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Temperature Dependence of Dynamic Light Scattering in the Intermediate Momentum Transfer Region

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ABSTRACT: Dynamic light scattering measurements have been made on dilute solutions of very high molecular weight polystyrenes in cyclohexane at 35.4, 45.0, and 55.2 °C. The data have been analyzed in terms of the first cumulant $\Omega(q)$ of the dynamic structure factor $S(q,t)$, with particular emphasis on the intermediate momentum transfer region ($R_g^{-1} \ll q \ll l^{-1}$), for which theoretical predictions yield $\Omega(q) \sim q^3$. The temperature dependence of the magnitude of $\Omega(q)$ is examined in terms of a "modified blob" model for the equilibrium distribution function and the preaveraged Oseen tensor description of hydrodynamic interaction. The temperature dependence of the experimental results is found to be in very good agreement with the theoretical calculations, although the magnitude of $\Omega(q)$ at each temperature falls consistently slightly below (~15%) the theoretical predictions, as reported previously for both good solvent and Θ conditions.

Introduction

Dynamic light scattering measurements on dilute macromolecular solutions have traditionally been performed in the so-called diffusion region described by $qR_g \ll 1$, where q is the momentum transfer vector and R_g is the radius of gyration. In these experiments the dynamic structure factor (or intermediate scattering function) $S(q,t)$ is extracted from the measured correlation function and subsequently modeled as a single exponential with decay constant $\Gamma = q^2D$, where D is a measure of center-of-mass translational diffusion. However, where measurements are made such that $qR_g > 1$ the internal motions of polymer chains may also be investigated. Inasmuch as the available q range is governed by the incident wavelength, for visible light this region only becomes accessible for high molecular weight polymers.

In the intermediate q region defined by $R_g^{-1} \ll q \ll l^{-1}$, where l is the statistical length, Dubois-Violette and de Gennes showed that the normalized $S(q,t)$ for a Gaussian chain may be scaled as $\exp\{[\omega_c(q)t]\}$, where the shape function f is expressed as a function of the dimensionless time $\tau \equiv \omega_c(q)t$(1). For an unperturbed Gaussian chain in non-free-draining conditions they found that the characteristic frequency $\omega_c(q)$ was proportional to q^3; this power law dependence was first investigated experimentally by Adam and Delsanti.[2] However, it is difficult to satisfy strictly the requirements $qR_g \gg 1$ and $ql \ll 1$ simultaneously in order to establish the correct exponent rigorously.

Recently, Akcasu et al. developed a method for the interpretation of dynamic light scattering measurements throughout the entire q range.[3] The results are analyzed in terms of $\Omega(q)$, the first cumulant of $S(q,t)$, defined by $\Omega(q) \equiv -\lim_{t\to 0}\,[\partial \ln S(q,t)/\partial t]$. It is found that $\Omega(q)$ becomes proportional both to Dq^2 in the diffusion region and to $\omega_c(q)$ in the intermediate q region. In order to generate $\Omega(q)$ values for comparison with experimental results, it is necessary to adopt a dynamical operator to describe the time evolution of the system and an equilibrium monomer distribution function. The operator of choice is Kirdwood's diffusion operator,[4] and for the non-free-draining case, $\Omega(q)$ has been evaluated by using either a preaveraged or a nonpreaveraged Oseen tensor description of the hydrodynamic interaction, for both good solvent (fully developed excluded volume) and Θ solvent (Gaussian chain) limits.[5,6] The experimental results for polystyrene in toluene (23 °C) and cyclohexane (35.0 °C) were consistently slightly below the theoretical predictions and were in better agreement with the preaveraged Oseen tensor results.[6] The calculations of $\Omega(q)$ in the good solvent limit were carried out with the temperature blob model of Daoud[7] for the distribution function.

Table I

sample	$M_w \times 10^{-6}$	M_w/M_n	c, mg/mL
LF4	4.1	~1.1	0.275
F505	5.05	1.02	0.26
F720	7.5	1.05	0.175
F1300	13.4	1.17	0.24
LF44	44.0	~1.1	0.11

In this paper we report measurements on polystyrene in cyclohexane near the Θ temperature (35.4 °C) and at two higher temperatures, 45.0 and 55.2 °C. These data are compared with theoretical predictions obtained by using the preaveraged Oseen tensor description and a modified blob model.[8] The latter replaces the two discrete exponents ($\nu = 0.5$ and 0.6) appearing in the original form of the blob model[7] for short and long portions of the chain with a (presumably) more physically reasonable length-dependent swelling factor.

