Polymer Dynamics of Thin Films and Monolayers

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Summary: Surface viscoelasticity of polymeric thin films and monolayers at the air/water interface can be deduced from the propagation characteristics of spontaneously generated capillary waves. The characteristics are probed by the technique of surface light scattering. It is shown that vinyl polymers with hydrophilic pendant groups and polyethers give rise to the predominantly elastic monolayers and thin films whereas those with relatively hydrophobic pendant groups the more viscous monolayers and thin films.

Keywords: capillary waves; Doppler shifts of surface scattered light; surface light scattering; viscoelastic monolayers.

Introduction

This is to present polymer dynamics studies of thin films and monolayers at the air/water interface that have been our interest for about past two decades. The focus is to understand how polymer dynamics is affected by confinement in the quasi-two-dimension. A large number of vinyl polymers though not water soluble, is surface active, by virtue of having pendant groups that are water soluble, such as small alkanols, fatty acids, their esters; this amounts to a vinyl repeating unit having a "wet foot" whereby the entire polymer is surface active, rendering the chains confined to the interface of water and air. A parallel situation exists for polyethers although poly(ethylene oxide) can be amphiphilic in solubility in water and hydrocarbon. Hence, the static monolayer studies of vinyl polymers are extant since the mid-'40s.[1-3] With the advent of modern experimental techniques for probing surface dynamics, the polymer monolayer dynamics has been actively explored since mid-'80s. The method we used is commonly called “surface light scattering”, which relies on the propagation characteristics of spontaneous capillary waves on liquid/gas interface and it has now been well reviewed.[4,5]

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Briefly stated, the capillary waves are a mixture of surface dilational and shear waves, and the range of spatial wave length is in the order of 100 μm and the wave amplitude is that of surface roughness of the air/water interface, 3-4 Å. The power spectrum of scattered light is Doppler shifted by an amount proportional to the wave propagation rate and the spectral width is related to the wave damping. Thus we obtain two experimental parameters, the spectral shift f_s and spectral width Δf_s. With the aid of a dispersion equation, we extract dynamic dilational elasticity ε_d and the corresponding viscosity κ under the assumptions that transverse viscosity is negligibly small and the surface tension required in the dispersion equation is the same as that we determine by the Wilhelmy plate method. Finally, we have recently succeeded in deducing the structure effect on the viscoelasticity with different homopolymers and copolymers, upon comparing their expected f_s and Δf_s on a reference interface with known sets of ε_d and κ at different surface pressure Π.[6]

Results and Discussion

In order to show the above stated classification of vinyl polymers and polyethers, we need to specify the surface pressure-area (Π-A) isotherms by means of their good solvent and theta solvent behaviors on the air/water interface (A/W).[7] Briefly it can be shown that the static elasticity ε_s extracted from the first order derivative of Π with respect to A, $\varepsilon_s = -A(\partial\Pi/\partial A)_T$, is expressed as a simple proportionality, $\varepsilon_s = y\Pi$, with a proportionality constant y, which is the power law exponent of Π on A, $\Pi = CA^y$, where C is also an proportionality constant. As shown in Figure 1, the specification of two classes of polymers is well borne out by their scaling exponent y for Π vs. A; numerical predictions of the scaling exponents for good (y = 2.86) [8] and theta (y = 101) [9] solvent conditions are represented by solid and dashed lines.

We now retun to polymer monolayer dynamics as deduced from the surface light scattering method. Comparison of viscoelastic parameters, dynamic dilational elasticity ε_d and the corresponding viscosity κ, obtained by the experiment for different polymer monolayers is provided by a polar plot.[10] This is displayed in Figure 2 where various hydrodynamic limits are

identified. By this plot, we can compare different polymers via a reference surface.

