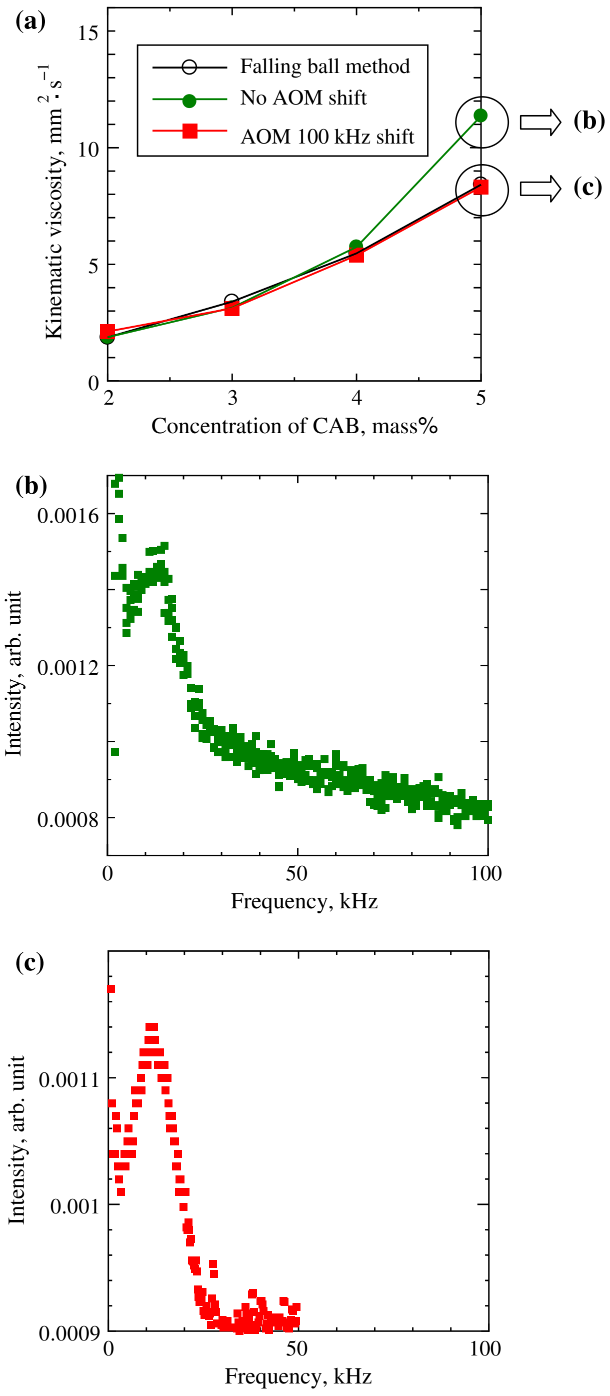

Fig. 7 (**a**) Kinematic viscosity as function of polymer CAB concentration. PS observed at CAB concentration of 5.0 mass%, (**b**) without AOM shift, and (**c**) with 100 kHz AOM shift

Stokes and anti-Stokes components symmetrically appear at about 30 kHz and 70 kHz with respect to 50 kHz.

The measured surface properties are shown in Fig. 6 as functions of the AOM-shift frequency. Both graphs show a comparison between the data obtained by the traditional contact method [4, 5] and by double-shift ripplon SLLS. Both the surface tensions and the kinematic viscosities obtained by ripplon SLLS show good agreement with the values measured by the contact method at all frequencies. This means that the accuracy of the measured surface tension and kinematic viscosity does not change at any AOM-shift frequencies, and the value of AOM-shift frequencies can be independently chosen between 25 kHz and 100 kHz.

Figure 7 shows the measured data for a polymer organic solvent. Figure7a shows the kinematic viscosity as a function of the concentration of the polymer cellulose acetate butyrate (CAB), and these are compared with data from the contact method and from the data obtained by using double-shift ripplon SLLS with and without the AOM shift. All kinematic viscosities measured by the three different methods show good agreement at a low polymer concentration and low kinematic viscosity. However, a difference in the measured kinematic viscosity is observed at higher polymer concentrations. The kinematic viscosity obtained without using the AOM shift is clearly higher than that obtained from the other two measurement methods. Figure 7b, c shows the PS observed at points (b) and (c), respectively, in Fig. 7a. A Lorentzian-shaped spectrum with a definite peak can only be obtained when using the AOM shift. The data obtained without the AOM shift are strongly affected by external vibrational noise. Thus, the double-shift method is effective in eliminating the influence of this noise, and it is further confirmed that this method extends the available measurement range of viscosities to higher values.

4 Conclusions

We developed a new optical measuring system for SLLS using an acousto-optic modulator. Experimental studies have shown that this system effectively extends the available measurement range of viscosities to higher values by reducing the influence of external vibrational noise. Therefore, the double-shift method considerably improves the sensitivity and accuracy of analysis of the low frequency beat signal of the ripplons detected in these experiments.

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