Collective Diffusion in Semidilute Gels at the Θ Temperature

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ABSTRACT: We report measurements by quasi-elastic light scattering at the Θ temperature of the concentration dependence of the collective diffusion coefficient D in semidilute polymer gels. The system investigated consisted of acrylamide–bisacrylamide copolymers with water/methanol (75%/25% (v/v)) as a solvent, the measurements being made at 13.5 °C. Both equilibrium-swollen samples and those in the prepared state are examined. We also reanalyze data from a previous experiment (*J. Phys. (Paris)* **1978**, *39*, 955) on a similar system, to take account of nonexponentiality in the correlation spectra and of the effect of solvent displacement. Within the semidilute range, all three sets of data concur to give a scaling relation of the form $D = D_0 c^m$, in which the value of m is equal to 0.97 ± 0.07. This result, which is in agreement with the theoretical scaling result, differs markedly from the previously reported value of 0.5. In the semidilute range, the correlation spectra are nonexponential; this feature is attributed to the mutual interpenetration of different polymer coils. Measurements of the shear modulus, which varies as c^3, indicate that entanglements play no significant role in these gels.

Introduction

Recent experimental evidence has established the existence of an elastic plateau modulus G in semidilute solutions of polymers at the Θ temperature.[1,2] In this condition, where the excluded volume interaction vanishes, the osmotic modulus K_{os} is determined by the three-body interactions and hence varies with concentration as c^3. The shear modulus G, on the other hand, is proportional to the density of entanglements, that is, to the probability of two polymer strands coming into contact, and so is expected[3] to be proportional to c^2. The fact that, in solutions, G is independent of solvent quality and the different behavior of G and K_{os} in Θ solutions demonstrate that these moduli are in no way coupled.

In chemically cross-linked gels, however, such a coupling must obviously exist by virtue of the permanent cross-links. For semidilute gels measured at the Θ temperature of the equivalent solution (Θ gels), both K_{os} and G are found experimentally to vary[5-7] as c^3. Except for the special case of gels swollen to equilibrium, the reason for this behavior is not obvious: why does the shear modulus not vary as c^2, as in solutions? On the other hand, if G does vary as c^3 and the polymer–solvent friction coefficient f varies as c^2 in Θ conditions,[8] then the collective diffusion coefficient[9] D $(=(K_{os} + {}^4/_3 G)/f)$ should vary as c. Early observations of D did not bear out this expectation, and the discrepancy was attributed at the time to the effects of a concentration-dependent solvent viscosity.[5] To the best of our knowledge there has been no subsequent work published on the concentration dependence of D in Θ gels, in which the initial gel concentration is varied. The experimental picture on this subject is therefore unclear, and even unsatisfactory.

Reanalysis of the spectra described in ref 5 reveals that $D(c)$ has a more complex behavior than indicated at the time. Three factors account for the differences. First, the concentration range explored extended far into the concentrated region ($c \leq 0.55$ g cm^{-3}), in which simple scaling is inappropriate. The true semidilute Θ region contained too few points to form a reliable basis. Second, although the majority of the correlation spectra gave fair approximations to single exponentials, systematic deviations from exponentiality occurred in the vicinity of $c \simeq 0.1$ g cm^{-3}, i.e. the upper limit of the semidilute range. The forced fitting procedure used at that time distorts these data from the resulting $D(c)$ curve. Lastly, no account was taken of the solvent displacement in the calculation of $D(c)$; the correction factor for this effect was proposed only later.[10]

In this paper, as well as presenting the reanalyzed data of ref 5, we report measurements by quasi-elastic light scattering of $D(c)$ in polyacrylamide–water/methanol gels similar to (but not identical with) those of ref 5. In order to provide answers to the above questions, the measurements were carried out both on the prepared gels and on gels that were swollen to equilibrium in the Θ solvent.

