Advances in Polymer Science

99

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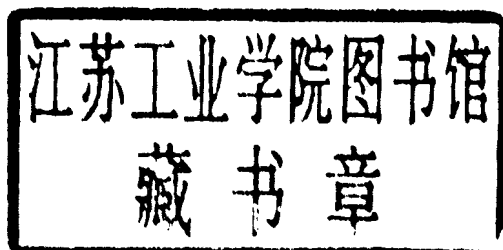
Part I

Molecular Interpretations of Sorption in Polymers

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By L. A. Errede

With 64 Figures

Springer-Verlag

Berlin Heidelberg New York
London Paris Tokyo
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Editors

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Table of Contents

The major part of this review is in fact a progress report of an ongoing research effort at 3M Laboratories aimed at a better understanding of polymer swelling by liquids. Since this effort builds naturally upon the many contributions of earlier investigators, Section 1 and 2 summarize the more important of these contributions. A sincere effort is made, however, to provide a good if not complete list of references to the original literature, and to several excellent in-depth reviews that describe these contributions in much more detail. Section 3 describes 3M contributions that lead to the concept of an adsorption parameter, α, the number of adsorbed molecules per monomer unit of polymer at liquid-saturation, which is calculated from the observed relative swelling power of a test-liquid for the sorbent polymer. The accumulation of data obtained in these investigations show that α (with respect to polystyrene) is consistent with expectation based on the molecular structures of the sorbed liquid and the monomer unit of sorbent polymer. Section 4 shows how α relates to the Hildebrand Solubility Parameter, δ, and the Flory-Huggins Interaction Parameter, χ, using δ and χ as reported in the literature and α for the corresponding polystyrene-liquid system as reported in Sect. 3. The relationships established thereby were used in turn to calculate values for δ and χ for polystyrene-liquid systems not yet reported in the literature. Section 4 also reports how α was used to gain better insight into the phenomenon of gel-formation from solutions of isotactic polystyrene in various liquids. Section 5 suggests ways in which might help in the understanding of other phenomena in which molecular adsorption plays an important role, such as polymer permeation, separations by polymer membranes, chromatography, catalysis, and perhaps even the kinetics and selectivity of organic reactions that occur in solution.

1 Introduction

The phenomenon of polymer swelling, owing to sorption of small molecules, was known even before Staudinger reported [1] in 1935 that crosslinked poly(styrene) swells enormously in certain liquids to form two-component polymer gels. The physical state of such systems varies with the concentration (C) and molecular structure of the sorbed molecules: thus, the system undergoes transition at constant temperature from a rigid state (glassy or partially crystalline) at $C < C_g$ to a rubbery state at C_g (the transition state composition). When $C > C_g$ and the second component is a liquid, its subsequent sorption proceeds quickly to gel-saturation; and of course a solution is produced if the polymer lacks covalently bonded crosslinks or equivalent restraints. Each successive physical state exhibits its own characteristic sorption isotherm and sorption kinetics.

So far most of the pertinent literature interprets interactions between polymer and a second sorbed component on the basis of the colligative properties of the system. This information is summarized in Sect. 2 of this review. From those reports, I inferred that some sort of association of the small penetrant molecules with the repeat unit of the polymer is a prerequisite condition for the sequential changes described above. This implies that the magnitude of polymer swelling should be directly related to how well the molecular structure of the small molecule can be accommodated by the molecular structure of the polymer repeat unit in view of the macrostructure of that polymer (i.e. the crosslink density). The results obtained in our laboratory, which are summarized in Sect. 3 of this Review, are thoroughly consistent with that hypothesis. In Sect. 4 these interpretations are extended to correlate the colligative properties of Sect. 2.

