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Light Spectroscopy Investigation of Dilute and Semidilute Poly(dimethylsiloxane) Solutions

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ABSTRACT: The hydrodynamic radius and the hydrodynamic correlation length of dilute and semidilute poly(dimethylsiloxane) solutions have been measured by light spectroscopy as a function of temperature and for various solvents. The results show that the hydrodynamic behavior of these systems cannot be described by the reduced temperature parameter alone and demonstrate specific polymer–solvent interactions.

Introduction

Recently, a number of papers have been devoted to the study of dilute and semidilute solutions of flexible polymers by light scattering.[1-8] In these studies, new experimental results as well as collected data were used to test the recent theories based on scaling concepts.[9] More especially, the radius of gyration R_G and the hydrodynamic radius R_H of macromolecules in dilute solutions were investigated as a function of molecular weight M_w and of temperature T. The scaling arguments developed by de Gennes[9] predict that both R_G and R_H are proportional to N^ν in a good solvent and for large values of N, which is the equivalent number of links in the statistical chain, and the most accurate value of ν is 0.588 ± 0.001.[10] From the experimental studies on the molecular weight dependence of R_G for different systems, the results give values of ν which are rather close to the theoretical one.

On the other hand, measurements of the translational diffusion coefficient of macromolecules using either an interferometric method[11] or, more recently, the light spectroscopy technique[12,13] led to a N^{ν_H} variation of R_H, with $\nu_H < \nu$ $(0.54 < \nu_H < 0.58)$.

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This discrepancy was interpreted by des Cloizeaux and Weill[14] as a consequence of the fact that R_H does not reach its asymptotic power law behavior within the investigated molecular weight range. However, very recent results show that for very high chain length, polystyrene in toluene essentially has reached the limiting exponent in the decade between 4×10^6 and 40×10^6.[15]

Quantitative comparisons of the theoretical and experimental behaviors of R_G and R_H in the nonasymptotic ranges were recently performed by Akcasu and Han[4] and by Nose and Chu[7] for polystyrene in various solvents at different temperatures. Single-chain properties, such as expansion factors of R_G and of R_H, were expressed in terms of a unique parameter $N/N_\tau \sim N\tau^2$, where the number of statistical segments N_τ of a thermal "blob" characterizes the crossover between Gaussian and excluded-volume regimes and τ is the reduced temperature: $\tau = 1 - \Theta/T$. The main conclusion of these analyses is that the R_H data fall in the nonasymptotic domain of the theoretical curve. As a consequence the apparent exponent obtained for $R_H = f(N/N_\tau)$ in a log-log plot is significantly lower than the theoretical value of 0.2. It must also be stressed that the experimental values of R_H obtained for different solvents are rather scattered when they are plotted vs. N/N_τ, contrary to what is observed for R_G.

The aim of this paper is to examine the influence of the nature of the solvent on the hydrodynamic radius of a macromolecule of given N in a large domain of τ. Measurements of the zero-concentration translational diffusion coefficient D_0 were carried out on solutions of a poly(dimethylsiloxane) (PDMS) of molecular weight $M_w = 148\,000$ in bromocyclohexane, chlorobenzene, and toluene over a temperature range 20–90 °C. According to the experimental data, the variation $R_H(\tau)$ cannot be described in terms of the single parameter τ and depends obviously on specific interactions between solute and solvent.

We also investigated the dynamic properties of semidilute solutions of high molecular weight PDMS ($M_w = 5\,000\,000$) in chlorobenzene and toluene. As in the case of dilute solutions, the data cannot be expressed in terms of only the τ parameter.

Experimental Section

A. Materials. The PDMS sample of $M_w = 148\,000$ was prepared by anionic polymerization of hexamethylcyclotrisiloxane (D_3) under high vacuum. With addition of the (221) macroheterobicyclic ligand (2.0×10^{-3} mol·L^{-1}) to a benzene solution of D_3 (0.96 mol·L^{-1}) after reaction with n-butyllithium (1.5×10^{-3} mol·L^{-1}) at 20 °C, narrow molecular weight distribution PDMS ($M_w/M_n = 1.16$, measured by GPC in toluene) was obtained after 16.5 h at 20 °C in 48% yield. Under these conditions, the amount of cyclic byproducts is negligible.[16-18] The high molecular weight PDMS sample was prepared by bulk polymerization of highly purified D_3 on a sodium mirror at 80 °C. Light scattering measurements made on benzene solutions of this polymer give the following values: $M_w = 5\,000\,000$, $R_G = 140$ nm, and $A_2 = 6 \times 10^{-5}$ mol·cm^3·g^{-2}. Reagent grade solvents (Merck) were used without further purification. The "Θ" temperatures are equal to 301,[19] 255,[20] and 240 K[21] for PDMS solutions in bromocyclohexane, chlorobenzene, and toluene respectively.

