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DYNAMIC BEHAVIOR OF ULTRAHIGH MOLECULAR WEIGHT POLY(METHYL METHACRYLATE) IN SEMIDILUTE SOLUTIONS

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ABSTRACT

The paper presents some rheological investigations on ultrahigh molecular weight (u.h.m.w.) ($M_w > 10^7$) poly(methyl methacrylate) in semidilute solutions. The main interest was to study the viscoelastic behavior of the semidilute solutions at different concentrations and temperatures. In the 60 – 600 rad/s frequency range, the experimental data show a predominantly elastic response ($G' > G''$) for the long poly(methyl methacrylate) chains in toluene.

Key Words: ultrahigh molecular weight poly(methyl methacrylate);
semidilute solutions; dynamic behavior.

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INTRODUCTION

Polymer rheology in fast flow is an area of active investigation, as demonstrated by many recent theoretical and experimental papers. A central topic is whether a constitutive instability could take place in shear flow, where the flow rate would become double valued at a single stress value. Presumably, a constitutive instability would occur at a constant shear rate involving the coexistence of entanglement and disentanglement states [1, 2]. Under controlled stress, a flow instability would correspondingly take place at a critical level whose magnitude would increase with increasing the molecular weight.

During processing of polymeric materials in the liquid state, flow can modify the structural features of the final products. Polymers are viscoelastic materials, they respond to an applied force or displacement by exhibiting both elastic and viscous behavior. The dynamic mechanical measurements provide a simultaneous measure of both elastic and viscous contributions. Also, the experimental data can be linked to the characteristics of the macromolecular chains (molecular weight, polydispersity, degree of branching, etc.) which control polymer processability and materials performance.

The dynamics of high molecular weight polymers solutions is dominated by topological interactions (or entanglements) [3-5]. However, the nonlinear effects shown by these systems in fast flows are not completely understood.

In the entangled regime, the motion of linear synthetic polymers is strongly slowed down by neighbouring chains, which form a tube within which the chain moves. Polymer dynamics in this regime can be described by the reptation model [6-8]. In this approach, it is assumed that the viscous and elastic behavior are governed by a system of coupled polymer chains exhibiting a homogeneous segment distribution; all chains move independently, the role of the network being played by neighbouring chains, to provide for each chain a tube with sufficiently long lifetime.

As for the rheological behavior of moderate-to-high molecular weight polymers the entangled and non-entangled states present strongly different features. Due to the very large dimensions, the polymer-polymer interactions occur at a lower concentration for ultrahigh molecular weight polymers [5]. Thus, the molecular architecture and dynamics of the long chains are more complicated as compared to those of usual chain lengths. On the other hand, the flow of infinitely dilute solutions is fundamentally different from that of concentrated solutions. In infinitely dilute solutions, which contain isolated macromolecules, the solvent can affect their conformations and effective sizes. In concentrated solutions, the macromolecules interact with each other, resulting in a network whose formation may be very strongly dependent on the nature of the solvent and polymer characteristics.

For semidilute solutions, the density of chains is large enough to accept that certain thermodynamic and hydrodynamic interactions become progressively screened with increasing concentration, the intermolecular entanglement effects depending on the molecular weight. The behavior of ultrahigh molecular weight (u.h.m.w.) polymers liable to mechanical deformations involves a series of new and unexpected aspects as compared to their homologous having lower molecular weights. Thus, in the semidilute regime, the response acquires some special characteristics which can be attributed to the beginning of chains entanglements that dominate the flow properties.

According to new theoretical predictions [1-4, 8-10] the plot of the shear stress as a function of the shear rate presents three regimes (linear, constant and linear). The nonlinear behavior occurs at very high shear rates for polymer melts and entangled polymer solutions. Our previous experimental data [11] obtained with a cone-and-plate Instron 3250 Rheometer for u.h.m.w. PMMA samples in semidilute solutions show for the shear stress and first normal stress difference vs. shear rate, at intermediate shear rates, the existence of plateau. Also, measurements carried out with a Physica Rheometer using a double gap measuring system geometry for u.h.m.w. PMMA in semidilute solutions revealed nonlinearities in the dependences of the shear stress and the viscosity *versus* shear rate, at high shear rates [5].