2 Background: Colligative-Property Interpretations

2.1 Sorption and Diffusion in Polymeric Systems

2.1.1 Before Transition to the Rubbery State

The economic importance of polymers as physical barriers to fluids in the packaging industry and in separation processes is well known [2, 3]. Consequently sorption of small molecules by a rigid polymer, i.e. in the glassy or crystalline state, has been studied more extensively than has the subsequent sorption after the transition to the rubbery state. It was pointed out by Meares [4] and later by Barrer [5] that sorption of gases and vapors by a polymer in the glassy state ($C < C_g$) is represented best by a dual-mode process [6], i.e. the observed sorption isotherm is a combination of a Henry's law "dissolved" component term, C_D, and a Langmuir "hole filling" term, C_H, the latter pertaining to the so-called free-volume in the rigid state of polymers. The relations are:

$$C = C_D + C_H, \tag{1}$$

$$C = k_D + C_H' bP/(1 + bP), \tag{2}$$

where k_D is the Henry's law constant, P is the partial pressure of the sorbed component, and C' and b are the Langmuir capacity constant and affinity constant respectively. As the concentration, C, of sorbed material approaches C_g, the concentration at which the system changes from the glassy to the rubbery state, the dual-mode sorption isotherm passes through a positive inflection point and thereafter follows the Flory-Huggins mode [7], owing to plasticization of the system by the second component.

So long as the concentration of penetrant molecules at the surface of the polymer in contact with penetrant in a fluid state is less than C_g, the flux, F, of these molecules [down the concentration gradient (dC/dx) in the direction normal to and away from the interface] is given by Fick's law:

$$F = DS(dC/dx),\qquad\qquad\qquad\qquad\qquad (3)$$

where D and S are the diffusivity and solubility respectively of the penetrant molecules in the "rigid" matrix.

Berens [7] reported that under such conditions the logarithm of diffusivity is a linear function of the molecular diameter of the penetrant molecule. This is consistent with the hypothesis discussed in detail by Stern and Frisch [8, 9] that diffusion through a rigid polymeric matrix is proportional to the energy required to expand (i.e. swell temporarily on a molecular scale) the polymeric chains sufficiently to allow "peristaltic" motion of the penetrant molecules along these chains. This energy is presumed to be proportional to the molecular diameter of the penetrant.

2.1.2 After Transition to the Rubbery State

When the concentration of sorbed molecules at the interface of polymer and fluid penetrant is greater than C_g, plasticization occurs at this interface; and the domain of rubbery-state polymer progresses in step with the permeation front, thereby complicating the kinetics of diffusion accordingly. In the case that the contacting fluid is a liquid, the rubbery state is followed by rapid swelling to saturation such that the front of "swelled-to-saturation" polymer trails closely behind the diffusion front, the progress of which is diffusion-controlled in accordance with Fick's law (Eq. 3). The concentration gradient between the two fronts remains almost constant and very steep. The overall kinetics of diffusion, therefore, is modified Fickian, i.e. Case II diffusion [10], which is typical for glassy polymers, such as poly-(methacrylates) and poly(styrenes), immersed in swelling liquids [11-13].

The physics of sorption and diffusion through polymeric materials in the rigid and rubbery states is discussed thoroughly in several outstanding reviews [14-18].

2.1.3 Sorption of Liquid to Attain Gel-Saturation

In the case that the fluid in contact with the polymeric surface is a liquid, the amount of that liquid sorbed to attain gel-saturation (or solution) after C becomes C_g is of course considerably greater than the amount sorbed to attain C_g. The kinetics of sorption thereafter, however, is dependent upon the history of the

polymeric sample [16], and therefore difficult to interpret. This is especially true in the case of water-swellable polymers such as poly(acrylamide) [19], because trace impurities sorbed on the surface affect wetting characteristics and therefore affect the rate of water uptake accordingly.

Although the kinetics of liquid uptake to attain gel-saturation is history-dependent, the composition at the true end-state (i.e. thermodynamic equilibrium in excess liquid) is not; therefore the observed end-state is usually reproducible [19]. Gel-saturation is attained when the restraining force (per unit area) of the polymeric crosslinked network becomes equal and opposite to the osmotic pressure that causes the system to swell [20]. In other words saturation is achieved when the chemical potential of swelling liquid, μ_1, in the swollen network is equal to the chemical potential of the excess pure liquid, μ_1^0, outside the network. It was logical to anticipate that the volume of liquid sorbed per gram of polymer, at this state of thermodynamic equilibrium with excess liquid, would correlate with the molecular structure of the liquid. In fact two parameters already exist which relate the sorption affinity to the molecular structure, namely the solubility parameter, δ, first proposed by Hildebrand [21], and the interaction parameter, χ, introduced by Flory [22] and Huggins [23–26].