B. Correlation Time Measurements. The optical source of the light scattering apparatus was a Spectra-Physics argon ion laser operating at 488 nm. The scattered light was collected at a predetermined angle by a lens–apparatus system and was focused on a photomultiplier (ITT, FW 130) cathode. The time-dependent correlation function of the scattered intensity was derived by using a 96-channel digital correlator (Precision Devices and Systems LTD Malvern System 4300).

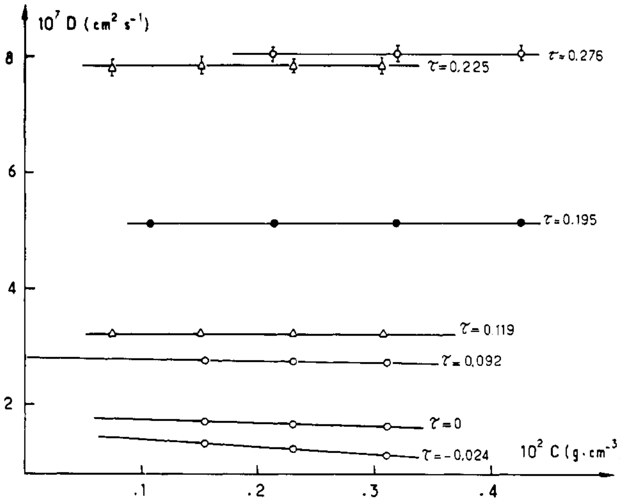

Figure 1. Concentration dependences of the diffusion coefficient D for the dilute PDMS solutions at various temperatures ($M_w = 148\,000$): (○) bromocyclohexane; (△) chlorobenzene; (●) toluene.

The polymer solutions were freed from dust by centrifugation of the scattering cells for 30 min at 10 000 rpm. Intensity correlation data were routinely processed by using the method of cumulants[22,23] in order to provide the average decay rate $\bar{\Gamma}$ and the variance v. The latter is a measure of the width of the distribution of the decay rates and is given by

$$v = (\overline{\Gamma^2} - \bar{\Gamma}^2)/\bar{\Gamma}^2$$

where $\overline{\Gamma^2}$ is the second moment of the distribution.

The diffusion coefficient D was determined from the average decay rate $\bar{\Gamma}$ according to

$$\bar{\Gamma} = 2k^2D$$

The magnitude of the scattering vector k is given by

$$k = [4\pi n \sin(\theta/2)]/\lambda$$

where θ is the scattering angle, λ is the wavelength of the incident light in a vacuum, and n is the index of refraction of the scattering medium.

Results and Discussion

A. Dilute Solutions. The autocorrelation function of light scattered from the dilute solutions of PDMS in the three solvents used in the present investigation can be well described by a single exponential with a decay rate varying like k^2. The variance is equal to 0.01–0.025 for solutions in toluene and chlorobenzene and slightly larger (0.02–0.035) for bromocyclohexane solutions. The index of polydispersity M_z/M_w (M_z, z-average molecular weight; M_w, weight-average molecular weight) as deduced from the experimental values of the variance[23] is found to be of the order of 1.09 ± 0.05, that is, a value slightly lower than that of the index M_w/M_n determined from GPC (1.16). The concentration dependence of the diffusion coefficient D for the dilute solutions of PDMS is reported in Figure 1 at various temperatures. Within the range of low concentrations, $D(C)$ can be expressed by