Experimental Section[20]

Five different polystyrene samples were used in this study. Samples LF4 and LF44 were kindly provided by Professor L. J. Fetters of the University of Akron, while samples F505, F720, and F1300 were obtained from Toyo Soda Co. The molecular weight and polydispersity ratio M_w/M_n for each sample (as provided by the supplier) are listed in Table I, as are the concentrations of the solutions used. In all cases the solvent employed was ACS spectrograde cyclohexane from Eastman Kodak Co. To avoid shear degradation of the high molecular weight polymers used in this study, the solutions were not filtered directly. Instead, the solutions were prepared by filtering solvent (0.22-μm Millipore filters) directly into scrupulously clean sample cells containing the polymer. These cells were then sealed and stored at 40 °C until use.

Dust should not be a factor in these experiments because the quantity of interest is the initial decay of the correlation function at large angles (i.e., $qR_g > 1$). In addition, the very small quantities of polymer employed serves to reduce the amount of dust introduced into solution. No evidence for a significant contribution to the scattered intensity from dust was found, either from direct observation of the light beam passing through the solution or by examining the slow excess intensity fluctuations at small angles.

Solvent viscosities were measured with a Cannon capillary viscometer incorporated into a Hewlett-Packard 5901B autoviscometer system at a series of temperatures in the range from

25.0 to 65.0 °C. Flow times were maintained at or above 100 s to obviate the need for kinetic energy corrections. The measured values of the solvent viscosity η_0 were scaled to a reference value of 0.797 cP at 30.0 °C. This yielded values of η_0 of 0.729, 0.628, and 0.542 cP at 35.4, 45.0, and 55.2 °C, respectively.

All scattering data were obtained in the homodyne mode using full photon-counting detection and a 128-channel Malvern 7025 correlator. Incident radiation at 488 nm was provided by a Coherent Super-Graphite 4-W argon ion laser. The cylindrical sample cells were mounted in a bath of index of refraction matching fluid. Temperatures were controlled to within ±0.1 °C at all temperatures and were determined by a copper-constantan thermocouple. $S(q,t)$ was obtained from the experimental correlation function $C(q,t)$ according to the relation $C(q,t) = 1 + \beta[S(q,t)]^2$,[9] where β is an adjustable parameter. It typically assumes values in the range 0.01–0.1. $\Omega(q)$ may be extracted from $S(q,t)$ either by cumulant analysis or by shape function analysis, as previously described.[6] In this paper shape function analysis was not used, even though it would improve the precision of the results at large values of qR_g, because the shape function itself is known precisely only under Θ conditions and for $qR_g > 4$. In cumulant analysis $S(q,t)$ may be represented as $\exp[-\Omega t(1 + A_1t + A_2t^2 + ...)]$[10] or as $(\exp(-\Omega t))[1 + B_1t^2 + B_2t^3 + ...]$[11] and $\Omega(q)$ determined by nonlinear regression. Alternatively, $\Omega(q)$ may be determined by linear regression on $\ln S(q,t)$ fits to $-\Omega(1 + A_1t...)$. All three of these approaches have been used in these experiments to ensure that consistent results are obtained. From the previous results the experimental time range was restricted so that $\Omega t < 0.6$ for all but the highest values of q at 45.0 and 55.2 °C. Under these conditions two terms in the above expressions were deemed sufficient. The base line of the correlation function was determined both from the correlator monitoring channels and as an adjustable parameter. No significant difference in the resulting values of $\Omega(q)$ was observed.

