in glasses. However, none of these theories has demonstrated the ability of predicting a variety of thermal histories over a broad time and temperature range without changing the input structural parameters. The search for quantitative prediction has been the focus of recent intensive investigations.[21] We have achieved for the first time a favorable comparison between the present molecular kinetic theory near the glass transition and experimental data on the isothermal annealing, $\tau_{\text{eff}}$, and memory effects for PVAc. All the kinetic phenomena were calculated from the same set of five input parameters, eq 21.

The study reveals that the physical aging of PVAc is dominated by the nonequilibrium structure-dependent part of relaxation times and, in contrast to recent reports in the literature,[21] that the distribution of relaxation time is actually independent of temperature. This is consistent with eq 12 and Figure 2 which relate the distribution of relaxation times to the fixed distribution of hole energies of a given system. Therefore, it supports the idea of representing the relaxation spectrum by a single parameter $\beta$. Through detailed comparison between theory and experiment, the new equation for the apparent relaxation time, eq 20, and our basic physical picture of relating the glass relaxation to the mean energy of hole formation, its statistical distribution, and the reference conditions have received experimental verification.

There is a subtle difference between the KAHR equations and our molecular kinetic equations, eq 6, which explicitly incorporate temperature-dependent thermal expansion coefficients ($\bar{\alpha}_i$). The present study reveals that the structural parameters ($\theta$, $X$) of Tool's equation should not be constants but a function of $\beta$ or temperature. These may explain why the phenomenological models had difficulty[10,22] of predicting several experiments by one set of structural parameters.

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# Osmotic Compressibility Measurements on Semidilute Polystyrene–Cyclohexane Solutions

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ABSTRACT: The thermodynamic properties of semidilute solutions of polystyrene of molecular weight ranging from $4.22 \times 10^5$ to $20.6 \times 10^6$ in cyclohexane are studied as a function of concentration ($2 \times 10^{-2} \lesssim C$ (g/cm$^3$) $\lesssim 0.1$) and temperature ($\Theta \leq T < 65$ °C) by intensity light scattering. The corresponding scaling laws for the inverse of the osmotic compressibility $\partial\pi/\partial C$ are verified.

## 1. Introduction

Using general concepts of scaling theory,[1,2] theoreticians and experimentalists have studied the thermodynamic properties and conformation of polymer chains in solution (see, e.g., ref 3–5). The results have led to the construction of the universal temperature–concentration diagram.[5] In this paper, we will be interested in a part of this diagram, namely, the semidilute $\Theta$ solutions and the transition from $\Theta$ to good solvent system. With respect to concentration, polymer solutions are classified as dilute or semidilute, the crossover between both regimes being located at the overlap concentration:[1,2]

$$C_{\text{T}}^* \simeq MR_{\text{G}}^{-3}(T) \sim M^{1-3\nu} \qquad (1)$$

$R_{\text{G}}$, the radius of gyration of a single coil, is linked to the molecular weight of the polymer $M$ by the relation $R_{\text{G}} \sim M^{\nu}$. At the $\Theta$ temperature ($\nu = {}^1/_2$) we have

$$C_{\Theta}^* \sim M^{-1/2} \qquad (2)$$

In the semidilute regime, the diagram is divided into good solvent and $\Theta$ regions, with the boundary[5] located at $\tau^{**} \sim C$, where $\tau$ is the reduced temperature ($\tau = (T - \Theta)/\Theta$, $\tau > 0$).

The thermodynamic state of the system is characterized by the osmotic pressure $\pi$. Two predictions of the scaling theory for good solvent semidilute solutions have already been confirmed:[6,7] (a) $\pi$ is independent of molecular weight and (b) $\pi$ scales as $\pi \sim C^{2.32}$.

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Data on semidilute solutions in the $\Theta$ region are scarce and do not cover a large enough concentration range in units of $C_\Theta^*$. Due to the fact that $C_\Theta^*$ is much larger than $C^*$ in good solvent, we have to use very high molecular weight polymers in order to have $C > C_\Theta^*$ but low values of $C$.

The purpose of this work is to study the thermodynamic properties of semidilute polymer solutions at the $\Theta$ temperature and for $T > \Theta$ by intensity light scattering measurements.