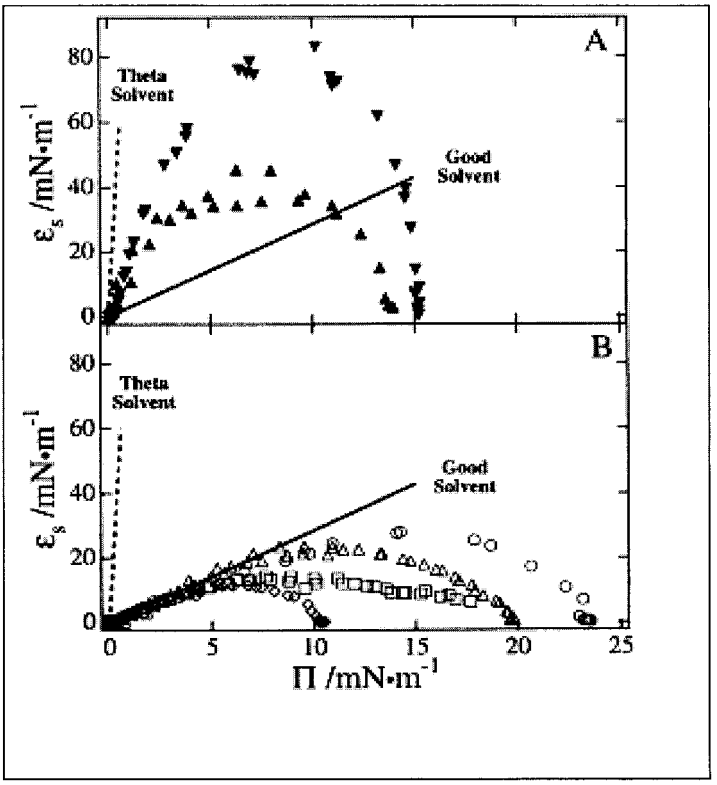

Figure 1. ε_S - Π for polymeric monolayers at A/W. The symbols correspond to data for poly(*t*-butylmethacrylate) (PtBMA) (▼), poly(methylmethacrylate) (PMMA) (▲), poly(vinylacetate) (PVAc) (○), poly(methylacrylate) (PMA) (△), poly(tetrahydrofuran) (PTHF) (□) and poly(ethyleneoxide) (PEO) (◇). Expected values of ε_s for the cases where A/W is a good or theta solvent are provided for comparison.

