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Chemistry of Polymers

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ABSTRACT

A brief examination of some issues of current interest in polymer physical chemistry is provided. Emphasis is placed on topics for which the interplay of theory and experiment has been particularly fruitful. The dominant theme is the competition between conformational entropy, which resists distortion of the average chain dimensions, and potential interactions between monomers, which can favor specific conformations or spatial arrangements of chains. Systems of interest include isolated chains, solutions, melts, mixtures, grafted layers, and copolymers. Notable features in the dynamics of polymer liquids are also identified. The article concludes with a summary and a discussion of future prospects.

INTRODUCTION

1.A. General Remarks. Macromolecules form the back- bone of the U.S. chemical industry, and are essential functional and structural components of biological systems.[1] Yet, the very existence of long, covalently bonded chains was in dispute only 70 years ago. The past 50 years has seen a steady growth in understanding of the physical properties of chain molecules, to the point that the field has achieved a certain maturity. Nonetheless, exciting and challenging problems remain. Poly- mer physical chemistry is a richly interdisciplinary field. Progress has relied on a combination of synthetic ingenuity, experimental precision, and deep physical insight. In this article, we present a brief glimpse at some interesting current issues and acknowledge some notable past achievements and future directions.

1.B. Basic Concepts. When N monomers join to form a polymer, the translational entropy is reduced. However, the entropy associated with a single molecule increases dramatically, due to the large number of different conformations the chain can assume.[2–11] Conformational changes occur at both local and global levels. Local conformational states with differing energies depend on the chemical nature of substituent atoms or side groups, X, as sketched in Figure 1. Typically, there are three rotational conformers at every C–C bond. These states, and the torsional energy as a function of rotation about the middle C–C bond, are represented in Figure 2. If Δ kT, there exists complete static (i.e., equilibrium-averaged) flex- ibility. Even for higher values of Δ /kT, where the trans conformation is preferred, the chain will still be flexible for large N. We can define a statistical segment length, b, over which the local stiffness persists; b depends on the value of Δ /kT.[12] But, beyond this length, bond orientations are uncor- related. The parameter which determines the overall chain flexibility is b/L, where L, the chain contour length, is $\sim N$. If b/L 1, the chain has complete static flexibility; for b/L 1, the chain is a rigid rod. Similarly, $\Delta E/kT$ determines the dynamical flexibility. If $\Delta E/kT$ 1, the time $\tau_{seg} \sim \exp(\Delta E/kT)$ required for trans T gauche

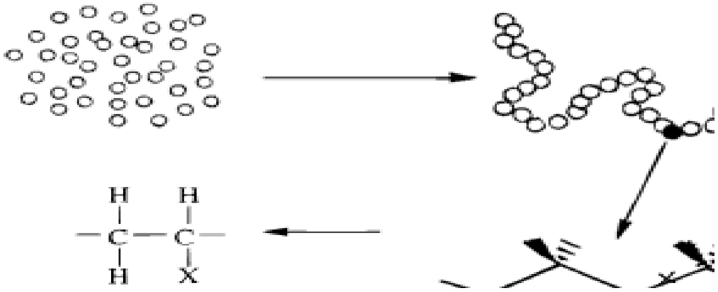

Figure 1. N monomers combine to form one linear chain, here with an all-carbon backbone and a pendant group denoted X.

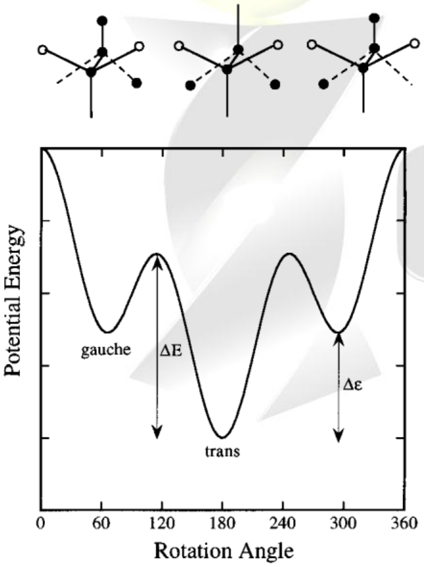

Figure 2. Schematic of the potential energy as a function of rotation about a single backbone bond and the corresponding trans and gauche conformers.