## 2. Theoretical Background

**2.1. Scaling Concepts.** We are interested in the osmotic pressure $\pi$ and the correlation length $\xi$ of semidilute polymer solutions. The reduced osmotic pressure $\pi M/CRT$, where $R$ is the gas constant, is a function of the reduced concentration $C/C^*$ only;[1] in semidilute solution ($C/C^* > 1$), we have[8,9]

$$\pi M/CRT \simeq (C/C^*)^y \qquad (3)$$

($y = 2$ in a $\Theta$ solvent and $y = 1.31$ in a good solvent ($\nu = 0.588$[10])). The exponent $y$ is determined from the requirement that $\pi$ is independent of the molecular weight.

The above conclusion can be extended to the inverse of the osmotic compressibility $\partial\pi/\partial C$ deduced from light scattering experiments:

$$\frac{M}{RT}\frac{\partial \pi}{\partial C} \simeq \left(\frac{C}{C^*}\right)^y \qquad (4)$$

The dependence of $\pi$ and of $\partial\pi/\partial C$ with respect to the reduced temperature variable $\tau/\tau^{**}$ is

$$\frac{\partial\pi/\partial C}{(\partial\pi/\partial C)_\Theta} \simeq \left(\frac{\tau}{\tau^{**}}\right)^x, \qquad x = 0.691 \qquad (5)$$

if $\tau/\tau^{**} \gg 1$, but $\tau \ll 1$ (where the exponent $x$ is determined by using values of $y$ and the definition of $\tau^{**} \sim C$),[11] or

$$\frac{\partial\pi/\partial C}{(\partial\pi/\partial C)_\Theta} \simeq 1 + a\frac{\tau}{\tau^{**}} \qquad (6)$$

if $\tau/\tau^{**} < 1$.

The correlation length $\xi$ in semidilute solutions is the screening length of the concentration–concentration correlation function. The concentration dependence of $\xi$ at $\Theta$ is well-known:

$$\xi \sim C^{-1} \qquad (7)$$

It has been verified by neutron scattering.[12]

**2.2. Light Scattering.** The intensity $I$ of light scattered at an angle $\phi$ from a polymer solution, at a concentration $C$ in g/cm$^3$, is expressed through the Rayleigh ratio $R_{90}$ ($\sim I/I_0$) as[13]

$$\frac{KC}{R_{90}} = \frac{1}{RT}\frac{\partial\pi}{\partial C}S^{-1}(q) \qquad (8)$$

where $I_0$ is the intensity of the incident light, $K = 4\pi^2n^2(\partial n/\partial C)^2/(N_A\lambda_0^4)$, $n$ is the refractive index of the solution, $\lambda_0$ is the wavelength of the incident light, $N_A$ is the Avogadro number, and $\partial n/\partial C$ is the refractive index increment. $S(q)$ is the particle scattering factor, which depends on the scattering vector $q = 4\pi n \sin(\phi/2)/\lambda_0$ and on the size of scattering centers. In a semidilute solution the scattering factor is approximated by

$$S^{-1}(q) = 1 + q^2\xi^2 \qquad (9)$$

This was shown by neutron scattering[12,14] for $0.3 < q^2\xi^2 < 30$.

Thus the scaling laws obtained for $\partial\pi/\partial C$ as a function of $C$ and $\tau$ can be checked through the inverse of the scattered intensity, measured at $q\xi \ll 1$ or extrapolated at $q = 0$, if one neglects the variation of $K$ with temperature.

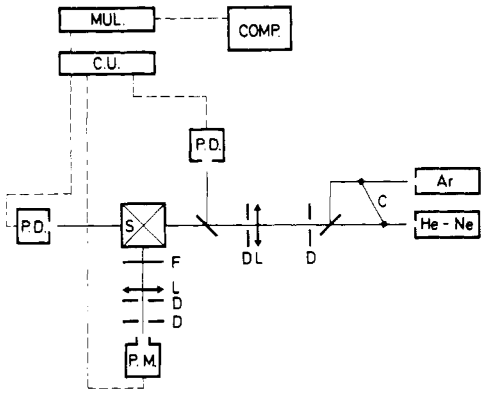

**Figure 1.** Block diagram of the light scattering apparatus: C, chopper; L, lens; D, pinholes; S, sample cell; F, 4880-Å filter; P.D., photodiodes; P.M., photomultiplier; MUL., multimeter; C.U., control unit; COMP., computer; Ar, Ar$^+$ laser; He-Ne, He-Ne laser.