Theory

In Θ solutions, two distinct crossover concentrations exist between the dilute and the semidilute regions. The coil overlap concentration[11] c^*, at which the overall solution concentration is the same as that inside the unperturbed coil (molecular weight M, radius $R_0 \propto M^{-1/2}$), is

$$c^* = M/R_0^3 \propto M^{-1/2} \tag{1}$$

The second crossover concentration is the critical entanglement concentration, c_e. It is a consequence of the fact that the plateau modulus of the solution[12]

$$G = G_N^0 c^2/\rho^2 \tag{2}$$

also defines the mass between entanglements, M_e:

$$G = (RT/M_e)c \tag{3}$$

In the above expressions, G_N^0 is the plateau modulus of the pure polymer melt, ρ its density, R_0 the unperturbed radius of gyration, and R the gas constant. Equation 2, which expresses the probability of forming an entanglement as being proportional to the probability of finding two polymer strands in contact, has been amply verified.[4,12] The limiting concentration c_e at which $M = M_e$ and below which there are no entanglements is given from eq 2 and 3; namely

$$c_e = RT\rho^2/MG_N^0 \propto M^{-1} \tag{4}$$

On account of their different molecular weight dependences in Θ solutions, at large M, c_e becomes much smaller than c^* and the effects of the shear modulus can become appreciable, especially at low concentrations.

In the case of acrylamide–bisacrylamide copolymer gels, however, M_n, the number-average molecular weight, is small, being, roughly speaking, equal to the ratio of acrylamide to bisacrylamide in the precursor solution.

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Calculations based on a recent two-phase model[13] of this gel in the Θ condition indicate that M_n in the weakly cross-linked (majority) phase is approximately 100–200 acrylamide units. This value is close to the critical molecular weight for entanglements in a number of molten polymers with similar side-group size.[12] In a 10% solution, eq 4 indicates that 10 times this number would be necessary to obtain an entangled state. Thus, even allowing for a broad distribution of molecular weights between cross-links, it is clear that M_n is too small in these gels for their elastic properties to be appreciably influenced by entanglements.

When a cross-linked gel absorbs excess solvent from its surroundings, swelling proceeds initially by the separation of the interpenetrating coils constituting the gel.[14] This unfolding process can be envisaged as involving three characteristic distances in the gel (or, equally, in a polymer solution): the mean spatial distance between cross-links, R_s; the distance R_t between two topologically connected cross-links; and the correlation length ξ of the polymer density fluctuations. If M_e denotes the molecular weight between cross-links (or between entanglements in a solution), then if A is a constant of the order of unity

$$c = A(M_e/R_s^3) \tag{5}$$

is the overall polymer concentration. In the language of scaling theory,[11] each chain is pictured as consisting of n noninteracting blobs of radius ξ. Thus the mean end-to-end distance R_t of a given chain is

$$R_t^2 = n\xi^2 \tag{6}$$

However, the mass of such a polymer chain is defined by the total volume of the blobs composing it and their concentration:

$$M_e = n\xi^3 c \tag{7}$$

Combining eq 5–7 leads to the relation[15]

$$R_s^3 = AR_t^2\xi \tag{8}$$

The value of A depends upon the functionality of the cross-links.

In Θ conditions, ξ is inversely proportional to the polymer concentration c, while, for a given gel, R_s^3 also varies as c^{-1}. Thus R_t is invariant as the gel swells or deswells in Θ conditions. This conclusion can be checked by measurements of the radius of gyration R_G of polymer coils in gels as a function of swelling. For a Gaussian chain consisting of N independent units of length b, the radius of gyration is related to the end-to-end length of R_t of the coil by[16]

$$\begin{aligned} R_G^2 &= Nb^2/12 + R_t^2/12 \\ &= R_0^2/2 + R_t^2/12 \end{aligned} \tag{9}$$

where, in the absence of external forces, $R_t^2 = 6R_0^2$. Neutron scattering measurements[17] show that the radius of gyration R_G of a chain of given molecular weight is independent of whether the polymer coil is end-linked in a gel swollen in a Θ solvent or in the dry state or, on the contrary, is unconstrained in dilute solution with a Θ solvent, i.e.

$$R_G = R_0 \tag{10}$$

in Θ gels. It may be recalled, for the sake of comparison, that the corresponding variation of R_G in gels swollen in a *good* solvent, predicted on the basis of eq 8 and 9, is very small;[18] experimentally, R_G is found to vary by less than 30% in gels swollen up to 15 times their dry volume.[14,18]

If one now considers a series of gels of different concentrations prepared under the same conditions, the shear modulus G is equal to the thermal energy per active chain;[19] that is

$$G = RTc/M_e = RT/AR_t^2\xi \tag{11}$$

This gives, from eq 9 and 10, if the temperature of preparation is close to the Θ temperature

$$G \simeq RT/R_0^2\xi \tag{12}$$

It follows that if the prepared state of the gel coincides with that of the equilibrium swelling state in the Θ solvent, then the gel concentration c is just equal to the coil overlap concentration c^*, at which point scaling theory stipulates that[11]

$$R_0 \simeq \xi \tag{13}$$

and under these conditions, since $\xi \propto c^{-1}$, eq 12 predicts that

$$G \propto c^3 \tag{14}$$

This result is of course a consequence of the equality at swelling equilibrium of the elastic restraining force and the osmotic pressure, the latter being proportional to c^3.