isomerizations is short (i.e., picoseconds to nanoseconds in solution), and the chain is dynamically flexible. For higher values of $\Delta E/kT$, dynamical stiffness arises locally. However, for large scale motions, involving times much greater than τseg, the chain can still be taken to be dynamically flexible The chemical details of the monomers and solvent affect the local properties, b and τseg. Macroscopic, or global, properties do

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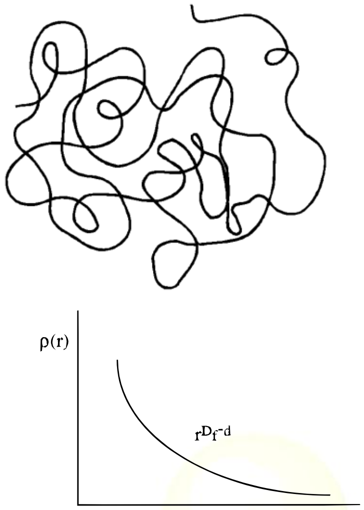

Figure 3. Schematic of a random coil polymer, and the density distribution F(*r*) for $b \ll r \ll Rg$.

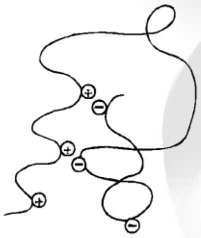

Figure 4. Illustration of (a) complete registry and (b) entropic frustration for a chain bearing both positive and negative charges.

not depend directly on the local static and dynamic details and can be represented as universal functions (*i.e.*, independent of chemical identity) by "coarse-graining" the local properties into phenomenological parameters. Polymer physical chemistry deals with both the macroscopic properties, dictated by global features of chain connectivity and interactions, and the phenomenological parameters, dictated by the local details.

Connectivity leads to long-range spatial correlations among the various monomers, irrespective of potential interactions between monomers.[13,14] Such a topological connectivity leads naturally to statistical fractals,[15] wherein the polymer structure is self-similar over length scales longer than b but shorter than the size of the polymer. For the ideal case of zero potential interactions, the monomer density F(r) at a distance r from the center of mass decays in three dimensions as $1/r$,[6,7] as shown in Figure 3. Consequently, the fractal dimension of the chain D_f ❩ 2. This result is entirely due to chain entropy, but the long-ranged correlation of monomer density can be modified by potential interactions. In general, F(r) decays as $(1/r)^{d-D_f}$, where d is the space dimension. Equivalently, the scaling law between the average size of the polymer, *e.g.*, the radius of gyration R_g, and N is $R_g \sim N^{\nu}$, where ν ❩ $1/D_f$. The value of D_f is determined by the compromise between the entropy arising from topological connectivity and the energy arising from potential interactions between monomers. For example, most polymer coils with nonspecific short-ranged interactions undergo a coil-to-globule transition upon cooling in dilute solutions, such that the effective fractal dimension increases to about 3. Or, the chain backbone may be such that b increases at low T; in this case the chain can undergo a coil-to-rod transition, where D_f decreases monotonically to about 1. This competition between conformational entropy and monomer–monomer interactions represents a central theme of this article.