$$D(C) = D_0(1 + \gamma C)$$

where γ is a virial coefficient which accounts for both excluded volume and hydrodynamic interactions. The plots of Figure 1 show that γ is negative for small values of τ and is equal to zero for $\tau \gtrsim 0.1$. It has been recently established from theory as well as from experiments that the value τ_0 at which γ vanishes is much larger than the crossover temperature τ^*, which delimits Gaussian and excluded-volume regimes.[8] For the polystyrene–cyclohexane system, the following molecular weight dependence of τ^* was obtained from the temperature–concentration diagram determined by neutron scattering experiments:[24,25]

$$\theta\tau^* = 3 \times 10^3 M^{-1/2}$$

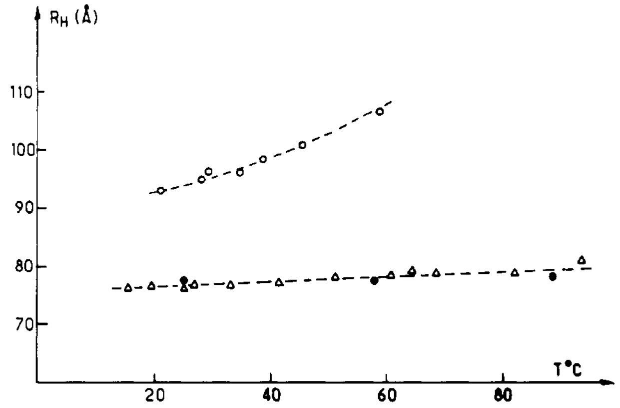

Figure 2. Hydrodynamic radius of PDMS vs. temperature: (○) bromocyclohexane; (△) chlorobenzene; (●) toluene.

Assuming that the same law can be applied for the PDMS solutions, one finds τ^* to be equal to 0.025 for M_w = 148000. This value is much smaller than τ_0 and is in good agreement with previous results.[8]

Furthermore the variation of γ with τ for PDMS solutions in bromocyclohexane is very similar to that observed for polystyrene solutions. For instance, the value of $(\gamma_{\tau=0.09} - \gamma_{\tau=0})/\gamma_{\tau=0}$ observed for the PDMS–solvent systems investigated here is 0.81 whereas it was found to be equal to 0.78 for the polystyrene–cyclohexane system.[8]

On the other hand, the results for chlorobenzene and toluene solutions show that γ does not increase with τ and remains equal to zero over a large range of τ. The hydrodynamic radius R_H can be obtained from the value of $D(C)$ extrapolated at zero concentration, according to the Stokes–Einstein relation:[26]

$$D_0 = k_B T/6\pi\eta_0 R_H$$

where k_B is Boltzmann's constant, T is the absolute temperature and η_0 is the viscosity of the solvent.

The temperature dependences of R_H for PDMS solutions are reported in Figure 2. The striking feature of this figure is that the hydrodynamic radius of PDMS in bromocyclohexane is larger than in chlorobenzene or toluene, which are better solvents. In other words, the hydrodynamic radius is not a function of only τ, as is the case for the static radius of gyration R_G.[4] This implies that the friction between monomeric units and the solvent involves some specific solute–solvent interactions. It must be underscored that such behavior has already been observed in the case of polystyrene solutions.[27,30] For instance, the hydrodynamic radius of polystyrene samples of molecular weight $M_w < 670000$ is smaller in butanone solutions than in Θ conditions.[31] This effect is even more pronounced if the Θ solvent is a mixture of two solvents.[29,30,32]

The large scattering of the data in the previously reported variation of R_H with N/N_τ for polystyrene systems also gives evidence of a solvent dependence of the friction coefficient.[4,7] Intrinsic viscosity measurements have also demonstrated the presence of specific solvent–polymer interactions.[33-35] Generally this effect is observed for polar polymers.

Variations of R_H vs. τ on a log–log scale for the PDMS solutions are reported in Figure 3. Slopes of the least-squares straight lines are 0.06, 0.05, and 0.025 for bromocyclohexane, chlorobenzene, and toluene solutions, respectively. These values are considerably smaller than the theoretical value of 0.2, thus confirming previous results on polystyrene systems. This can be expected since the limiting regime is not reached in the investigated range of reduced temperature.