2.2 Parameters that Relate to Swelling Power

2.2.1 Hildebrand Solubility Parameter

Hildebrand and Scott [21] have shown that the solubility of a non-electrolyte in non-ionic solvents depends on the similarity of the thermodynamic properties of solute and solvent. They pointed out that *when entropic effects can be ignored,* the free energy of mixing of solute in solvent is determined by the sign and the magnitude of the enthalpy (ΔH). According to Hildebrand, ΔH per unit volume for such endothermic mixing is given by:

$$\Delta H = \phi_1 \phi_2 (\delta_1 - \delta_2)^2 , \tag{4}$$

where ϕ_1 and ϕ_2 are the volume fractions of the solvent and solute respectively, and $(\delta_1 - \delta_2)$ is the difference in solubility parameters. Hildebrand defined δ to be the square root of the cohesive energy density (δ^2) of the molecular species.

$$\delta^2 = \Delta E/V = (\Delta H - P \, \Delta V)/V , \tag{5}$$

where ΔE is the internal energy, which is equal to the enthalpy when $P \, \Delta V$ is zero, and V is the molar volume.

Thermodynamic relationships stated in Eqs. 4 and 5 imply that the more equal the cohesive energy densities of solute and solvent the greater is their mutual compatibility [21] (i.e. like dissolves like).

Marked differences between observed and predicted results occur, however, when the entropy effects are too great to be ignored. In the derivation of Eqs. 4 and 5, only dispersion forces between molecular components were taken into

account. The cohesive energy, however, is also dependent upon associations between polar groups and especially hydrogen bonding. It was suggested [27, 28], therefore, that the "total solubility parameter" (δ_t) is represented better by the combined effect of three components.

$$\delta_t^2 = \delta_d^2 + \delta_p^2 + \delta_h^2 , \tag{6}$$

where δ_d refers to the contribution by non-polar London dispersion forces (as considered by Hildebrand), δ_p refers to the combined Keesom dipole-dipole forces and Debye dipole-induced-dipole forces, and δ_h refers to Lewis acid-base or hydrogen-bonding forces. Fowkes [29] pointed out that δ_h for polymer-liquid systems can be calculated accurately from the acid-base relationships established by Drago [30, 31].

The solubility parameters of many volatile liquids have been calculated directly from their respective heats of vaporization and molar volumes (Eq. 5). Hoy [32] has shown that δ for relatively non-volatile liquids can be calculated from vapor pressure data using a modification of the Haggenmacher Eq. [33]. Large numbers of such data have been reported and these are collected in extensive tables [27, 28, 34].

Since the cohesive energy density (Eq. 5) is a function of the molecular structure, it was logical to attempt establishment of solvent power for a given liquid as an additive function of the molecular component contributions to the thermodynamic properties. Scatchard [35] has shown that in a homologous series of the type $R(CH_2)_nH$ [where R is H, X, Ph, OH, or OR], $(EV)^{1/2}$ is a linear function of n. Small [36] applied this observation to find additive constants for the more common groups in organic chemistry, which he termed molar attractive constants, i.e. $F_i = (E_iV_i)^{1/2}$. When the F_i constants are summed over the groups present in the molecule, the $(EV)^{1/2}$ is obtained for one mole of the substance, i.e. $\Sigma F_i = (EV)^{1/2}$; the molar cohesive energy, E, cohesive energy density, δ^2, and solubility parameter are then given by:

$$E = (\Sigma F)^2/V ; \qquad \delta^2 = (\Sigma F/V)^2 ; \quad \text{and} \quad \delta = \Sigma F/V .$$

Small [36] showed that most of the reported δ can be estimated by the last of the above three relationships, on the basis of the molecular structure of the solvent. He used this method to calculate the solubility parameter of poly(styrene) to obtain a value, $\delta_{pol} = 9.12$ $(cal/mL)^{1/2}$, which is within the range of the experimental δ-values [8.6 to 9.7 $(cal/mL)^{1/2}$] reported for this polymer [34, 37–39], [note that $(joule/mL)^{1/2} = 2.046$ $(cal/mL)^{1/2}$].