## 3. Experimental Section

**3.1. Light Scattering Apparatus.** The measurements were performed on a light scattering photometer whose block diagram is given in Figure 1.

The sample cell was placed in a cyclohexane bath in the center of a thermostated copper block. It was drilled with channels through which circulated water from an external regulated bath. The temperature was measured by a chromel–constantan thermocouple placed in the cyclohexane. The temperature stability was better than 0.05 °C. Flat optical windows (2 cm$^2$) were located at angles of 0°, 90°, 180°, and 270°, through which passed the incident, scattered, and transmitted light beams.

The polarized light source was either a He-Ne laser (Spectra Physics, Model 120) or an Ar$^+$ laser (Coherent Radiation, Model CR3) which were alternately selected. The light power incident on the sample cell was always less than 3 mW. The intensity of the reference and transmitted light beams was detected by photodiodes (Hamamatsu S.875-33R) and the intensity of the light scattered at an angle of 90° was detected by a photomultiplier (RCA 8852). A 4880-Å filter was placed in the scattered beam when the Ar$^+$ laser beam was incident on the sample in order to eliminate the fluorescence of polystyrene.

The outputs of the photodiodes, photomultiplier, and thermocouple were alternately measured by a digital multimeter (Fluke 8520A) and registered in the memory of an on-line computer (Hewlett-Packard 85). The reference ($I_r$), scattered ($I_d$), and transmitted ($I_t$) intensities were measured for both wavelengths and the ratios $I_d/I_r$ and $I_d/I_t$ calculated. No difference was observed between the two ratios, thus making corrections for beam attenuation in the sample unnecessary.

Using laser light of two different wavelengths enabled us to evaluate the correlation length $\xi$ through the relation

$$r = \left(\frac{I_d}{I_r}\right)_1 \Big/ \left(\frac{I_d}{I_r}\right)_2 = X\left(\frac{1 + q_2^2\xi^2}{1 + q_1^2\xi^2}\right) \qquad (10)$$

The subscripts 1 and 2 refer to $\lambda = 6328$ Å and $\lambda = 4880$ Å, respectively. $X$ is a normalization constant determined experimentally from measurements on a benzene sample: $X = 0.299 \pm 0.005$.

The experimental reproducibility is 2.5%. When $\xi > 100$ Å this lack of reproducibility becomes troublesome and one has to impose a Lorentzian shape in order to determine $\xi$ (eq 10), then $S(q_2)$ (eq 9), and $\partial\pi/\partial C$ (eq 8).

As an example, if $\xi = 350$ Å and $\delta I/I = 2.5\%$, one makes an error of 10% in the $\xi$ determination and of 20% in the $\partial\pi/\partial C$ determination.

However, this reproducibility is acceptable when $\xi < 100$ Å because one has a supplementary check: the two different wavelengths must lead to the same osmotic compressibility value.

**Table I**
**Molecular Weight ($M_w$), Polydispersity $M_w/M_n$, and Overlap Concentration $C_\Theta$* for the Polymers Used**

| $M_w \times 10^{-6}$ | $M_w/M_n$ | $C_\Theta$*, g/cm$^3$ |
|---|---|---|
| 0.422 | 1.05 | $6.15 \times 10^{-2}$ |
| 1.26 | 1.05 | $3.56 \times 10^{-2}$ |
| 3.84 | 1.05 | $2.04 \times 10^{-2}$ |
| 6.77 | 1.14 | $1.54 \times 10^{-2}$ |
| 20.6 | | $8.81 \times 10^{-3}$ |