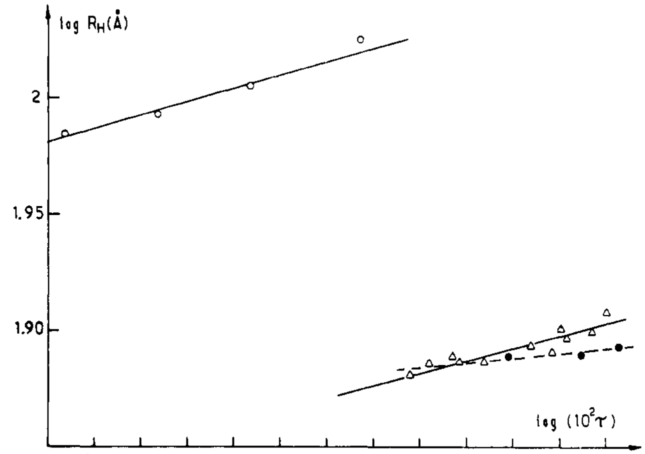

Figure 3. Variations of log R_H vs. log τ for dilute PDMS solutions: (○) bromocyclohexane; (△) chlorobenzene; (●) toluene.

B. Semidilute Solutions. The development of the scaling theories has also initiated many studies on semidilute solutions of macromolecules.[1-3,5-8,36-39] The semidilute regime appears at polymer concentrations higher than the overlap concentration $C^* \sim N/R_G^3$ (R_G = radius of gyration), where chains begin to interpenetrate each other. The semidilute solution can be visualized as a temporary network where the mesh size is given by the screening length ξ, which is independent of molecular weight and decreases with concentration.[8]

The concentration fluctuations of the pseudolattice are described by a diffusion equation, and their autocorrelation function is predicted to decay exponentially with a time constant $(D_c k^2)^{-1}$, where D_c is a cooperative diffusion constant given by[9]

$$D_c = k_B T/6\pi\eta_0\xi_H$$

ξ_H is the hydrodynamic correlation length.

The temperature and concentration dependences of ξ_H in the temperature domain $\tau > \tau^*$ are predicted to be

$$\xi_H \sim C^{-0.75}\tau^{-0.25}$$

The above relationship is only valid in the asymptotic limit, which is not reached in the concentration range presently investigated.

As a matter of fact, light spectroscopy experiments have demonstrated that the temperature and concentration dependences of ξ_H are described by

$$\xi_H \sim C^{-a_H}\tau^{-b_H}$$

where a_H and b_H are apparent exponents smaller than 0.75 and larger than 0.25, respectively.

The determination of ξ_H from light scattering experiments raises some important difficulties inherent in the fact that the autocorrelation function exhibits large deviations from the single-exponential behavior in the case of most of the investigated systems. The exact shape of the autocorrelation function is not yet established. In several studies two relaxation processes characterized by two distinct relaxation times were reported.[3,6,39] The fast mode was attributed to the gellike fluctuations whereas the origin of the slow mode was unidentified. A detailed analysis of the data obtained for several systems was performed by Mathiez et al.,[39] who claimed that the relative amplitude and the relaxation time of the slow mode increase with concentration. Furthermore the amplitude of this mode was shown to decrease with the time elapsed since the sample preparation, which suggests a locally

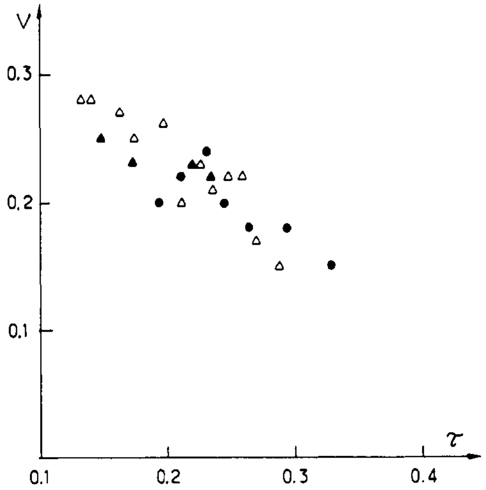

Figure 4. Temperature dependence of the variance for semidilute PDMS solutions (M_w = 5 000 000): (△) chlorobenzene, $C = 1.5 \times 10^{-2}$ g·mL^{-1}; (▲) chlorobenzene, $C = 3 \times 10^{-2}$ g·mL^{-1}; (●) toluene, $C = 1.5 \times 10^{-2}$ g·mL^{-1}.

incomplete dissolution of the polymer. In other studies the autocorrelation function was analyzed by using the cumulants method, which assumes a continuous distribution of the relaxation times.[36-38]

Our samples were kept in solution for 6 months before measurements were performed. The concentrations were sufficiently low so that the amplitude of the slow mode could be neglected according to the results of Mathiez et al.[39] At these concentrations, the centrifugation method was efficient enough to eliminate all the dust from the sample solutions. This was checked by comparing the autocorrelation functions obtained in the homodyne and heterodyne configurations, respectively.