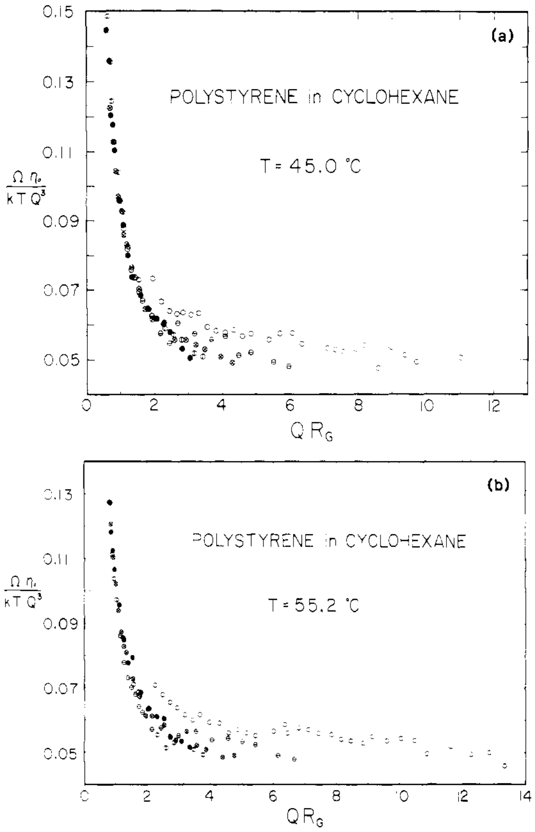

Figure 1. Plot of $\Omega(q)\eta_0/k_BTq^3$ vs. $qR_g(T)$ for five polystyrenes in cyclohexane: (○) $M_w = 44 \times 10^6$; (⊖) $M_w = 13.4 \times 10^6$; (⊗) $M_w = 7.5 \times 10^6$; (⦶) $M_w = 5.05 \times 10^6$; (●) $M_w = 4.1 \times 10^6$; (a) 45.0 °C; (b) 55.2 °C.

Theory

Theoretical predictions for $\Omega(q)$ have been determined by using a modified blob model for the equilibrium monomer distribution function.[8] In the Akcasu–Gurol formalism, $\Omega(q)$ is defined by

$$\Omega(q) \equiv \frac{\sum_{i,j}\langle \mathbf{D}_{ij}e^{i\mathbf{q}\cdot\mathbf{R}_{ij}}\rangle:\mathbf{qq}}{\sum_{i,j}\langle e^{i\mathbf{q}\cdot\mathbf{R}_{ij}}\rangle} \qquad (1)$$

where $\mathbf{D}_{ij}$ is the diffusion tensor and $\mathbf{R}_{ij}$ is the vector connecting the ith and jth links. In the modified blob approach chain expansion is introduced by

$$\langle|\mathbf{R}_{ij}|^2\rangle = l^2|i-j|\alpha^2(i,j) \qquad (2)$$

where l is the statistical length and $\alpha(i,j)$ is the local swelling factor of the chain. Subsequently, $\alpha(i,j)$ is assumed to be a function of $n = |i-j|$ only and is approximated for all n by a formula similar to that of Flory:[12]

$$\alpha^5(n) - \alpha^3(n) = (n/N_\tau)^{1/2} \qquad (3)$$

In this equation N_τ, the number of segments within a blob, is proportional to the reduced temperature $\tau = (T-\Theta)/T$. This expression for $\alpha(n)$ thus differs from both Peterlin's uniform expansion model,[13] where $\alpha^2(n) = n^\epsilon$,[13] and the blob model,[7] where $\alpha^2(n) = 1$ for $n < N_\tau$ and $\alpha^2(n) = (n/N_\tau)^{2\nu-1}$ for $n > N_\tau$. For given values of n and N_τ, eq 3 may be solved to arbitrary precision by means of a straightforward iterative procedure. Incorporation of eq 2 and the preaveraged Oseen tensor description of hydrodynamic interaction in eq 1 leads to the result

$$\frac{\Omega(q)}{q^2D_m} = \frac{1 + 2(2^{1/2})h^*\sum_{n=1}^{N}(1-n/N)n^{-1/2}\alpha^{-1}(n)e^{-y^2n\alpha^2(n)}}{1 + 2\sum_{n=1}^{N}(1-n/N)e^{-y^2n\alpha^2(n)}} \qquad (4)$$

where $y^2 = q^2l^2/6$, D_m is the segmental diffusion coefficient, which is equal to k_BT/ζ, and h^* is the hydrodynamic interaction parameter defined as[14]

$$h^* = \zeta/\eta_0 l\pi(12\pi)^{1/2} = B/2^{1/2}$$

with ζ the monomer friction coefficient, B the Flory draining parameter,[12] k_B the Boltzmann constant, and N the number of statistical segments in the chain. To facilitate numerical computation and comparison with experimental results, eq 4 may be rewritten as