Clearly, however, relation 14 cannot be universally valid for Θ gels. For example, if for gels of a given acrylamide content, the concentration of the cross-linking agent, bisacrylamide, is reduced, then ξ is found to decrease slightly,[20] while R_0 must increase on account of the higher degree of polymerization between cross-links. Condition 13 thus no longer holds, and the prepared state of the gel does not coincide with the swelling equilibrium state; the shear modulus in this situation falls below the value expected from relation 14.

An interesting—and unverified—corollary of this discussion is that in Θ gels, on account of the invariance of R_t upon swelling, the shear modulus should simply be inversely proportional to the swelling ratio V: the standard argument[19] assumes an affine deformation of the end points of each elastic chain upon swelling, thus giving rise to a shear modulus which varies as $V^{-1/3}$. In this investigation it was not possible to provide an answer to this test, since highly deswollen polyacrylamide gels are in the glassy state at room temperature.

Experimental Details

One of the chief constraints in this experiment is the narrowness of the accessible semidilute Θ range in gels: to avoid the effects of the concentrated regime, the concentration should be kept below about 10%. Poly(acrylamide-*co*-bisacrylamide) is one system which forms a gel in near-Θ conditions below this concentration.

The gels were prepared by using as solvent a mixture of 75% water/25% methanol (v/v), containing in addition 0.1 M NaCl. The Θ temperature for polyacrylamide in this solvent is about 13.5 °C.[8] Several gels were prepared with differing monomer concentrations. In all of these, the ratio of acrylamide/bisacrylamide was set equal to 75 by weight; this value was chosen because it had been found previously[5] that greater bisacrylamide concentrations caused excessive turbidity in the samples, while lower cross-linking densities led to highly nonexponential light scattering correlation functions. The precursor solutions were catalyzed with 0.7 mg/mL ammonium persulfate and 0.28 μL/mL TEMED. Use of such small quantities of TEMED reduces the incidence of hydrolysis, while the presence of salt screens any residual coulombic effects. The polymerization was carried out at room temperature (20 °C), which, for the low molecular weights and relatively high gel concentrations investigated here, lies well within the Θ range as described by Daoud and Jannink.[21]

The quasi-elastic light scattering measurements were performed with a standard apparatus, working in the heterodyne mode. Although it is generally an easy matter to prepare optically clear

Table I
Summary of Reanalyzed Data from Ref 5

sample	concn, g cm^{-3}	$\bar{\Gamma} \times 10^{-3}$,[a] s^{-1}	$\Delta\bar{\Gamma} \times 10^{-3}$,[b] s^{-1}	$\mu_2/\bar{\Gamma}^2$ [c]	$D \times 10^7$,[d] cm^2 s^{-1}	$M_{os} \times 10^{-5}$, dyn cm^{-2}
1	0.067	2.92	0.70	0.10	0.860	0.265
2	0.072	3.16	0.42	0.15	0.931	0.340
3	0.076	3.90	0.45	0.17	1.15	0.350
4	0.089	4.74	0.61	0.15	1.41	0.707
5	0.094	4.61	0.53	0.16	1.38	0.753
6	0.111	4.98	0.70	0.11	1.50	1.36
7	0.114	5.73	0.50	0.20	1.73	1.06
8	0.134	4.80	0.38	0.06	1.47	2.34
9	0.146	5.13	0.50	0.10	1.58	2.42
10	0.161	4.87	0.58	0.07	1.51	3.84
11	0.185	5.51	0.37	0.09	1.74	6.17
12	0.198	5.35	0.47	0.07	1.70	7.82
13	0.206	5.68	0.24	0.08	1.82	9.00
14	0.245	5.95	0.47	0.06	1.95	14.1
15	0.245	6.30	0.98	0.08	2.07	11.8
16	0.265	6.25	0.65	0.05	2.08	20.7
17	0.290	7.20	0.58	0.06	2.43	30.5
18	0.321	7.55	0.41	0.08	2.61	41.7
19	0.382	8.73	0.93	0.09	3.16	93.1
20	0.456	9.12	0.89	0.06	3.50	226
21	0.547	9.90	1.11	0.07	4.12	744

[a] Value of first cumulant for scattering angle of 90°. [b] Scatter in measurements of first cumulant. [c] Mean ratio of second cumulant/(square of first cumulant). [d] D defined by eq 15, taking the density of the pure polymer as 1.35 g cm^{-3}. [e] Longitudinal osmotic modulus derived from measurement of the intensity of the dynamically scattered light (see ref 5).