The overlap concentration C^* of the PDMS solution in toluene was estimated from previous light spectroscopy experiments to be about 2×10^{-3} g/mL:[3] that is considerably lower than the concentrations used in this study (1.5 $\times 10^{-2}$ and 3×10^{-2} g/mL).

The autocorrelation function of light scattered from PDMS solutions was found to be nonexponential. It did not show any evidence of the presence of two discrete relaxation processes but it fits a second-order cumulant expansion. The variance decreases slightly when τ increases as shown in Figure 4.

The τ dependence of the average correlation length ξ_H is reported on a log–log scale in Figure 5. Contrary to theoretical predictions, ξ_H depends not only on τ but also on the chemical nature of the solvent. Furthermore the apparent exponent of $\xi_H = f(\tau)$ differs from one solvent to another one ($b_H \sim 0.4$ for chlorobenzene solutions and $b_H \sim 0.17$ for toluene solutions). Of course, it must be kept in mind that ξ_H represents an average value and thus it seems difficult to draw some conclusions about the scaling behavior of ξ_H as long as the time dependence of the autocorrelation function is not fully understood.

Conclusion

The results reported in this paper show that the hydrodynamic behavior of both dilute and semidilute solutions of PDMS of a given molecular weight cannot be described by the reduced temperature parameter alone. Contrary to the geometrical radius of gyration R_G, the hydrodynamic radius of a single chain in the Θ domain cannot be considered as a constant characteristic of the polymer molecule. The average hydrodynamic correlation length in entangled solutions is also sensitive to specific polymer–solvent interactions.

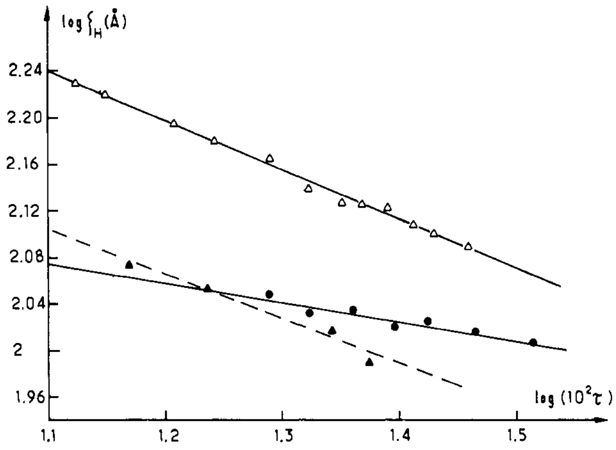

Figure 5. Temperature dependence of the hydrodynamic correlation length for semidilute PDMS solutions (M_w = 5 000 000) (symbols are the same as in Figure 4).

Moreover, the autocorrelation function of semidilute solutions in moderately good solvents cannot be described by a single-exponential decay. The variance characterizing the width of the distribution of relaxation times increases when the reduced temperature τ decreases.

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(32) For instance, the ratio between the hydrodynamic radii of a polystyrene of molecular weight M_w = 670 000 dissolved in cyclohexane at 35 °C and in a "Θ" mixture of benzene-methanol, respectively, is found equal to 0.8. This ratio decreases with the molecular weight (Munch, J. P.; Candau, S., unpublished results).

