

QUASIELASTIC LIGHT SCATTERING FROM POLY(STYRENE)-DIBUTYL PHTHALATE SOLUTIONS

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Temperature and concentration behaviour of the dynamic structure factor of poly(styrene) was measured in a marginal solvent (dibutyl phthalate) by quasielastic light scattering. Both the concentration and temperature dependences of the hydrodynamic radius of the polymer coil and of the hydrodynamic blob size were found to follow the scaling laws predicted by theory. A relation $m + b = -1$ between exponents m and b for the concentration and temperature dependence of the blob size in semidilute solutions has been derived, and its validity was checked experimentally.

Using general concepts of the scaling theory¹⁻⁴, the conformation of polymer chains in solution has been studied both theoretically and experimentally (see *e.g.* refs⁵⁻⁷). The results led to the construction of a universal temperature-concentration (T - c) diagram⁸ (Fig. 1). Variation of the hydrodynamic radius, R_H , and the blob size^{1,2}, ξ_H , in various regions of the T - c plane is shown in Table I, which also defines the relevant scaling exponents.

If we keep in mind the difference between static (ν_G) and dynamic (ν_H) values of the exponent ν (here called the basic exponent), a_H , b_H , and m_H for a dynamic method may be expressed as⁸

$$a_H = 2\nu_H - 1, \quad m_H = \nu_H/(1 - 3\nu_G), \quad b_H = -1 - \nu_H/(1 - 3\nu_G). \quad (1a,b,c)$$

The four regions of the diagram (Fig. 1) are delimited in the following way:

a) The two regions I and II are separated by a crossover concentration^{1,2} (c^*),

$$c^* = M/(4/3) \pi R_G^3 N_A \sim N^{1-3\nu_G} \tau^{3(1-2\nu_G)}, \quad (2)$$

where R_G is the radius of gyration of the coil, M is the molar mass of the polymer, N is its number of statistical segments, N_A is the Avogadro number and τ is the reduced temperature, $\tau = (T - \Theta)/T$; T and Θ are the absolute temperature and the Θ -temperature of the polymer-solvent system, respectively.

b) The lines $\tau^* = \pm N^{-1/2}$ separate the Θ -solvent range (I') (where $R_H = R_{H\Theta}$ is predicted, in the first approximation, to depend only on molar mass) from the dilute region (I) and the bad solvent region (IV), respectively.

c) The boundaries of regions II and III (c^{**}), and III and IV, respectively, are symmetrical with respect to the axis $\tau = 0$. The latter is the asymptote to the coexistence curve of the solution (curve K in Fig. 1), while $\tau^* \sim -N^{1/2}$ is the ordinate of its maximum. For polystyrene, empirical relations have been derived⁹ for c^{**} .

The lines mentioned above, with the exception of the coexistence curve, do not define a sharp change in behaviour as in the case of a phase transition, but indicate rather a broad crossover region between two systems with different characteristic behaviour.

The purpose of this paper is to present further data on the behaviour of a polymer chain in different temperature and concentration regions and especially in the crossover regions and to propose a more uniform view of some regions of the diagram.

EXPERIMENTAL

Apparatus. The principles of the light beating spectroscopy have been amply described¹⁰. Here, an apparatus used for homodyne detection is described schematically only: A Spectra Physics 125 A He-Ne laser with an output power of about 50 mW was used as the light source. Light scattered from the sample was detected by a cooled photomultiplier which gives less than 20 dark photon counts *per* second. The scattering angle was always 90°. The output signal of the photomultiplier was analyzed on a 100 channel Hewlett-Packard correlator 3721A. The auto-correlation function was fitted to a single exponential using Koppel's method for polydispersity analysis¹¹. The sample cell was placed in a thermostated sample holder. By combining cooling by nitrogen vapour and electrical heating, the temperature could be set to any value in the range