Table II
Summary of Experimental Results

sample	c_0, g cm^{-3}	V	$10^{-4}G$ at c_0, dyn cm^{-2}	10^7D at c_0, cm^2 s^{-1}	$\mu_2/\bar{\Gamma}^2$	10^7D(swollen), cm^2 s^{-1}	$\mu_2/\bar{\Gamma}^2$
1	0.604	1.135	1.09	1.22	0.24	1.07	0.20
2	0.0714	1.097	2.40	1.27	0.18	1.33	0.15
3	0.0863	1.077	2.44	1.38	0.23	1.49	0.17
4	0.0946	1.108	3.97	1.82	0.24	1.68	0.11
5	0.1057	1.110	5.69	2.08	0.26	1.85	0.07

gels in a good solvent, the same is not true in Θ solvents on account of their tendency to form microscopic inhomogeneities throughout the material of the gel. Although the turbidity caused by this effect is small in the present samples, it is sufficient to prohibit operating fully in the homodyne mode. The samples were therefore not filtered, and heterodyning was ensured by scattering from suspended dust particles; this procedure was checked by introducing a supplementary static scatterer into the laser beam at the point of observation: the correlation functions remained unchanged.

In spite of the bisacrylamide content of these gels, the spectra displayed appreciable nonexponentially, and accordingly these were analyzed by using a three-cumulant fit. For an infinitely dilute gel, the diffusion coefficient is related to the first cumulant $\bar{\Gamma}$ and the scattering wave vector $\mathbf{K}$ by

$$\bar{\Gamma} = DK^2 \tag{15'}$$

Figure 1 shows the angular dependence of $\bar{\Gamma}$ predicted by eq 15'; that is, $\bar{\Gamma}$ is proportional to $\sin^2(\theta/2)$, where θ is the scattering angle. On account of the finite volume fraction ϕ of the polymer in the gels investigated here, the apparent diffusion coefficient D of eq 15' must be divided by $(1 - \phi)$ to accommodate for the displacement of the solvent in the motion of the polymer:[10]

$$D = \frac{\bar{\Gamma}}{K^2(1 - \phi)} \tag{15}$$

In eq 15, ϕ is taken as c/ρ, where ρ is the density of the pure polymer. The majority of the observations were made with θ = 90° from gels contained in fluorescence cells of square cross-section, using as source as 15-mW SP 124 He–Ne laser.

Two sets of samples were investigated: The first was measured in the prepared state, while the other was removed from the fluorescence cells in which they were made and then allowed to come to swelling equilibrium for 3 weeks in excess solvent at 13.5 °C. A second series of light scattering measurements was performed on the swollen samples.

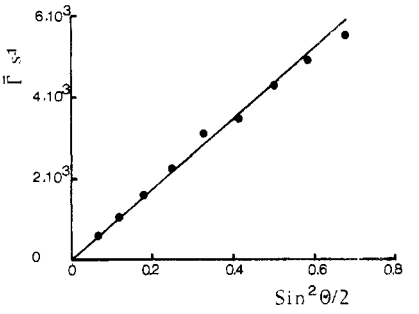

Figure 1. Angular variation of the first cumulant $\bar{\Gamma}$ of the correlation spectra obtained from a polyacrylamide–water/methanol gel of concentration 0.08 g cm^{-3} at 13.5 °C. Wavelength of incident light 632.8 nm.

The shear modulus G of the gels was measured by placing the parallelepiped-shaped samples in a frame holding a light, vertically sliding piston, which pressed on the gel. The underside of the piston was coated with a thin Teflon film to allow the gel in contact with it to spread laterally and hence avoid barreling of the sample. The shear modulus was obtained by adding appropriate weights to the piston and observing the resultant deformation of the gel through a microscope.

Results and Discussion

The reanalyzed data of ref 5 are listed in Table I, while the results of the present experiment are summarized in Table II. We discuss the former first.