When specific, strong interactions such as hydrogen-bonding or electrostatic forces are present, chain conformations can suffer entropic frustration, as illustrated in Figure 4 for charge-bearing monomers.[16,17] In the process of forming the fully registered state (a) between the oppositely charged groups, the chain, via random selection, can readily form a topological state such as (b). The chain is entropically frustrated in state (b) since the two registered pairs greatly reduce the entropic degrees of freedom of the chain. The chain needs to wait until the pairs dissociate, accompanied by a release of entropy, and the process of registry continues. This feature of entropic frustration is common in macromolecules containing chemically heterogeneous subunits and in polymers adsorbing to an interface. When a chain is frustrated by topological constraints, not all degrees of freedom are equally accessible, and standard arguments based on the hypothesis of ergodicity may not be applicable. The identification of the resulting equilibrium structure is a challenge to both experiment and theory. The kinetics of formation of such structures is also complicated by the diversely different free energy barriers separating the various topological states. In general, the distance between different trajectories of the system diverges with time, and the presence of free energy minima at intermediate stages of evolution delays the approach to the final optimal state.17 Several of these features are exemplified by biological macromolecules.

1.C. Recent Developments. *Synthesis.* Conventional poly- merization methods, either of the step-growth (*e.g.*, polycon- densation) or chain-growth (*e.g.*, free radical) class, produce broad molecular weight distributions and offer little control over long-chain architectural characteristics such as branching. Although of tremendous commercial importance, such approaches are inadequate for preparing model polymers, with tightly controlled molecular structures, that are essential for fundamental studies. For this reason, living polymerization has become the cornerstone of experimental polymer physical chemistry. In such a synthesis, conditions are set so that growing chain ends only react with monomers; no termination or chain transfer steps occur. If a fixed number of chains are initiated at t) 0, random addition of monomers to the growing chains leads to a Poisson distribution of chain length, with a polydispersity (Mw/Mn) that approaches unity in the high N limit. Block copolymers can be made by sequential addition of different monomers, branched chains by addition of polyfunctional terminating agents, and end-functionalized polymers by suitable choice of initiator and terminator. Examples of chain structures realized in this manner are shown in Figure 5.

The most commonly used technique, living anionic poly- merization, was introduced in the 1950s.18,19 It is well-suited to several vinyl monomers, principally styrenes, dienes, and methacrylates. However, it suffers from significant limitations, including the need for rigorously excluding oxygen and water, a restricted set of polymerizable monomers, and reactivity toward ancillary functionalities on monomers. Consequently, there is great interest in developing other living polymerization protocols.20 Over the past 15 years, group transfer,21 ring- opening and acyclic diene metathesis,22-24 cationic,25,26 and even free radical27 living polymerization methods have been demonstrated. Soon a much broader spectrum of chemical functionalities will become routine players in the synthesis of model polymers, and commercial products will rely increasingly on controlled polymerization techniques.

Theory. The genesis of polymer theory is the realization that a conformation of a polymer chain can be modeled as the Physical Chemistry of Polymers