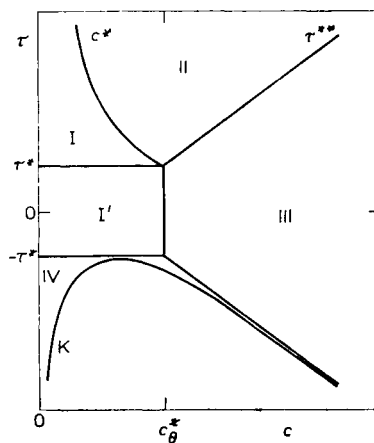


FIG. 1

Temperature (τ)-concentration (c) diagram of a polymer-solvent system. Individual regions of the diagram are described in Table I. After Daoud and Jannink⁷

between -140 and $+250^\circ\text{C}$. The long-term temperature stability as measured by a calibrated thermocouple was better than 0.1 K .

Solution preparation and characterization. The studied polymer was atactic poly(styrene) obtained from Pressure Chemical Company with molar mass $M_w = 2 \cdot 10^6$ and polydispersity $M_w/M_n < 1.30$ (producer's values). The solvent used was dibutyl phthalate, which is a marginal (moderately good) solvent of poly(styrene). This fact is demonstrated, *e.g.*, in refs^{12,13}. From the data in ref.¹² we derived an approximate value of the Θ -temperature, $\Theta = -14^\circ\text{C}$. The solvent was carefully purified and distilled before use. The solutions were filtered with a Jena 65 bacterial filter at 80°C and then degassed *in vacuo* at 80°C for 1 hour. It was verified by GPC analysis that no degradation of the polymer occurred during filtration. The solutions were characterized by weight concentrations and the concentration in g cm^{-3} involved in the scaling formulas was calculated for each temperature.

RESULTS AND DISCUSSION

Estimation of the characteristic length

The dynamic structure factor is given by the formula¹⁴

$$S(q, t) = S(q, 0) \exp(-2Dq^2t) \quad (3)$$

in the case of the homodyne detection. Here, D is the diffusion coefficient, t is time, $q = (4\pi n/\lambda) \sin(\theta/2)$ is the scattering vector, λ is the wavelength of the incident light, n is the refractive index of the medium and θ is the scattering angle.

Provided that $qR < 1$ and with D known from the single exponential fit of the dynamic structure factor, the hydrodynamic radius, R_H , of the coil in dilute solution may be calculated via the Stokes–Einstein relation^{1,5,14}

$$D = kT/6\pi\eta R_H, \quad (4)$$

where k is the Boltzmann constant and η is the viscosity of the solvent. The viscosity was measured at several temperatures ranging from 2°C ($\eta = 49.5\text{ mPa s}$) to 130°C ($\eta = 1.6\text{ mPa s}$) with an Ubbelohde-type viscometer and interpolated using a Vogel–Fulcher¹⁵ relationship $\log(\eta) = A + B/(T + C)$.

In the semidilute region, D represents the collective diffusion coefficient of transient polymer network and is related to the hydrodynamic size of blobs, ξ_H , by a relation similar to (4)

$$D = kT/6\pi\eta\xi_H, \quad (5)$$

provided that the following inequalities hold: $(c/c^*)^{-1.125} < qR < (c/c^*)^{0.75}$ (see *e.g.* ref.⁹).

In the crossover region, where neither the coil nor the blob description may be used, the characteristic length (L_H) is simply inversely proportional to the diffusion coefficient determined from the quasielastic light scattering experiment according to the Stokes-Einstein formula.