The purpose of the present paper is to investigate the dynamic mechanical properties of u.h.m.w. poly(methyl methacrylate) (PMMA) solutions. The main interest was to study the viscoelastic behavior of the semidilute solutions at different concentrations and temperatures.

EXPERIMENTAL PART

Low polydispersity, atactic, u.h.m.w. PMMA samples were prepared by plasma-induced polymerization [12]; the molecular weights range between $10.48 \cdot 10^6$ and $23.84 \cdot 10^6$. The molecular heterogeneity $1.2 \leq M_w/M_n \leq 1.3$ was obtained from light scattering measurements at 27°C, in CCl_4 (theta condition). Dilute solution studies were performed by light scattering and viscometry to observe polymer conformational characteristics in solvents with different thermodynamic quality [13, 14].

For this investigation, toluene was choosen as solvent. The rheological measurements were carried out at four temperatures, i.e., 0°C, 10°C, 20°C and 30°C, at three different concentrations - 0.08, 0.20 and 0.40 g/dl - which correspond to the semidilute regime [5].

Oscillatory measuremets were performed with a Physica Rheometer, using a double gap measuring system geometry with the length of measuring bob 111 mm, the inner and outer radii of measuring bob of 22.75 mm and 23.50 mm, respectively, and the inner and outer radii of measuring cup of 22.25 mm and 24.00 mm, respectively, in the frequency range 10 - 100 Hz (60 – 600 rad/s). The rheometer performs oscillatory tests by turning the cup back and forth in a sinusoidal manner. The shear stress in the sample is measured by measuring the deflection in the bob. The phase angle shift (δ) is automatically computed from the time displacement (Δt) between the sin waves of stress and strain, i.e. $\delta = \omega \cdot \Delta t$, where ω is the frequency in radians ($\omega = 2\pi\nu$) and ν is the frequency in Hz.

RESULTS AND DISCUSSION

In the strain experiment, the sample is submitted to sinusoidal deformations. Within a few cycles of start-up and often much less, the stress will also oscillate sinusoidally at the same frequency, but in general will be shifted by a phase angle δ with respect to the strain wave. The complex modulus G^*, storage modulus G' and loss modulus G'' are calculated from the stress and strain amplitudes (τ_0 and γ_0 respectively) and from the phase angle shift δ, according to:

$$G^* = \tau_0/\gamma_0 \tag{1}$$

$$G' = G^* \cos\delta \tag{2}$$

$$G'' = G^* \sin\delta \tag{3}$$

$$G^* = G' + iG'' \tag{4}$$

A useful parameter which is dimensionless and conveys no physical magnitude but is a measure of the ratio of energy lost to energy stored in a cyclic deformation is the loss tangent, tanδ (equation (5)):

$$\tan\delta = G''/G' \tag{5}$$

In oscillating measurements, the frequency is initially fixed and the rheological parameters are measured as a function of strain amplitude. This enables the linear viscoelastic region, where G*, G′ and G″ are independent of applied strain, to be obtained at any given frequency. The frequency dependence of G′ and G″ for u.h.m.w. PMMA solutions in toluene was determined at very low strain amplitude ($\gamma = 0.1\%$) where the solutions exhibit linear viscoelasticity.

Figures 1 and 2 give the variation of G′, G″ and tanδ as a function of frequency for two concentrations (0.20 and 0.40 g/dl) of PMMA in toluene at 0°C. In the range of studied frequency, the experimental data show a predominantly elastic response, G′ > G″. Also, in all studied cases, the values of the complex modulus G* have been found to be very closed to the values of the storage modulus G′.