$$\frac{\Omega(q)\eta_0}{q^3k_BT} = \frac{1}{h^*qR_\Theta}\left(\frac{N}{72\pi^3}\right)^{1/2} \times \frac{1 + 2(2^{1/2})h^*\sum_{n=1}^{N}(1-n/N)n^{-1/2}\alpha^{-1}(n)e^{-q^2R_\Theta^2(n/N)\alpha^2(n)}}{1 + 2\sum_{n=1}^{N}(1-n/N)e^{-q^2R_\Theta^2(n/N)\alpha^2(n)}} \qquad (5)$$

where $R_\Theta^2 \equiv Nl^2/6$ and denotes the radius of gyration under Θ conditions.

Results and Discussion

Figure 1a presents the data for the five polystyrenes in cyclohexane at 45.0 °C, and Figure 1b the 55.2 °C results. The first cumulant $\Omega(q)$ has been divided by q^3 so that the results will be independent of q in the intermediate q region if a q^3 dependence is followed; in addition, the data have been normalized by η_0/k_BT. The abscissa is the dimensionless product qR_g, where R_g is the temperature-dependent radius of gyration. Values of $R_g(T)$ have been calculated, rather than measured, according to the relation

$$R_g(T) = R_g(\Theta)\alpha(N) \qquad (6)$$

$R_g(\Theta)$ for polystyrene in cyclohexane is taken to be 3 ×

Table II

	45.0 °C			55.2 °C		
$M_w \times 10^{-6}$	N/N_τ	$\alpha(N)$	$R_g \times 10^5$, cm	N/N_τ	$\alpha(N)$	$R_g \times 10^5$, cm
4.1	9.74	1.434	0.871	37.4	1.589	0.965
5.05	12.0	1.456	0.982	46.0	1.616	1.089
7.5	17.8	1.500	1.232	68.3	1.668	1.370
13.4	31.8	1.569	1.723	122	1.750	1.922
44.0	105	1.728	3.439	401	1.938	3.857

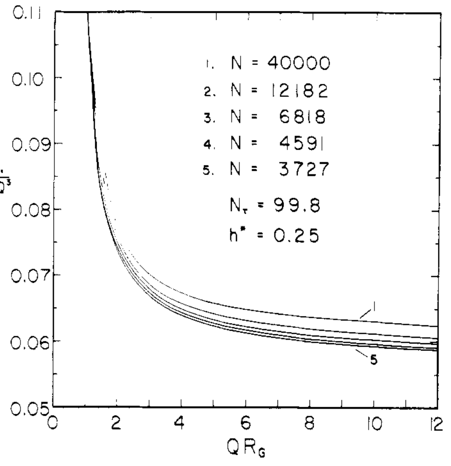

Figure 2. Plot of $\Omega(q)\eta_0/k_BTq^3$ vs. qR_g according to eq 5 with T = 55.2 °C.

$10^{-9}M_w^{1/2}$ cm,[15] and $\alpha(N)$ is obtained by the iteration procedure referred to previously. In order to calculate $\alpha(N)$, it is necessary to select a value of the ratio N/N_τ, which is given by

$$\frac{N}{N_\tau} = \frac{\tau^2 M_w}{\alpha n M_0}$$

where M_0 is the monomer molecular weight, n the number of monomers in a statistical length, and α a proportionally constant. The product αn is the only adjustable parameter needed to permit comparison of experiment with theory; results for $R_g(T)$ and $R_g(\Theta)$ for polystyrene in cyclohexane using the original blob theory yield a value of $\alpha n \approx 4$.[16] Strictly, αn should be redetermined with the modified blob approach; however, the difference is calculated to be small (<1%) for determination of $\Omega(q)$ in the intermediate q region. The values of $R_g(T)$ for the five molecular weights thus determined are presented in Table II, for both 45.0 and 55.2 °C, along with the corresponding values of N/N_τ and $\alpha(N)$.