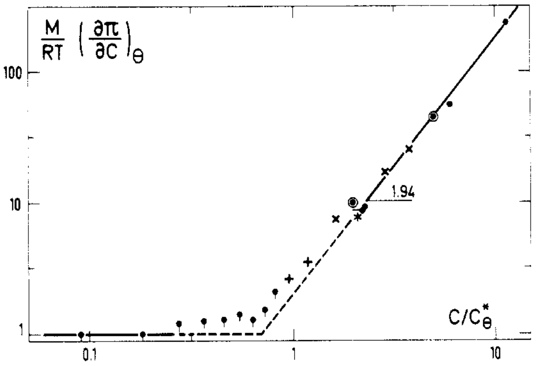

**Figure 2.** Dependence of the inverse of the reduced osmotic compressibility $(M/RT)(\partial\pi/\partial C)_\Theta$ on the reduced concentration variables $C/C_\Theta$* (log–log scales). The following symbols are used for the different molecular weights: (+) $4.22 \times 10^5$; (*) $1.26 \times 10^6$; (⊙) $3.84 \times 10^6$; (×) $6.77 \times 10^6$; (●) $20.6 \times 10^6$. Reduced osmotic compressibility deduced from osmotic measurements: (ɸ) ref 20; (–●) ref 21.

Using the ratios $(I_d/I_r)_{2PS}$ and $(I_d/I_r)_{2BZ}$ measured at 4880 Å with polystyrene solutions and benzene sample, respectively, we deduced $\partial\pi/\partial C$ from relations 8 and 9 and the numerical values $n = 1.423$ (at 35 °C),[15] $\partial n/\partial C = 0.179$ (35 °C),[16] and $R_B = 38 \times 10^{-6}$ cm$^{-1}$ [17] for the benzene Rayleigh ratio. We obtain

$$\frac{\partial\pi}{\partial C} = 5.052 \times 10^8 \frac{(I_d/I_r)_{2BZ}}{(I_d/I_r)_{2PS}} CS(q) \quad ((\text{dyne cm})/\text{g}) \quad (11)$$

**3.2. Materials.** The polystyrene fractions used were furnished by Toyo Soda Inc. Their characteristics are compiled in Table I; values of $C_\Theta$* are calculated from the relation $C_\Theta$* (g/cm$^3$) = $M/N_A R_{G\Theta}{}^3$. The experimental results for $R_{G\Theta}$[18] lead to $C_\Theta$* (g/cm$^3$) = 40 $M^{-1/2}$. Cyclohexane of analytical grade (R.P. Normapur) was used as furnished by Prolabo. Samples were prepared without any filtration in the unsealed scattering cell, and the monomer concentration $W$ was determined by weighting.[19] However, $X$ values are identical (0.299 ± 0.005) for the benzene sample, PS samples at high concentration ($W > 6\%$) at the Θ temperature, and PS samples at high temperatures ($T > 45$ °C); thus the intensity scattered by dust at $\phi = 90°$ is not detectable in this experiment.

## 4. Results and Discussion

At the Θ temperature the scaling hypothesis (4) that the quantity $C/C_\Theta$* is a reduced variable for the inverse of the reduced osmotic compressibility $(M/RT)(\partial\pi/\partial C)_\Theta$ is tested in Figure 2. A good superposition is observed throughout the concentration range. The figure is drawn with log–log scales, which enables us to find the power law

$$\frac{M}{RT}\left(\frac{\partial\pi}{\partial C}\right)_\Theta = 2\left(\frac{C}{C_\Theta^*}\right)^{1.94\pm0.07} \quad (12)$$

for $2.2 < C/C_\Theta^* < 11$. This law is the one expected for semidilute solutions (see eq 4). This infers that the asymptotic regime is obtained, experimentally, for $C > 3C_\Theta$*.

It is interesting to compare our results with those obtained by osmotic pressure measurements. We calculate the derivative of $\pi_\Theta/RT$ at each experimental point obtained in the same system when numerical results are available.[20] We use also the osmotic pressure measurements of ref 21 at two concentrations near enough to be able to calculate $\Delta\pi/\Delta C$. The corresponding points are plotted in Figure 2; it is seen that all experimental data considered are in agreement.