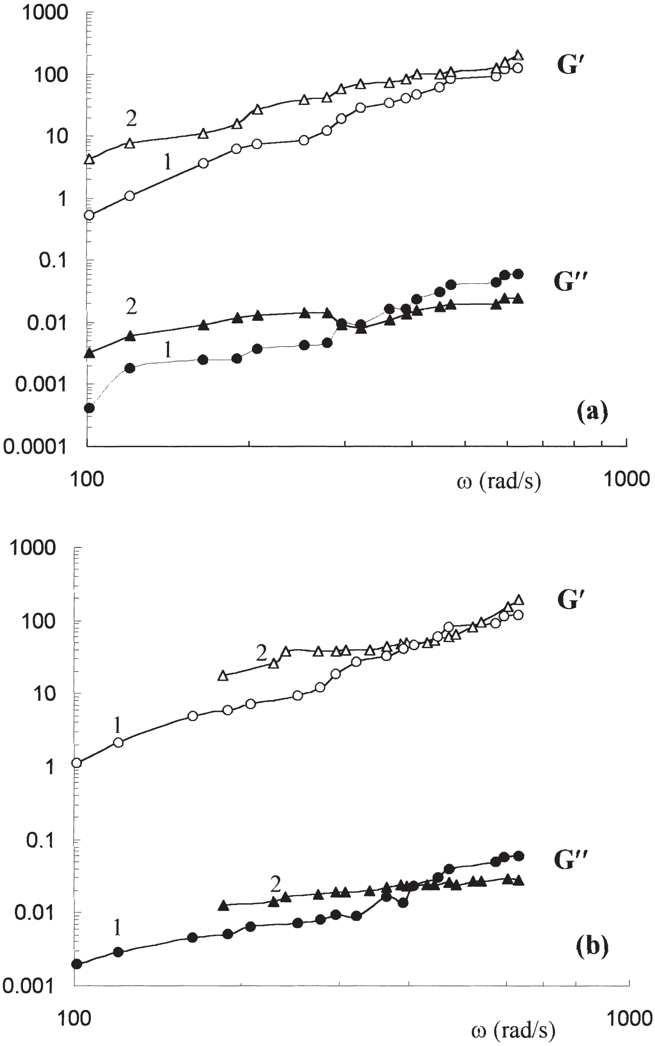

Figure 1. Dynamic shear moduli G′ and G″ (Pa) as a function of frequency ω (rad/s) at constant strain amplitude $\gamma = 0.1$ % for solutions of PMMA with $M_w = 10.480 \cdot 10^6$ (1) and $M_w = 18.178 \cdot 10^6$ (2) in toluene at 0°C for c = 0.2 g/dl (a) and c = 0.4 g/dl (b).

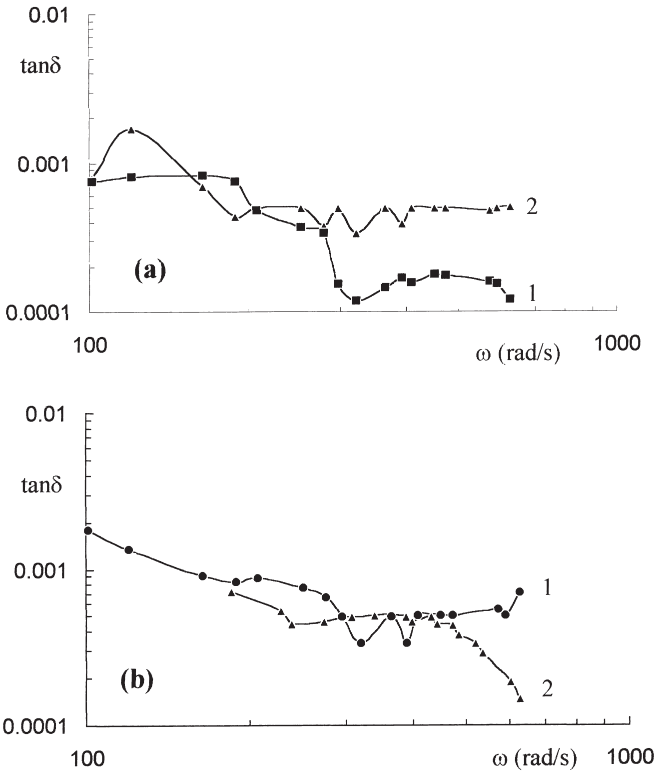

Figure 2. Plot of tanδ *vs.* ω for solutions of PMMA with $M_w = 10.480 \cdot 10^6$ (1) and $M_w = 18.178 \cdot 10^6$ (2) in toluene at 0°C for c = 0.2 g/dl (a) and c = 0.4 g/dl (b).