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Intramolecular Motion in Flexible Cycloalkyl Rings, Ranging from Cycloheptyl to Cyclododecyl, Contained in the Side Chains of Poly(dicycloalkyl itaconates)

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ABSTRACT: The dynamic mechanical behavior of a series of poly(itaconic acid diesters) containing pendant cycloalkyl rings has been investigated. Ring sizes vary from the cycloheptyl to the cyclododecyl. In these polymers, substantial damping, measured at 1 Hz, in the glassy state is observed in the temperature range 100-200 K, and the apparent activation energy for a number of these damping processes has been either measured experimentally or estimated. It has been found possible to attribute some or all of the observed damping in a particular polymer glass to intramolecular motion in the flexible cycloalkyl groups. By comparing the energy requirements of these molecular relaxations, measured from either NMR studies or strain energy calculations, with our experimental data, we have been able to propose which of the various molecular mechanisms are likely to occur in the glassy state for the several derivatives. While such relaxations can account for most of the damping peaks in the spectra, there are a few damping processes which remain unexplained by intramolecular motions in the ring, particularly in the dicyclononyl and dicyclododecyl derivatives.

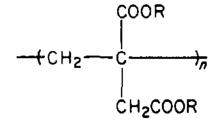
Introduction

It is now well established that the relaxation of small groups can occur in glassy polymers at temperatures well below the glass transition temperature. These are often detected by locating a loss process in a dynamic mechanical spectrum, and various suggestions have been made as to the molecular origin of these relaxations. To date the exact molecular mechanisms involved in these relaxations have been established in only a few systems with some degree of accuracy, and of these perhaps one of the best documented is the chair → chair′ transition of the cyclohexyl ring, identified by Heijboer[1] in poly(cyclohexyl methacrylate).

The molecular interpretation proposed by Heijboer has been confirmed by our own work[2] on a series of poly(dicyclohexyl itaconates) and by Seefried and Koleske,[3] who studied poly(vinylcyclohexane) and related structures. In all these investigations it was observed that polymer chains containing pendant cyclohexyl rings exhibited damping peaks in their dynamic thermomechanical spectra which were absent in the spectra of comparable structures containing rigid, pendant, phenyl rings. Furthermore, measurment of the apparent activation energy, ΔH^*, for this damping process yielded values in the range 48-65 kJ mol^{-1}, depending on chain structure, which compare well with the value of $\Delta H^* = 47$ kJ mol^{-1} reported by Anet and Bourn[4] for the ring inversion of the cyclohexane molecule.

There is further evidence to suggest that the type of intramolecular ring motion observed in pendant cyclohexyl rings is not confined to this group and that other cycloalkyl rings can also behave as flexible units.[5] The conformational changes which are possible in large isolated cycloalkyl rings have been studied by a number of workers[6] and it is of interest to investigate the behavior of polymers containing similar ring systems. It should also be particularly instructive to compare the energy requirements for an observed relaxation process in the polymer glass with that calculated for the possible and various ring inversions in the corresponding small molecules.

This consideration has been studied in some detail by using a series of diesters of poly(itaconic acid) substituted with cycloalkyl units ranging in size from 7 to 12 carbon atoms. The basic structural unit is



$$\left[CH_2-\overset{\overset{\displaystyle COOR}{|}}{\underset{\underset{\displaystyle CH_2COOR}{|}}{C}}\right]_n$$

where R is the cycloalkyl ring.

Experimental Section

Monomer Preparation. Dicycloalkyl esters of itaconic acid were prepared either by reacting the acid (1 mol) with the appropriate alcohol (3 mol) in the presence of an acid catalyst such as sulfuric acid/*p*-toluenesulfonic acid or by making use of the diacid chloride of itaconic acid in a toluene solution under a nitrogen atmosphere.[3] The dicycloheptyl diester was isolated by vacuum distillation of the reaction mixture after neutralization with aqueous sodium carbonate. In all other cases a silica gel column had to be used and the diester was separated with a chloroform eluent. The purified monomers were characterized by NMR and IR spectroscopy.

Polymerization. All monomers were polymerized in bulk, using a radical initiator [α,α'-azobis(isobutyronitrile)]. Reactions were carried out under vacuum at temperatures between 333 and 343 K for periods of 24-48 h. The product was dissolved in chloroform and isolated by precipitation with methanol. Purification was achieved by repeated dissolution and precipitation, followed by drying in vacuo. Each polymer was characterized by IR spectroscopy, and number-average molecular weights were obtained by osmometry.

Dynamic Mechanical Measurements. Two techniques were used to obtain the dynamic thermomechanical spectra of the samples: torsional braid analysis (TBA) and a Rheovibron viscoelastomer (RV). Both techniques have been described in detail elsewhere.[7] The TBA has a nominal frequency of 1 Hz while the

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