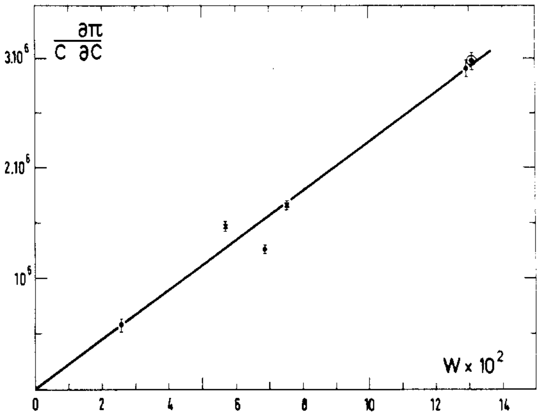

**Figure 3.** Concentration dependence of $(1/C)(\partial\pi/\partial C)$ at the Θ temperature and with samples having a concentration $C > 3C_\Theta$* (linear scale). The solid line is the empirical determination corresponding to eq 13; for symbols see caption to Figure 2.

In the semidilute regime ($C > 3C_\Theta$*) at $T = \Theta$, the dependence on concentration and the molecular weight independence of the inverse of the osmotic compressibility are shown in Figure 3. The values corresponding to a given concentration (e.g., $W = 13\%$) but of different molecular weights ($M_w = 3.84 \times 10^6$ and $20.6 \times 10^6$) are identical within experimental error. Moreover, we see that for $C > 3C_\Theta$* whatever the molecular weight, the experimental points can be described empirically by

$$\frac{1}{C}\frac{\partial\pi}{\partial C} = 2.24 \times 10^7 W \quad (13)$$

where $\partial\pi/\partial C$ is expressed in (dyn cm)/g.

A subsidiary result is the determination of the correlation length $\xi$. The results obtained on three different samples having a concentration of $W = 2.57\%$, 3.28%, and 5.26% lead to $\xi W = (6.73 \pm 1.4) \times 10^{-8}$ cm g/g. This value is in agreement with neutron scattering measurements:[12]

$$\xi W = 7.1 \times 10^{-8} \text{ cm g/g} \quad (14)$$

As a function of the reduced temperature $\tau/\tau^{**}$ eq 5 predicts that the plot of $(\partial\pi/\partial C)_\Theta/(\partial\pi/\partial C)$ should be a single curve independent of molecular weight and concentration. The reduced temperature scale $\tau^{**}$ for the system polystyrene–cyclohexane in the range of temperature investigated (35–65 °C) is proportional to the concentration. This can be deduced from the numerical values given in ref 12: the variation of $\xi/\xi_\Theta$ with the reduced temperature $\tau/C$ is a single curve, independent of the concentration.

In Figure 4 we plot, in a linear representation, the variation of $(\partial\pi/\partial C)_\Theta/(\partial\pi/\partial C)$ as a function of $\Theta\tau/W$. We must remark that with the two samples studied ($W = 2.57\%$, $M_w = 20.6 \times 10^6$ and $W = 13\%$, $M_w = 3.84 \times 10^6$) for a given value of $\Theta\tau/W$ (≈90, corresponding to $T - \Theta = 2.2$ and 12.2) we obtain identical values of $(\partial\pi/\partial C)_\Theta/(\partial\pi/\partial C)$ (≈0.4); thus $\Theta\tau/W$ is the reduced temperature variable.

The boundary between the Θ region and the good solvent region has been located by neutron scattering experiments[12] at $\Theta\tau^{**} \approx 30W$.

For $0 < \Theta\tau/W < 40$ the osmotic compressibility variation could be described by

$$(\partial\pi/\partial C)_\Theta/(\partial\pi/\partial C) = 1 - 1.27 \times 10^{-2}(\Theta\tau/W) \quad (15)$$