The predominance of elastic character for the long chains of PMMA in semidilute solutions of good solvents (in our case toluene) can be attributed to entanglements formation. The concentration value of 0.08 g/dl PMMA in toluene corresponds to the transition zone from dilute to semidilute regime, while the values of 0.20 and 0.40 g/dl mean that the solution is in the semidilute state.

In dilute solutions, the rheological units are the individual particles. As concentration increases, they must touch or even penetrate each other due to the lack of space, the chains cross each other (coupling points) and entanglements are formed. As for the nature of the coupling point, two types of entangled regions are possible for PMMA - toluene solutions: purely geometrical entanglements (characterized by a mean lifetime and slippage factor) and entanglements by intermolecular attractive forces (physical bonding network). By increasing the concentration, an infinite entanglement network (made up of shorter and longer segments of the coiled macromolecules) are produced. For high molecular weights and extended molecules (good solvent conditions), both the starting of chain entanglements and the network state are realized at much lower concentrations as compared to usual length polymers.

Entangled solutions give rise to a pronounced shear rate dependence of viscosity [5] and to elastic effects. This is due to the fact that, during flow, the hydrodynamic forces will interact with entanglement couplings. They will partly destroy them and thus change the characteristics of the network. Thus, the data obtained during flow and their dependence on flow conditions allow the elucidation of macromolecular dynamics in solution.

The nature and the extent of molecular mobility are controlled by the temperature. As temperature rises, the thermal energy acquired determines the movement of segments and large deformations, characteristic for the viscoelastic state, occur. Figure 3 evidences that the temperature influences the dynamic shear moduli of an u.h.m.w. PMMA semidilute solution up to $\omega = 200$ rad/s. At higher frequencies the curves are very close to each other.

Figure 4 shows the evolution of dynamic moduli as a function of frequency for different concentrations of PMMA in toluene at 30°C. At low frequencies, G' and G'' are higher for the higher studied concentration (0.4 g/dl). For $\omega > 200$ rad/s, G' and G'' seem to be independent on polymer concentration.

The dynamic behavior of long macromolecules in the semidilute regime of concentrations is different as compared to those in the dilute state, and thus the viscoelastic properties are different. For linear chains, the relevant dynamical difference of the entangled state is that the chain can only diffuse “longitudinally” and not “laterally”. Indeed, any attempt of the chain to move sideways is soon frustrated by the cumulative effect of the topological constraint due to the surrounding chains. The chain can diffuse, however, by moving essentially along its own contour, as no topological obstacles will then be found, motion characteristic to the entangled state.