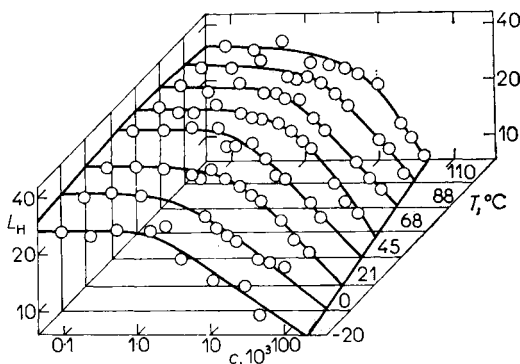
The concentration dependence of the characteristic lengths was studied in the range from 10^{-4} to $4.2 \cdot 10^{-2}$ g/g at several temperatures from -20 to 150°C . (Solutions of higher polymer concentration could not be filtered, which rendered the measurements by homodyne technique impossible.) The concentration dependence of L_H is plotted in Fig. 2, in double logarithmic scales, for several temperatures. As the polymer concentration is lowered, L_H approaches asymptotically the value of $L_H(c = 0) = R_H(c = 0)$. With increasing concentration L_H approaches ξ_H , the concentration behaviour of which is described by the corresponding scaling law (see Table I), and in a log-log plot it is represented by a straight line with slope m_H (Fig. 2). This line

TABLE I

Theoretical predictions of the scaling theory⁷. Symbols: l is the length of the equivalent Kuhn statistical segment, N is the number of these segments in a single polymer chain, $N \sim M$ (M is polymer molar mass), τ is the reduced temperature $(1 - T/\theta)$, T , and θ are the absolute temperatures of polymer and the theta point, respectively, ν_H , m_H , b_H , and a_H are scaling exponents

Region	Solvent	Characteristic unit	Dilute solution	Semidilute solution
I	good	coil	$R_H \sim lN^{\nu_H}\tau^{a_H}$	—
I'	theta	coil	$R_H \sim N^{1/2}$	—
II	good	blob	—	$\xi_H \sim c^{m_H}\tau^{b_H}$
III	Θ -like	blob	—	$\xi_H \sim c^{-1}$
IV	bad	globule	$R_H < R_H(\Theta)$	—

FIG. 2
Dependence of the hydrodynamic characteristic length, L_H (nm), on concentration, c (g cm^{-3}), and temperature, T ($^\circ\text{C}$). Results for temperatures -10°C , 10°C , and 30°C are not shown but appear in Table II



can again be considered as an asymptote to the experimental curve. The simplest analytical curve having two asymptotes is a hyperbola. If we wish the asymptote of the curve on the dilute side to be parallel to the axis of concentrations, the equation of the hyperbola in variables $y = \ln L_H$, $x = \ln c$ reads

$$y = a - (m/2) \{x - [(x - x_0)^2 + d^2]^{1/2}\}. \quad (6)$$

The asymptotes intersect at the point $(x_0, y_0 = a - mx_0/2)$; $m = m_H$ is the slope of the asymptote in the semidilute regime, $y_0 = \ln(R_H(0))$, x_0 roughly locates the crossover between the dilute and semidilute regions and d (the distance between the intersection of asymptotes and the curve on a line parallel to the $\ln L_H$ axis) is a measure of the sharpness of the crossover. An example of such a curve is in Fig. 3. The four parameters describing the hyperbola were calculated by means of a least squares fit to the experimental data. Curves for several temperatures in a three-dimensional diagram in Fig. 2 were analyzed; the parameters of hyperbolas are compiled in Table II.

Data presented in Fig. 2 were reanalyzed in order to establish the temperature dependence of the characteristic length, L_H , at various concentrations. In the dilute region (I, see Table I) the scaling theory predicts a linear temperature dependence with slope a_H , and in the semidilute region it again predicts a linear temperature dependence with the slope b_H (both in log-log scales). The full curve including the crossover region has the two above-mentioned straight lines as asymptotes and may thus be approximated also by a hyperbola. Experimental data at a fixed concentration were again fitted to such a curve by an iterative least squares procedure (Fig. 4). For a sample of fixed concentration c^0 we can assume that the maximum of the hyperbola indicates the temperature τ^0 at which $c = c^0 = c^*$. The temperature τ^0 and the slopes a_H and b_H of both asymptotes were calculated. The value of a_H is