Small's success in calculating δ_{pol} for poly(styrene) encouraged others to attempt calculation of the corresponding δ_{pol} for a variety of other polymers and copolymers by means of component contributions. The value of such calculations are suspect, however, because the component contributions used to calculate the corresponding δ_{pol} were deduced from cohesive energy density data for small molecules, for which the entropy effects are not very significant; this is not the case, however, for high molecular weight multifunctional molecules, especially polymers.

The classical method for measuring the solubility parameter of a polymer is to determine the solubility of that polymer in a large number of liquids with known solubility parameters, and then to plot the observed solubility as a function of the solubility parameters of the test liquid. The solubility parameter where the polymer solubility is maximal [40] is by definition the solubility parameter of the polymer, δ_{pol}.

Gee [41] has shown that the same is normally true for swellability of crosslinked polymers, i.e. the magnitude of swelling exhibited by a polymer with δ_{pol} in a liquid with δ_{liq} increases as $(\delta_{pol} - \delta_{liq})$ approaches zero. Such correlations have been used to establish the solubility parameters of many polymers and these data are also collected in extensive tables [27, 28].

2.2.2 Flory-Huggins Interaction Parameter, χ

The Flory-Huggins theory [20, 22–26, 42, 43] considers the change in potential energy in going from the pure states of polymer and liquid to a mixture thereof. In the original form of this theory, the interaction parameter, χ, between liquid and polymer was defined as

$$\chi = z \, \Delta w_h / kT , \tag{7}$$

where k is the Boltzmann constant, z is the "number of nearest neighbors", Δw_h is the exchange interaction energy defined as the difference between the intermolecular potential, w_{12}, for a molecule of solvent interacting with a neighboring segment of polymer and the mean of the energy of interaction, w_{11}, between two molecules of solvent and the energy of interaction, w_{22}, between two segments of polymer, i.e.:

$$\Delta w_h = w_{12} - 0.5 \, (w_{11} + w_{22}) . \tag{8}$$

Originally χ was stated to be independent of polymer concentration. The χ-parameters determined by many investigators using one or another of the methods for measuring colligative properties of polymer-liquid solutions (mentioned below) show that this is not the case (see Tables 3–22 of Reference 43); nor does χ vary linearly with $1/T$ as stated in Eq. 7. Later [44] a quantity Δw_s representing an entropic contribution from contact interaction was added to the Flory-Huggins definition of χ to produce a relationship linear in $1/T$.

$$\chi = z(\Delta w_h - w_s)/kT . \tag{9}$$

Despite the above shortcomings, the Flory-Huggins theory has served as a useful model for predicting a large number of colligative properties, and has had remarkable success in providing qualitative if not quantitative descriptions of polymer-solvent systems.

Flory and Huggins have shown that the magnitude of association between polymer and sorbed liquid is reflected in the colligative physical properties of the resultant mixtures. In such cases, χ is given by:

$$\chi = (\mu_1 - \mu_1^0)/RT\phi_2^2 - [\ln(1 - \phi_2) + \phi_2(1 - V_1^0/V_2^0)]/\phi_2^2, \qquad (10)$$

where μ_1 and μ_1^0 are the chemical potentials of the liquid in solution and in pure state respectively, R is the gas constant, T is temperature, ϕ_2 is the molar fraction of the polymer and V_1^0 and V_2^0 are the volume fractions of the liquid and polymer respectively. The interaction parameter has been used as a semiquantitative measure of the "goodness" of a solvent in a given polymer-solvent system [42, 43]. A value of $\chi < 0.4$ indicates that the liquid has a relatively good affinity for the polymer, whereas a value of $\chi > 0.8$ indicates the opposite.

The χ-parameter has been related to gas sorption phenomena in polymers using a variation of Eq. 10 obtained by substituting $RT \ln(P/P_0)$ for $(\mu_1 - \mu_1^0)$ to give:

$$\chi = [\ln P_1/(1 - \phi_2) P_1^0] - \phi_2(1 - V_1^0/V_2^0)]/\phi_2^2 \qquad (11)$$

which enables one to establish χ from the sorption isotherm [44], or conversely to use a known χ to charcterize the sorption isotherm exhibited by sorbed components that cause plasticization of glassy polymers [45].