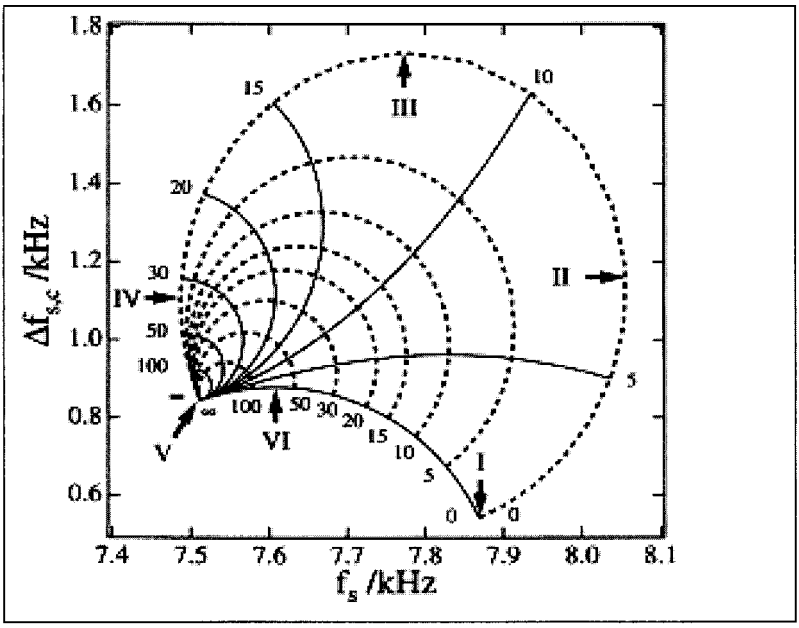

Figure 2. Calculated values of *f*s,c vs. *f*s for water at 25°C (reference state) and *k*ref=324.3 cm-1 according to Hard and Neuman[10] using the dispersion equation. The solid curves correspond to constant values of ε_d in mN·m^{-1} while the dashed loops show values of constant κ~10^{-5} in mN·s/m. Other important parameters used in the calculation were η_{ref}=0.894 cP, ρ_{ref} =0.997 g cm^{-3}, $\varepsilon_{d,ref}$=71.97 mN/m. The limits correspond to I = Pure Liquid Limit, II = Maximum Velocity Limit for a Purely Elastic Surface Film (PESF), III = Maximum Damping Coefficient for a PESF, IV = Minimum Velocity Limit for a PESF, V = Surface Film with an Infinite Lateral Modulus and VI = Maximum Damping Coefficient for a Perfectly Viscous Surface Film.

Thus, we can now compare the six polymers in terms of their dynamic behavior by means of the polar plot. As is apparent in two plots in Figure 3, two clearly delineated dynamic behaviors are well correlated with the static behaviors. PEO, PTHF, PMA and PVAc give rise to all highly elastic films whereas PMMA and PtBMA provide predominantly viscous films that is in accord with that shown in Figure 1.

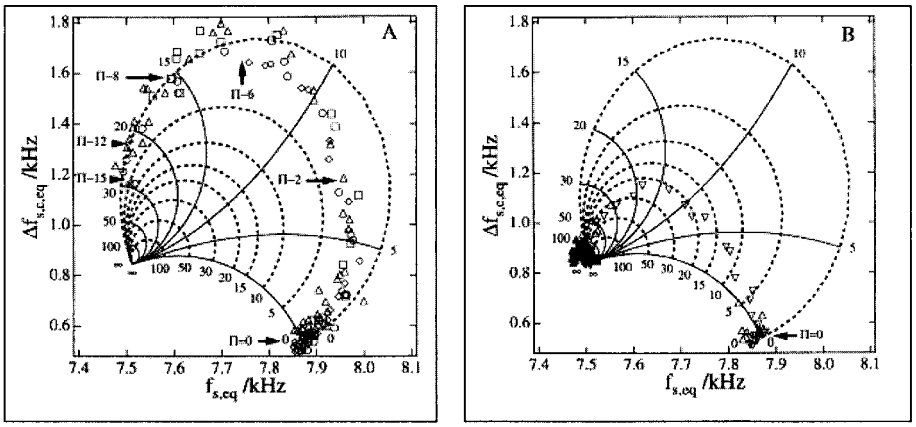

Figure 3. $\Delta f_{s,c,eq}$- $f_{s,eq}$ for poly(ethylene oxide) (PEO) (◇), poly(tetrahydrofuran) (PTHF) (□), poly(methylacrylate) (PMA) (△) and poly(vinylacetate) (PVAc) (○) up to $\varepsilon_{s,max}$ for each polymer in part (A). Part (B) of the figure shows the same data for poly(methylmethacrylate) (PMMA) (△) and poly(*t*-butylmethacrylate) (PtBMA) (▽) for Π<2 (open symbols) and Π>2 (filled symbols) in mN m^{-1}. The solid radial lines represent the dynamic elasticity, ε_d in mN m^{-1}, while the dashed polar curves correspond to the surface viscosity, $\kappa \times 10^5$ in mN·s·m^{-1}. The surface pressure is increasing counter-clockwise starting at Limit I. The overall trend in (A) shows excellent agreement with the limiting behavior of predominantly elastic surface films. In stark contrast, (B) shows both PtBMA and PMMA approach infinite lateral modulus dynamics (ε_d and $\kappa \rightarrow \infty$, Limit V) for Π>2 mN·m-1. Whereas PtBMA exhibits a smooth transition but with a larger viscosity relative to (A) as increases from ε_d=0 mN·m^{-1}, PMMA shows a discontinuous change which can be explained by the coalescence of PMMA patches existing as a heterogeneous film prior to the monolayer state..

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