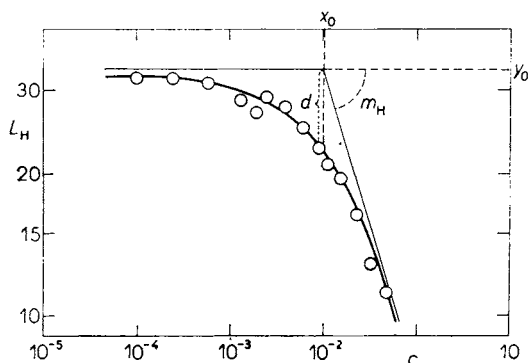


FIG. 3

Hyperbolic fit to the concentration dependence (g cm^{-3}) of the hydrodynamic characteristic length, L_H (nm), at 21°C . The different parameters of the hyperbola (Eq. (6)) are indicated

nearly constant, 0.094 ± 0.02 . Values of τ^0 and b_H are collected in Table III; at low and high concentrations only a linear regression was used.

Crossover concentrations. According to Eq. (2), $A = c^*/(\tau^0)^{3(1-2\nu_G)}$ is a constant. For the generally accepted value $\nu_G = 0.59$ we have $A = c^*/(\tau^0)^{-0.54}$. Values of A

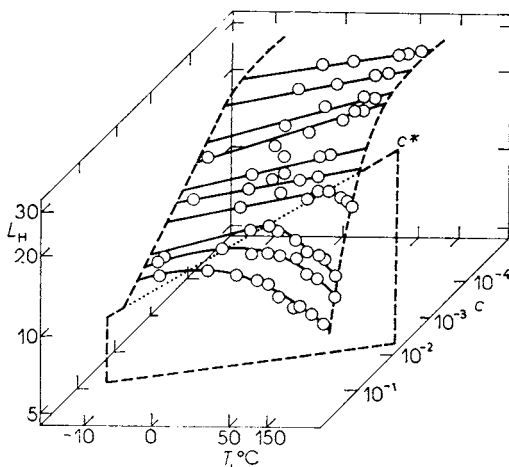
TABLE II

Parameters y_0 , $R_H(0) = \exp(y_0)$, x_0 , m , and d in the general equation of a hyperbola (6) for indicated temperatures

$T, ^\circ\text{C}$	y_0	$R_H(0)$	x_0	m	d
155	2.86 ^a	17.46 ^a	—	—	—
130	3.50	33.11	-5.14	-0.66	1.72
110	3.62	37.34	-4.53	-0.65	1.84
89	3.60	36.60	-5.87	-0.58	1.30
68	3.55	34.81	-5.22	-0.64	1.03
45	3.59	36.23	-5.76	-0.52	1.27
30	3.49	32.78	-5.91	-0.41	0.41
21	3.51	33.45	-4.71	-0.47	1.43
10	3.45	31.50	-5.40	-0.44	1.39
0	3.51	33.45	-6.77	-0.26	1.74
-10	3.32	27.66	-6.04	-0.33	0.50
-20	3.28	26.57	-6.52	-0.28	0.15

^a Results from linear regression.

FIG. 4
Dependence of the hydrodynamic characteristic length, L_H (nm), on temperature, T ($^\circ\text{C}$), and on concentration, c (g cm^{-3}). The three variables are in logarithmic scales, the temperature axis corresponds to $\log \tau$ with $\theta = -14^\circ\text{C}$



calculated for different samples of concentration $c = c^*$ and with the corresponding τ^0 taken from the hyperbolic fit are given in Table III. Disregarding the highest concentration, the quantity A is a constant within experimental error and leads to the following approximation valid for polystyrene in dibutyl phthalate: $c^* = 0.0049 (\tau^0)^{-0.54}$. Clearly, c^* has the correct temperature dependence predicted by Eq. (2) and provides a tool for calculating c^* at a given temperature.