Other relationships between χ and an observable physical property such as osmotic pressure [20, 43], freezing point depression of polymer [20, 52] or solvent [20, 53], and gas liquid chromatography [46–54], were established in like fashion. The relationship determined for swelling of cross-linked polymer to thermodynamic equilibrium in excess liquid has particular significance for the subject of this review. It is given here in the form of the Flory-Rehner equation.

$$\chi = [V_1^0(v_e/V_2^0)(\phi_2/2 - \phi_2^{1/3}) - \ln(1 - \phi_2) - \phi_2]/\phi_2^2, \qquad (12)$$

where v_e is the effective number of chains connecting crosslink points, and v_e/V_2^0 is the crosslink density of the polymer, which must be established by an independent method. Unfortunately the values of χ determined from swelling measurements are less reliable than those obtained from other observable physical properties [43]. Examination of χ-parameters collected in Tables $3-22$ of Ref. 43, however, show that even those determined by the other methods are not precise enough to permit good correlation of χ with the molecular structure of the liquid sorbed by a given polymer.

The solubility parameter theory (Eq. 4), first proposed by Hildebrand [21], was combined with the Flory-Huggins theory [43] to produce yet another means for determination of χ.

$$\chi = V_1^0(\delta_{pol} - \delta_{liq})/RT - z \Delta w_s/k, \qquad (13)$$

where the solubility parameters δ_{pol} and δ_{liq} are measures of the intermolecular attractions in the polymer and solvent respectively. As stated earlier the solubility

of a polymer in a liquid is taken as maximal when $\delta_{pol} = \delta_{liq}$. Usually the constant entropic contribution, $-z \, \Delta w_s/k$, has values [55] between 0.2 and 0.5.

Values of δ for many liquids have been reported, and these have been recorded in extensive Tables [27, 28, 32, 34, 56–59]. The availability of these data provide an easy means of estimating δ. The solubility parameter theory also has serious shortcomings, however, which limits further the reliability of thermodynamic properties computed by the combination of both theories. Nevertheless it does provide useful qualitative, if not quantitative, descriptions of polymer-solvent systems.

2.3 Forces of Molecular Association that Affect Swelling

Explicit in the Flory-Huggins theory [22–26] is the realization that forces of molecular association are responsible for the finite change in energy that accompanies transformation of pure polymer and pure liquid to a solution of the two components. This change involves rupture of a finite number of molecular liaisons between like molecules in the initial state and formation of a finite number of liaisons between unlike molecules in the end-state. The magnitude of energy change depends on the summation of these forces. There is uncertainty, however, in the definition of the kind and number of liaisons per unit species in the original states, especially that extant in the polymer, which may be crystalline or amorphous but usually is a mixture thereof. The energy required to disrupt the crystalline domains is greater than that required for disruption of amorphous domains. Moreover polymers classified as crystalline contain a finite amount of amorphous region, and conversely polymers classified as completely amorphous contain chain ordering even in solution [60]. Therefore it is difficult to define the initial state or even the true average number of nearest neighbors with respect to a given monomer unit. Also uncertain is the number of liaisons between monomer unit and small molecules in the final state, which presumably must relate to the molecular architectures of these associated species.

Unless the nature and number of the liaisons in the initial and final states are known with certainty, the reliability of the χ-parameter (based on Eq. 7 and relationships derived therefrom) suffers accordingly, even with the most accurate thermodynamic methods for measuring colligative physical properties of polymer-liquid systems. It would be well, therefore, to develop methods for defining the mode of complexation at the initial and final states on a molecular basis. Elucidation of the molecular nature of these complexations at gel-saturation (or in true solution) is an end-objective of the work described in Sect. 3 of this review.

Perhaps the first physical evidence that the force of association between polymer and sorbed liquid is indeed significant came from vapor depression data; for example the vapor pressure of toluene in a solution of 0.01 moles of poly(styrene) (number average molecular weight 290,000) per mole of toluene is 10 fold less than the expected value calculated on the basis of vapor pressure depression in solution [43]. That this force is strong enough to affect the rheological properties of such solutions was reported by Shrag [61] and also by Lodge [62], who studied

oscillatory flow birefringence of polymer solutions in high-viscosity solvents. They showed thereby that addition of only small amounts of polymer affect abnormally the solvent viscosity, owing to induced ordering of the surrounding molecules that apparently extends even beyond the first layer of adsorbed molecules. Consistent with this concept of induced ordering are the observations of Bastide [63, 64] and Edwards [65]. Their findings indicate that when high-molecular-weight polymer (MWt > 10^6) is plasticized with low-molecular-weight polymer (MWt < 10^3), and the system is stretched at its rigidification temperature to effect orientation of the high-molecular-weight component, the low-molecular-weight component is similarly oriented, which implies multidentate association of the repeat units in the low-molecular-weight component with the repeat units in the high-molecular-weight component.