The corresponding data obtained at the Θ condition have been presented elsewhere.[6] In accordance with expectation, a molecular weight independent master curve was obtained for this limiting case. At temperatures above Θ, however, a unique master curve should not be expected. This is due to the fact that the ordinate involves the hydrodynamic radius R_H ($=q^2k_BT/\eta_0 6\pi\Omega$), whic is a dynamic quantity, whereas the abscissa involves the static quantity R_g. Recent results have shown that the temperature dependence of R_H and R_g may be different, and the ratio of the respective swelling factors $\alpha_H(T)/\alpha_s(T)$ is not independent of N/N_τ (and therefore M) at intermediate temperatures.[7] This phenomenon is reflected in the results in Figure 1a,b, particularly for the polystyrene LF44. Figure 2 displays the predictions of eq 5 corresponding to the data in Figure 1b. N has been chosen somewhat arbitrarily on the basis of 10 monomers per statistical length, although for reasonably large N this selection is not critical. The value 0.25 was chosen as a typical value for h^*,[12] but the particular choice of h^* has no influence on the results in the intermediate q region for sufficiently large N. Qualitatively, these results may be seen to be in agreement with the data. In particular, it is evident that no master curve is obtained in the intermediate q region. In addition, for temperatures between the Θ and good solvent limits, $\Omega(q)$ is no longer simply proportional to q^3. Rather, $\Omega\eta_0/k_BTq^3$ decreases with increasing qR_g, with values near the good solvent limit at smaller q and approaching the Θ limit at high q. By plotting this quantity as a function of q rather than qR_g, one would obtain a master curve at sufficiently large q (i.e., $qR_g \gg 1$) within the intermediate region. However, only the data for the largest molecular weight polymer (LF44) meet this criterion; inasmuch as the primary purpose of this paper is to investigate the temperature dependence in the intermediate q region, the subsequent analysis is confined to this sample.

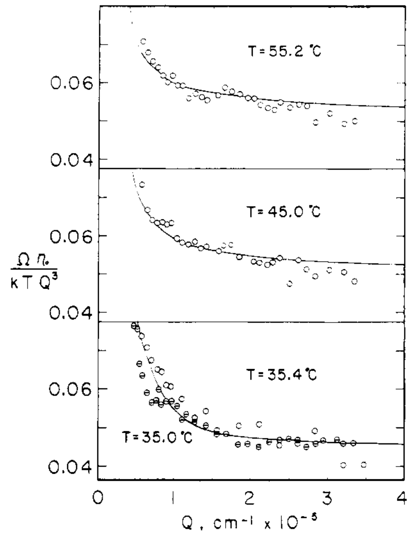

Figure 3. Plot of $\Omega(q)\eta_0/k_BTq^3$ vs. q for $M_w = 44 \times 10^6$ at four temperatures. Theoretical curves correspond to eq 5, except that each curve has been arbitrarily shifted by subtracting 0.0075.

In Figure 3 the data for LF44 at three temperatures (35.4, 45.0, and 55.2 °C) are presented. In addition, some previously published results at 35.0 °C are included.[6] The results are plotted as $\Omega\eta_0/k_BTq^3$ vs. q; for the sake of clarity the three temperatures (data for 35 and 35.4 °C were not separated) have been displaced along the ordinate. The theoretical predictions according to eq 5 have been superimposed on the data; however, in all three cases the theoretical curves have been shifted arbitrarily but uniformly by subtracting 0.0075. Again, N has been chosen on the basis of 10 monomers per statistical length and h^* maintained at 0.25. As observed in ref 6, under Θ and good solvent conditions the theoretical values of $\Omega/(q)/q^3$ lie consistently above the experimental results. However, once the shift is imposed, the data agree quite well with the theory at each temperature simultaneously. Thus the temperature dependence per se is apparently very well described by this approach. The source of the discrepancy in the magnitude of Ω in this regime remains unidentified.

As pointed out previously, correction for finite concentration effects can serve to reduce but not eliminate this difference.[6] For the $M_w = 44 \times 10^6$ sample the maximum correction ranges from 4% to 5% over this temperature range. However, such a correction procedure has not been justified in the intermediate q region, and is not attempted here.