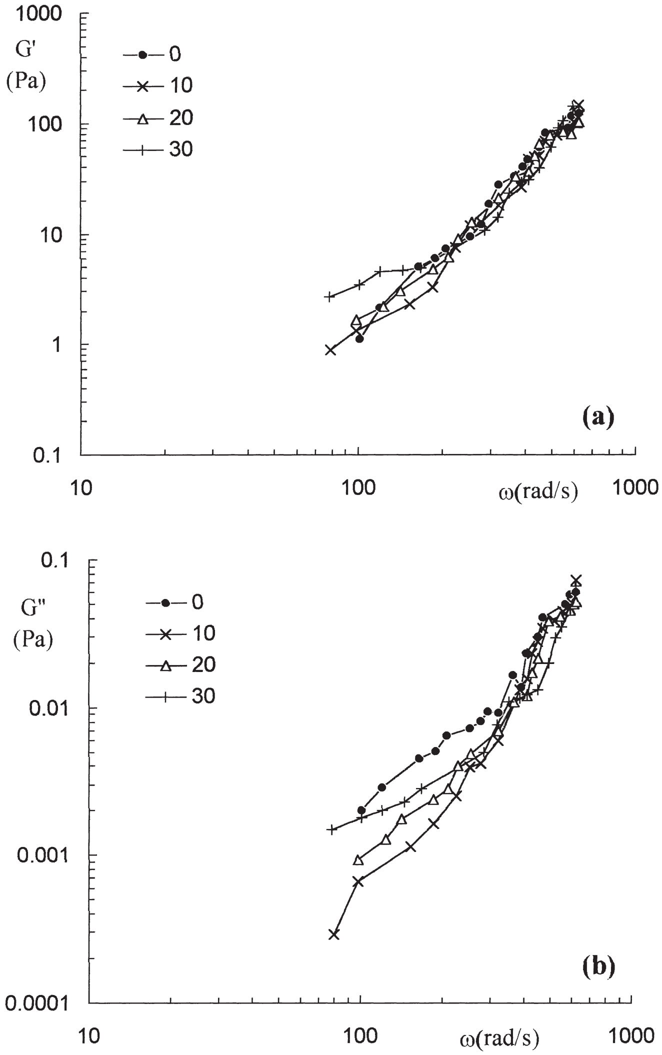

Figure 3. Dynamic shear moduli G′ (a) and G″ (b) as a function of frequency ω (γ = 0.1 %) for a solution of 0.4 g/dl PMMA in toluene at indicated temperatures (°C).

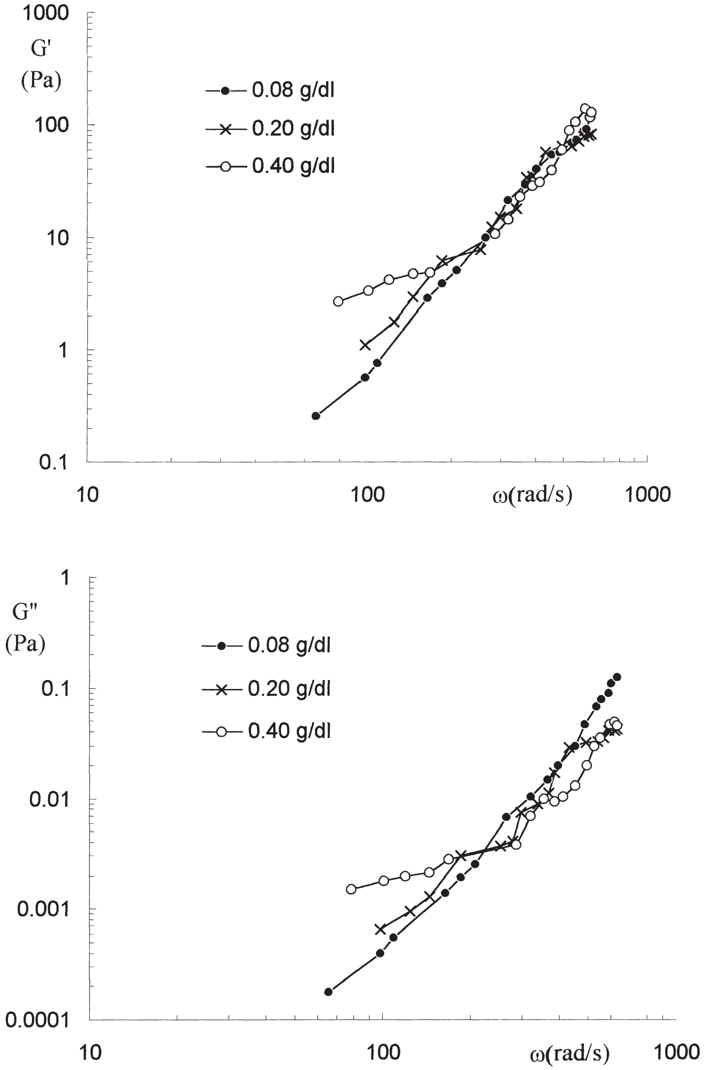

Figure 4. Dynamic shear moduli G′ (a) and G″ (b) as a function of frequency, ω, ($\gamma = 0.1$ %) for different concentrations of PMMA in toluene at 30°C.

CONCLUSION

U.h.m.w. polymers are an excellent material for testing the theories on polymeric systems in entangled state. This paper presents some new data obtained in semidilute solutions of u.h.m.w. PMMA, data necessary to achieve a quantitative interpretation of rheological phenomena occurring in solutions and melts of ordinary molecular weight PMMA (or polymers). The investigations shows that, in the frequency range of 60 – 600 rad/s, dynamic moduli G′ and G″ indicate a predominantly elastic response of long PMMA chains in toluene (good solvent) solutions and this behavior can be attributed to entanglements formation.

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