The effect of the cumulant analysis is to increase the value of D in the low-concentration region ($c \leq 0.114$ g cm^{-3}), while that of the factor $(1 - \phi)$ is to increase D in

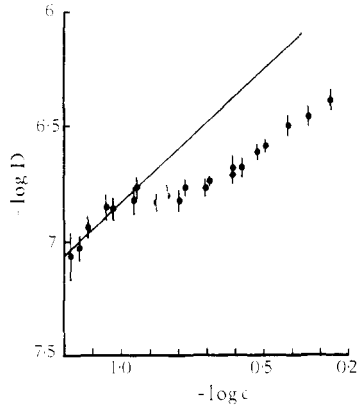

Figure 2. Double-logarithmic representation of $D(c)$ for the reanalyzed data of ref 5 (see Table I). The straight line shown is the least-squares fit to the seven data points of lowest concentration (eq 16). The slope of the average line through all the points is about 0.62. D is measured in units of cm^2 s^{-1}, and c in g cm^{-3}.

the high-concentration region. The resulting data points no longer form a straight line in a double-logarithmic plot but display a pronounced plateau in the region between 0.13 and 0.20 g cm^{-3} (Figure 2). The least-squares fit derived from the seven points of lowest concentration (i.e., $0.067 \leq c \leq 0.114$ g cm^{-3}) is given by

$$\log D = -(5.67 \pm 0.17) + (1.16 \pm 0.16) \log c \quad (16)$$

In the values of the longitudinal osmotic modulus $M_{os} = K_{os} + 4G/3$, derived from the measurement of the intensity, there is no kink corresponding to that observed in $D(c)$. The points form a monotonic curve that starts to deviate from linearity for c greater than about 0.15–0.20 g cm^{-3}. For the same concentration range as eq 16, one obtains for M_{os} (measured in dyn cm^{-2})

$$\log M_{os} = (7.86 \pm 0.26) + (2.91 \pm 0.24) \log c \quad (17)$$

If the concentration range for the latter measurements is extended to $c = 0.161$ g cm^{-3}, then the exponent m describing the concentration dependence of M_{os} improves in definition to become

$$m = 2.96 \pm 0.12 \quad (18)$$

Both values of m given by eq 17 and 18 are in accord with the value of 3 expected from scaling theory, and this result simply confirms the conclusion of ref 5 where the equivalent exponent was found to be 3.07 ± 0.07.

As for the measurements of the collective diffusion coefficient, the physical cause of the kink appearing at the crossover between the semidilute and the concentrated region is unexplained but is probably related to the specific nature of this polymer. Nonetheless, in the semidilute region, the exponent for D given in eq 16 is compatible with the scaling value of unity, although the associated error is somewhat large. The uncertainty attached to this result is the underlying motivation for our more recent measurements, which we shall now proceed to discuss.

From Table II it can be seen that the swelling ratio between the equilibrium swollen state and the prepared state is roughly 1.1. This implies that the samples are nearly at swelling equilibrium when they are prepared, and therefore relation 14 should be approximately applicable. Figure 3 traces the measured values of the shear modulus G in the prepared state as a function of concentration in a double-logarithmic plot. In spite of the scatter in the experimental points, it can be seen that G depends strongly upon c. The slope of the straight line drawn through the points is 3, in agreement with the value indicated in eq 14.

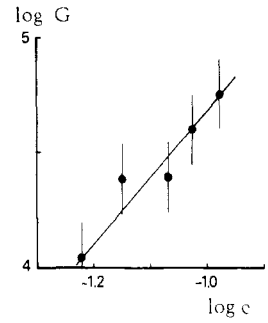

Figure 3. Measured values of the shear modulus G (in dyn cm^{-2}) vs. initial concentration c_0 for the unswollen Θ gels, shown in a double-logarithmic representation. The error bars displayed correspond to an estimated 15% error in the measurements. The straight line through the points has a slope of 3. The units of concentration c on the horizontal axis are g cm^{-3}.

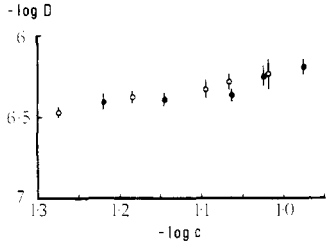

Figure 4. Double-logarithmic representation of $D(c)$ for the prepared gels (filled circles) and for the equilibrium-swollen gels (open circles). D is measured in units of cm^2 s^{-1}, and c in g cm^{-3}.