There is some suggestion in these results (particularly for $q > 2.5 \times 10^5$ cm^{-1}) that $\Omega(q)/q^3$ decreases more rapidly with increasing q than the modified blob calculation predicts. (It should be noted that the shift of 0.0075, determined by the 35 °C data, is assumed to be essentially temperature independent. If this assumption is not appropriate, the theoretical curves can, of course, be adjusted to coincide with the results in the larger q region. However, the previous results[6] support the notion that the shift is not strongly temperature dependent.) Three possible reasons for this trend can be considered: The first is the return to $\Omega(q) \sim q^2$ behavior due to the segmental diffusion as the crossover value $q^{-1} \sim l$ is approached. Since the experimental values of $q^{-1} > 300$ Å, this possibility should not be a major factor for a polymer as flexible as polystyrene, for which $l \sim 20$ Å. The second reason may be the systematic underestimation of $\Omega(q)$ at large q due the inadequacy of the cumulant fit and unfavorable signal-to-noise ratio. The use of the asymptotic shape function for the Θ solvent data[6] suggests that this is indeed a distinct possibility. Finally, it may be that the actual transition from excluded volume to Gaussian behavior as function of q (and thus $|i - j|$) is less gradual than the modified blob prediction.

To explore this possibility analytically, we have performed a perturbation analysis for $\Omega/q^3(k_BT/\eta_0)$ in the large-q limit, by approximating $\alpha(n)$ given in eq 3 by

$$\alpha^2(n) \simeq 1 + (n/N_\tau)^{1/2} \qquad (7)$$

Substituting this form into eq 4 and replacing sums by integrals, we have found

$$\frac{\Omega(q)\eta_0}{q^3k_BT} = 0.053\left[1 + \left(\frac{3\pi^{1/2}}{4} - \frac{1}{2\pi^{1/2}}\right)\frac{1}{qR_g}\left(\frac{N}{N_\tau}\right)^{1/2} + \ldots\right] = 0.053\left[1 + 1.05\frac{1}{qR_g}\left(\frac{N}{N_\tau}\right)^{1/2} + \ldots\right] \qquad (8)$$

Recently, Tanaka and Stockmayer[17] have obtained a similar expansion using the conventional first-order perturbation theory. In the preaveraged Oseen tensor case, corresponding to eq 8, they have found

$$\Omega(q)\eta_0/q^3k_BT = 0.053[1 + 6.46z/qR_g + \ldots] \qquad (9)$$

where z is the excluded volume parameter related to $(N/N_z)^{1/2}$ by $(N/N_z)^{1/2} = \gamma z$. The proportionality constant γ can be adjusted to reproduce a desired chain property correctly when it is calculated with the blob model. For example, γ was chosen as 2.49 in ref 16 to produce the large-z limit of the expansion factor α_s given by the Flory formula $\alpha_s^5 - \alpha_s^3 = 1.67z$. If we use this value to compare eq 8 and 9, we find that $\Omega(q)/q^3$ approaches its asymptotic Θ solvent value more slowly as a function of z/qR_g (slope 2.61), than predicted by the first-order perturbation theory (slope 6.46). The extreme case of the original blob model provides a crossover in Ω from good solvent to Θ solvent behavior[5] at a critical value of $q^* \sim \tau/l$. An element of such a crossover might be indicated by these data; however, no evidence of q^* increasing linearly with temperature is apparent. This conclusion may be at variance with the neutron spin-echo results of Richter et al.[19] Of these three explanations, it appears that the inadequacy of the data fitting is the most reasonable, although it is still a possibility that the transition from gaussian to good solvent behavior of the local swelling according to eq 3, as postulated in the modified blob model, may be too slow. We still believe that the dynamical problem cannot be considered solved until the full calculation of $S(q,t)$ at any temperature, molecular weight, and concentration can be obtained.

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(18) One can, of course, reproduce the first-order perturbation theory exactly by choosing $\gamma = 6.15$ in eq 8, at the expense of deviations in other quantities (such as the expansion factors for the radius of gyration and the hydrodynamic radius[8]) that can be calculated with the blob model without any additional adjustable parameters. For example, the asymptotic behavior of α_s for large z becomes $\alpha_s \rightarrow z^{1/5}$ instead of $\alpha_s \rightarrow 1.11z^{1/5}$ when γ is chosen as $\gamma = 6.15$ instead of $\gamma = 2.49$.
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(20) Certain commercial materials and equipment are identified in this paper in order to specify adequately the experimental procedure. In no case does such identification imply recommendation or endorsement by the National Bureau of Standards nor does it imply that the material or equipment identified is necessarily the best available for this purpose.