Dilute region. The temperature dependence of the coil size in the limit of infinite dilution can be examined by means of the parameter $y_0 = \ln(R_H(c=0))$ (Table II), plotted in log-log scales in Fig. 5. Omitting the experimental point at the highest temperature where polymer degradation was detected by GPC, the remaining data can be fitted well to a straight line whose slope found by linear regression is $a_H = 0.10 \pm 0.04$. Using (1), we find for the dynamic basic exponent

$$v_H = 0.551 \pm 0.016.$$

The same critical exponent a_H is obtained from the slopes of the asymptotes to the curves in Fig. 4. In the concentration range from $9.0 \cdot 10^{-5}$ g/g to 10^{-2} g/g the value of the exponent a_H is concentration independent within the experimental error with a mean value of $a_H = 0.094 \pm 0.02$, leading to $v_H = 0.55 \pm 0.01$. The values of the exponents may however be somewhat affected by the uncertainty in the Θ -temperature.

Our light scattering measurements in the vicinity of the expected Θ -temperature show that the actual Θ -temperature could be somewhat lower. In fact, its exact value is not of great importance in determining the scaling exponents from measurements made far from the Θ -temperature. It can be easily shown that the error of the scaling exponents due to the uncertainty $\Delta\Theta$ is of the order of $\Delta\Theta/T$ under such conditions. Provided that $\Delta\Theta = \pm 20^\circ\text{C}$, which is the upper limit for $\Delta\Theta$, the corresponding error in the scaling exponents a_H , b_H is about 6%. This possible systematic error should be added to the errors of a_H , b_H , and v_H given in Table IV.

Semidilute region. Calculation of the slope m_H of the asymptote to the experimental points in the semidilute region (Table II) corroborates the temperature dependence of the exponent m_H (Fig. 6); only at high temperatures does m_H ap-

TABLE III
Parameters τ^0 , A , b_H (see text) for different concentrations

c , g/g	0.010	0.019	0.029	0.042
τ^0	0.286	0.116	0.074	0.055
A	0.0048	0.0052	0.0049	0.073
b_H	-0.351	-0.360	-0.332	-0.328

proach -0.67 found, *e.g.*, by Adam and Delsanti⁵. It corresponds to $\nu_G = 0.6$ and $\nu_H = 0.55$. At lower temperatures the absolute value of m_H is significantly smaller. This anomalous temperature dependence of the exponent m_H can be explained by a shift of c^* with temperature. In the vicinity of room temperature, all our data fall into the crossover region around c^* ; in a log-log plot they do not lie on a straight line. The curvature is not apparent, owing to the experimental error. As a result of forcing the data to lie on straight lines, a lower value of the exponent is determined. Only at high temperatures was c^* so low, that measurements at high concentrations were carried out truly in the pseudogel region.

The values of the exponent b_H for different concentrations (given by the slopes of the corresponding asymptotes to the curves in Fig. 4) are compiled in Table III.

TABLE IV

Scaling exponents a_H , b_H , m_H , and ν_H determined by different procedures

Scaling exponent	ν_H	<i>Cf.</i>
$a_H = 0.10 \pm 0.04$	0.55 ± 0.02	Fig. 5
$b_H = -0.34 \pm 0.10$	0.51 ± 0.07	Table III
$m_H = -0.65 \pm 0.04$	0.51 ± 0.04	Fig. 7

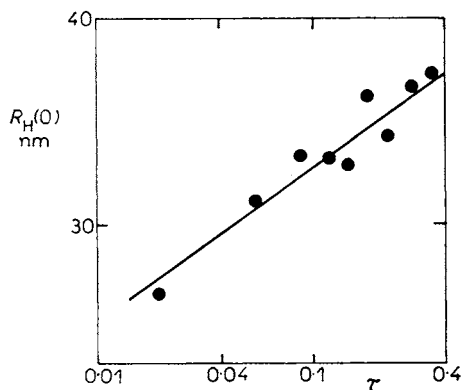


FIG. 5

Dependence of the hydrodynamic radius (R_H) of a polymer coil at infinite dilution obtained from the hyperbolic fit on the reduced temperature (τ)