There also subsists appreciable scatter in the measured values of D (Figure 4), particularly for the unswollen samples. For these the diffusion coefficient can be expressed as

$$\log D = -(5.78 \pm 0.26) + (0.96 \pm 0.24) \log c \quad (19)$$

where, as in eq 16, D is measured in cm^2 s^{-1}. The swollen samples give, in the same units,

$$\log D = -(5.79 \pm 0.08) + (0.92 \pm 0.08) \log c \quad (20)$$

Both of these results are compatible with the scaling exponent of unity.

The principal reasons for the large uncertainty in the observed exponents can be found, first, in the narrowness of the concentration range explored: this is a consequence of the difficulty of making low-concentration Θ gels. Second, the nonexponentiality of the correlation spectra, by increasing the number of parameters required to describe the curve, introduces extra uncertainty.

It can be seen from Table II that the dependence upon swelling of D is rather weak, as is to be expected from the different swelling dependence of G and K_{os}.[7,8,14] This means that the two curves described by eq 19 and 20 are not superimposable, but it is legitimate to average the exponents; in this average, there is not reason to exclude the previous results, embodied in eq 16. The resulting weighted mean of the exponents in eq 16, 19, and 20 is given by

$$D = D_0 c^p \quad (21)$$

with

$$p = 0.96_7 \pm 0.06_5 \quad (22)$$

An inference which may be drawn from the observed values of the swelling ratio V in Table II and the discussion leading to eq 14 is that the bisacrylamide/acrylamide ratio used in these gels is just sufficient to ensure that the

prepared state is close to swelling equilibrium. Larger ratios lead to significant syneresis and opalescence; smaller values favor polymerization of large coils, which consequently overlap each other. In this latter condition a wide range of center-of-mass motions can arise that are similar in nature, although limited in space, to translational diffusion in an un-cross-linked solution. The effect of these overlapping regions can be understood schematically as follows. In the regions of the coil where there is no overlap, the relaxation of the "breathing", or gel, modes is simply determined by the osmotic pressure gradient and the polymer–solvent friction coefficient, i.e., by the solvent viscosity. For the overlapping regions participating in the same breathing mode, however, relaxation proceeds via the separation and rearrangement of the two constituent coils, which, on account of the polymer–polymer friction, is a much slower process. Since these modes also contribute to the concentration fluctuations, they scatter light, giving rise to a nonexponential signal. In gels in a good solvent, the cross-linking removes such slow modes, provided the samples are sufficiently swollen; this condition seems to be difficult to attain in Θ gels.

In conclusion, for the semidilute range of the Θ gels investigated previously, and reanalyzed here, as well as for those described in this paper, the collective diffusion coefficient D is in accord with the predictions of simple scaling. The same conclusion also applies to the concentration dependence of the shear modulus G. Unlike Θ solutions,[1] there is no angular dependence of D, because the network is permanent. No effects were observed of contributions of entanglements to G; this is consistent with the fact that the polymer chains are too short for entanglements to occur.

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Segmental Mobility in the Equilibrium Liquid below the Glass Transition

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ABSTRACT: Volume and enthalpy recovery data from near the glass transition temperature are suggested to be useful for indicating segmental mobility below the glass transition temperature in the equilibrium liquid. The procedure makes use of a recent theory by Robertson, Simha, and Curro for the kinetics of aging of polymer glasses. The theory is fitted to recovery data at temperatures above the glass transition, and then the time–temperature shift parameter is adjusted to obtain a fit to recovery data at temperatures below the glass transition. Segmental mobility can be estimated for temperatures below that of the measurement of recovery through the use of the free volume distribution arising from thermal fluctuations. The procedure was applied to poly(vinyl acetate), for which the rapid decrease in mobility on cooling from temperatures above the glass transition was found to moderate below the glass transition. This is suggested to arise from the influence of motions associated with lower temperature mechanical and dielectric loss peaks.

Introduction

How does the segmental mobility of the equilibrium liquid depend on temperature below the glass transition temperature? The segmental mobility above the glass transition temperature has long been known. For polymer liquids as well as for many small-molecule liquids in the 100 °C or so temperature range just above the glass transition, the temperature dependence of the segmental mobility, whether expressed as a viscosity or the reciprocal of the relaxation time, is well described by an equation of the form[1-5]

$$\log a_T = -c_1 + c_1c_2/(T - T_g + c_2) \quad (1)$$

where a_T is the time–temperature shift parameter, c_1 and

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