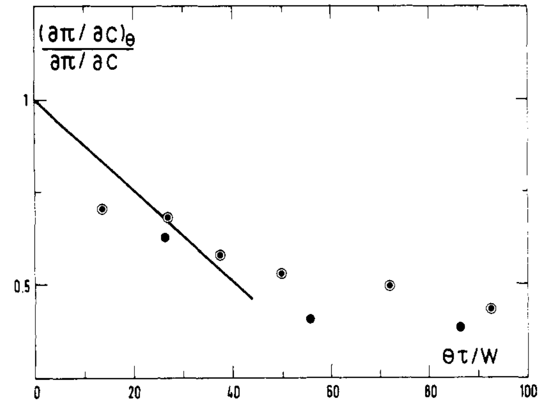

**Figure 4.** Dependence of $(\partial\pi/\partial C)_\Theta/(\partial\pi/\partial C)$ on the reduced temperature variable $\Theta\tau/W$ for two samples ((●) $M_w = 20.6 \times 10^6$ and $W = 2.57 \times 10^{-2}$; (⊙) $M_w = 3.84 \times 10^6$ and $W = 13.1 \times 10^{-2}$).

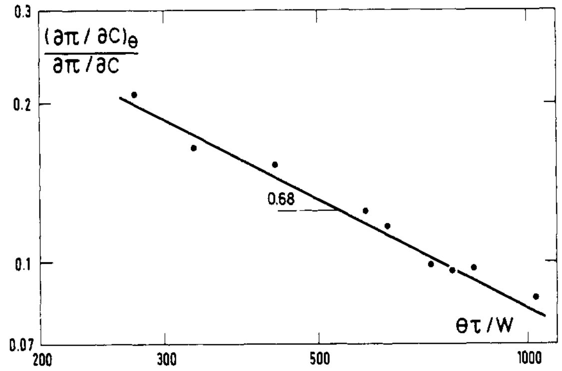

**Figure 5.** Dependence of $\partial\pi/\partial C$ ($M_w = 20.6 \times 10^6$, $W = 2.57 \times 10^{-2}$) on the temperature ($\Theta\tau/W > 200$) (log–log scale). The slope corresponds to the exponent determined by the best fit (eq 16).

In Figure 5, we present the variation of $(\partial\pi/\partial C)_\Theta/\partial\pi/\partial C)$ for one sample at low concentration ($W = 2.57 \times 10^{-2}$, $M = 20.6 \times 10^6$); we obtain[22]

$$(\partial\pi/\partial C)_\Theta/(\partial\pi/\partial C) = 8.85(\Theta\tau/W)^{-(0.68\pm0.08)} \quad (16)$$

for $\Theta\tau/W > 300$.

The universality of $(\partial\pi/\partial C)_\Theta/(\partial\pi/\partial C)$ as a function of $\Theta\tau/W$ cannot be checked in this range of $\Theta\tau/W$ because at a concentration of $W = 13\%$, the temperature maximum at which measurements were performed (65 °C) corresponds to $\Theta\tau/W < 300$.

For the $W = 2.57\%$ sample we evaluate a correlation length $\xi$ which decreases as temperature increases. As an example, $r = 0.36$ at 35 °C ($\xi = 340$ Å) and decreases to $r = 0.31$ at 42 °C ($\xi = 120$ Å). Thus for $\Theta\tau/W > 300$ (42 °C) the error due to extrapolation to $q = 0$ is no longer dramatic.

The temperature exponent (0.68) is in agreement with theoretical prediction if one considers the Θ to good solvent transition. Thus in the polystyrene–cyclohexane system, it seems that there is no evidence for a Θ to marginal solvent transition,[25] whose temperature exponent must be 1.5.

## 5. Conclusion

Static scaling laws for the inverse of the osmotic compressibility are confirmed experimentally in semidilute polystyrene–cyclohexane solutions. The exponent values are found to agree with those predicted theoretically. The molecular weight independence of the inverse of the osmotic compressibility is demonstrated: $\partial\pi/\partial C = 1.7 \times 10^7 C^2$. It is found that both $C/C_\Theta{}^*$ and $\tau/C$ are reduced variables for $(M/RT)(\partial\pi/\partial C)_\Theta$ and $(\partial\pi/\partial C)/(\partial\pi/\partial C)_\Theta$, respectively. In the concentration range $2 \lesssim C/C_\Theta{}^* < 11$ we find at $T = \Theta$, $(M/RT)(\partial\pi/\partial C) = 2(C/C^*)^{1.94}$. In the temperature range $10 < \tau/\tau^{**} \lesssim 33$, we find $\partial\pi/\partial C \sim \tau^{0.68}$.

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