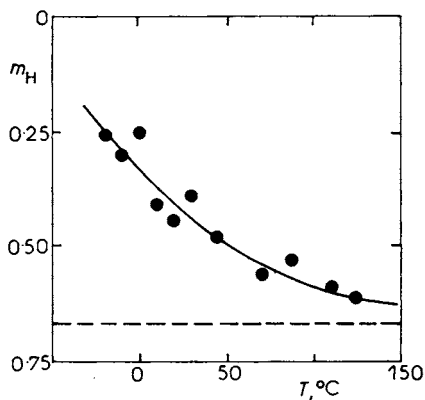


FIG. 6

Dependence of the exponent m_H in Eq. (1) on temperature

The exponent b_H is concentration independent with the mean value $b_H = -0.34 \pm 0.01$ leading to $\nu_H = 0.53 \pm 0.06$. If we examine in greater detail expressions (1) m_H and b_H , we immediately see that the following relation should hold:

$$m_H + b_H = -1. \quad (7)$$

(A similar relation holds, of course, for the static values of the exponents m_G and b_G .) This allows us to rewrite the expression for the blob size (II, see Table I) in terms of only one scaling exponent m_H :

$$\xi_H \sim c^{m_H} \tau^{-(1-m_H)}, \quad (8)$$

which may readily be transformed into

$$\xi_H \tau \sim (c/\tau)^{m_H}. \quad (9)$$

Experimental results for $c < 10^{-2}$ g/g at all measured temperatures have been replotted in variables $\xi_H \tau$ and c/τ in log-log scales in Fig. 7. All the points corresponding to the semidilute region (i.e. $c < c^*$ at a given temperature or $\tau < \tau^0$ at a given concentration) fall on a single straight line; linear regression yields the slope $m_H = -0.65 \pm 0.04$. This is a good proof of the validity of relation (9). Using (1) and $\nu_G = 0.59$, this gives $\nu_H = 0.52 \pm 0.04$. Experimental points below the straight line are not related to the semidilute regime. The temperature dependence of the exponent ν_H analyzed in the Weill-des Cloizeaux theory¹⁶ should result in a light curvature of the straight line, which could be calculated using the relevant expression

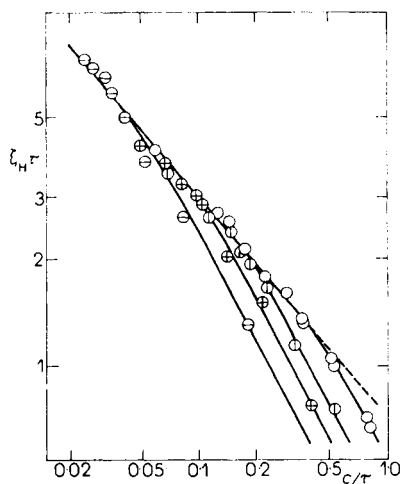


FIG. 7
Concentration and temperature dependences of the blob size in variables $\xi_H \tau$ and c/τ (Eq. (9)) \odot 0.010, \oplus 0.019, \ominus 0.029, \diamond 0.042

for v_H , but the accuracy of the data does not allow us to demonstrate this fact experimentally.

CONCLUSION

The exponents a_H , b_H , m_H and the corresponding basic exponent v_H obtained from our measurements compare well with the values of v_H reported previously (see, e.g.^{6, 11, 17-20}) and demonstrate that the Weill-des Coizeaux limit¹⁵ $v_H = v_G$ cannot be reached under our experimental conditions. The derived relationship $\xi\tau \sim (c/\tau)^m$ valid in the semidilute region describes both the temperature and concentration dependence of the blob size by a single scaling exponent m . On the basis of hyperbolic approximations proposed for the temperature and concentration dependences of the characteristic length, we have found (i) an experimental relation for the crossover concentration, $c^* = 0.0049\tau^{-0.54}$, for the system studied, (ii) the value of the coil radius in the limit of zero concentration as a function of temperature, and (iii) the value of the exponents a_H , b_H , and m_H .

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