The many studies of solvent effects in organic chemistry [66] have shown that liaisons between reactant molecules and the molecules of the solvent affect significantly the rate and even selectivity of reactions that occur in solution. These liaisons usually are between the functional groups in the reactant molecules and the functional groups of the solvent. This is especially apparent in those cases that involve strong associative forces such as hydrogen bonding. The same is true for polymer-liquid systems. Thus, poly(ethylene oxide) is readily soluble in water at room temperature owing to hydrogen bonding of the oxygen atoms in the polymer with the hydrogen atoms in the water. When the temperature of such solutions in raised to about 45 °C, however, the polymer separates from solution, owing to thermally induced dissociation of hydrogen bonding.

Dole [67, 68] observed that small molecules associate firmly with "functional" sites in polymeric materials. He studied sorption of water and organic vapors by synthetic high molecular weight polymers. He noted that the ratio (a/N) of sorbed molecules (a) to available adsorption sites (N, i.e. the total number of functional groups in the polymer) increases with the partial pressure of the vapor being sorbed. In the case of water sorption at 100% RH by poly(N-vinyl 2-pyrrolidinone) a/N was almost one, and in the case of water sorption by poly(vinyl methoxyacetal) [68] it was even greater than one.

Later Yokoyama and Hiraoka [69], who studied evaporation of aqueous solutions of poly(acrylic acid), observed that there is a well-defined ratio of adsorbed water molecules per carboxylic acid group, and that this ratio increases with percent neutralization of the acid groups, such that a/N increases from one at 0% neutralization to four at 100%.

Fowkes [29], who studied the solubility of chlorinated poly(vinyl chloride) in various liquid esters, noted that the solubility of such polymers in these solutions and the intrinsic viscosities thereof decrease with temperature. He interpreted this to mean that the increase in temperature caused dissociation of liaisons formed between acidic hydrogens in the polymer and basic ester groups of the solvent. His own observations and those reported by others, as discussed above, led him to articulate the hypothesis that the "true" solute in polymer-liquid solutions is not the "naked" polymer, but rather it is the polymer "adorned" with solvent molecules that are essentially immobilized by adsorption to the polymer. To be sure these molecules are in exchange equilibrium with the non-adsorbed molecules

that comprise the solution. In the above cases the increase in temperature causes displacement of the solvent-polymer-complex equilibrium in favor of dissociation into polymer and liquid, with concomitant self-association of polymer.

Additional evidence that monomer units in the polymer do "complex" with molecules of the solvent comes from studies of the gel-formation that occurs when polymer solutions are cooled well below room temperature [70–72] to induce spinodal phase separation. The polymer does not redissolve until the temperature is raised well above the formation temperature of the system. These gels are supported by interconnected rigid polymer domains, at least part of which are in the form of "helical bands" [72–74]. In the case of isotactic polystyrene these "helical bands" consist of 3_1-helices, which self-aggregate to form crystalline domains. Gelation also occurs with atactic polymer, presumably caused by some form of self-association that does not lead to the well-organized domains that are found for isotatic polymers [74–78] such as isotactic poly(styrene), isotactic poly(acrylates), and also for poly(N-vinylcarbazole), and poly(phenylene oxides). In such cases the structure of the helices that comprise the ordered domains is dependent upon the solvent in which the gel is formed [76–78]. The investigators of this phenomena ascribed the cause of association to dispersion force interactions between the functional groups in the polymer segments and the solvent molecules, such that the distance between segments is influenced by the size and shape of the solvent molecule.

The existence of a solvent-polymer complex in the "helical aggregate" domains was verified by Guenet and co-workers [79–83], who studied the thermal properties, enhanced small-angle X-ray scattering, neutron scattering, and electron photomicrographs of these ordered domains. They showed that a solvated 3_1 helix is formed initially and that this is transformed in turn to a more stable but markedly less solvated 3_1 helix on aging. They concluded that these ordered domains have a structure reminiscent of nematic polymers (i.e. liquid-crystalline material) associated with solvent molecules that affect chain-chain interactions [82]. They showed also that these domains have well-defined ratios of "guest" solvent molecules to monomer units in the "host" polymer. They suggested that the local organization of the solvent molecules around the polymer chain to form a "crystalline" complex strongly governs the ability for physical gelation.

Guenet suggested that this ratio may represent a parameter characteristic of the composition of the helix, which he designated as $\bar{\alpha}$, referring to the number of adsorbed molecules per monomer unit of polymer that separated from solution. If one accepts that the force of association between polymer and solvent is as significant in solution (as suggested by Shrag) as it is in the helix (as suggested by Guenet), then it should be possible to determine the ratio of adsorbed molecules per repeat unit of polymer in the non-crystalline region as well as in the crystalline region of such gels. Comparison of this ratio with the Guenet ratio ($\bar{\alpha}$) would help elucidate how nucleation and propagation of the ordered helical domains come about. To establish such a ratio requires an in-depth study of polymer swelling, which in turn requires a reliable, easy-to-use method for measuring polymer swelling quantitatively.

2.4 Methods of Measuring Polymer Swelling at Liquid Saturation

It is well-known that the volume of a given liquid sorbed at constant temperature by a cross-linked polymer varies inversely with the crosslink density of that polymer [1, 20, 84–90]. It is equally well known [1, 20, 39, 91–94] that determination of polymer swellability was, and still is, a very time-consuming procedure that often yields results of only limited reliability, owing primarily to the ill-defined dimensions and/or inability to measure accurately the weight of the gelled polymer sample at equilibrium swelling in excess liquid. The early investigators of poly(Sty-*co*-DVB) swelling [1, 39] waited 3 to 7 days for copolymer samples to equilibrate with solvent before removing the sample for damp-drying between absorbent materials and subsequent measurement of liquid uptake, either gravimetrically or volumetrically. The reproducibility of the measured volume or weight of the damp-dried gelled polymer samples was poor at best, and consequently as many as 40 replicated determinations were averaged together to obtain one reliable value [39] for the swelling ratio $(V_g - V_p)/V_p$, where V_g and V_p are the volumes of the polymer in the gelled and dry states, respectively.

Volumetric methods based on liquid displacement have been developed by Bobin [95], Garvey [96], Zhuravlev et al. [97], Schreiber et al. [98], and Buckley [84], which generally are more precise for measuring swelling than the earlier methods based on dimensional changes. Chicklis and Grasshoff [99] developed an optical device for measuring liquid uptake, which appears to improve the sensitivity of earlier devices for measuring swelling of very thin (1 to 10 µm) films, and the reduced dimension lessens the time required to attain equilibrium swelling before final measurement.

More recently it has been shown that it is possible to measure the dimensional changes of microbeads, upon relatively rapid saturation in a test liquid, by means of photomicrographic techniques [100–102]. Although considerably more precise than those noted above, these measurements are still very time consuming and require expensive instrumentation. Methods for measuring swelling volumetrically in "batch" quantities of microbeads have also been reported [103, 104], but these too entail a long and time-consuming protocol for each determination.

Owing to higher surface-to-volume ratio, the time to attain gel-saturation using microbeads or powders is even less than that for very thin films. Polymers in these forms have been used in gravimetric methods, which are especially useful for measurement of sorption of gases and vapors [7, 45, 105–116]. Peppas [117] has shown, however, that this may not be such an advantage in the case of liquids, because of a so-called "relaxation effect" [93], which results in an "overshoot"; i.e. the volume of sorbed liquid becomes maximal in a relatively short time as expected, but then decreases slowly thereafter to an asymptotic limit that is reached in about a month. Peppas attributes this slow decay in sorption capacity to "relaxation" of polymer chains. Such an "overshoot" was also observed much earlier by Boyer [39], who used relatively larger polymer samples, but the magnitude of the effect observed by Peppas was greater, owing to the much shorter time to reach maximal saturation, which minimizes slow "relaxation" during the interim. The total time required to attain the stable end state, however, was similar.