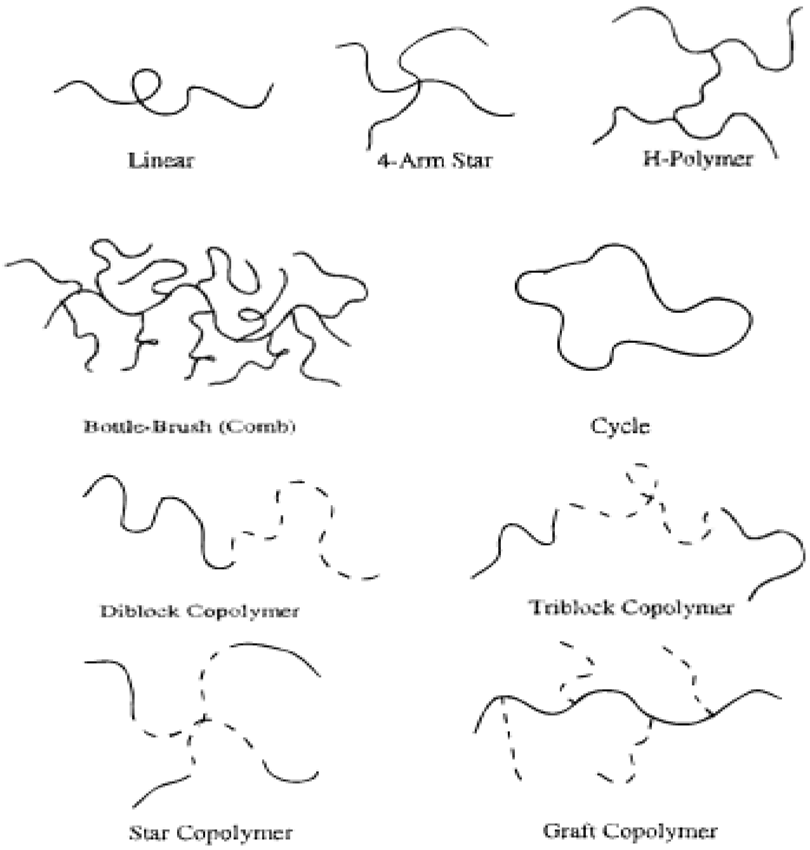

Figure 5. Various polymer topologies achieved by living polymerization techniques.

trajectory of a random walker.$^{2-11}$ In the simplest case, the apparent absence of any energy penalty for self-intersection, the statistics of random walks can be successfully applied. In the long-chain limit, the probability distribution $G(\mathbf{R},N)$ for the end-to-end vector of a chain, $\mathbf{R}$, is Gaussian, under these (experimentally realizable) “ideal” conditions. Now G satisfies a simple diffusion equation, analogous to Fick’s second law:

$$\frac{\partial}{\partial N} - \frac{b^2}{6}\frac{\partial^2}{\partial \mathbf{R}^2} \quad G(\mathbf{R},N)\ \mathbf{)}\ \delta(\mathbf{R})\ \delta(N) \qquad (1.1)$$

Thus, N corresponds to time, G to concentration, and $b2$ to a diffusivity. The right-hand side simply requires that the chain beginning at the origin arrive at RB after N steps. When there is a penalty for self-intersections, due to excluded volume inter- actions between monomers, it is possible to compose a pseudo- potential for segmental interactions. The diffusion equation now contains an additional potential term which, in turn, depends on G:13,28

$$\frac{\partial}{\partial N} - \frac{b^2}{6}\frac{\partial^2}{\partial \mathbf{R}^2} + \frac{V[G(\mathbf{R})]}{kT}\ G\ \mathbf{)}\ \delta(\mathbf{R})\ \delta(N) \qquad (1.2)$$

This requires a self-consistent procedure to determine G, from which various moments of experimental interest can be derived; in essence, this process amounts to making an initial guess for G, calculating the potential term, and numerically iterating until the chosen G satisfies eq 1.2 For multicomponent polymer systems, the local chemical key feature of SANS is the sharp difference in coherent scattering cross section between hydrogen and deuterium; isotopic substitution thus permits measurement of the properties of single chains, or parts of chains, even in the bulk state. All three experiments give information on the static structure details and the various potential interactions between effective segments can be parametrized by writing an appropriate “Edwards Hamiltonian” (see eq 2.1 and associated discussion).7-9 Standard procedures of statistical mechanics (with varying levels of approximation) are then employed to obtain the free energy as a functional of macroscopic variables of experimental interest.8,29-31 Such density functional approaches lead to liquid- state theories derived from coarse-grained first principles.8 The free energy so derived, reflecting a quasi-microscopic description of polymer chemistry, is also used to access dynamics.

Simulation. Lattice walks are used to determine *G* for a single chain with potential interactions, with some site potential energy to simulate chain contacts. A key feature of this approach is to use generating Function 34-35

$$P(x)\underset{N)0}{)}\; p\, x^{N} \qquad (1.3)$$

where *pN* are probability functions describing chains of *N* steps; this greatly reduces the computational complexity. For fully developed excluded volume, the exact method enumerates all possible nonintersecting random walks of *N* steps on a lattice; assuming all configurations are *a priori* equally probable, various averages are then constructed. In the alternative Monte Carlo method, a chain of successively connected beads and sticks is simulated on various lattices, or off-lattice, and statistical data describing the chain are accumulated. The stick can be either rigid or a spring with a prescribed force constant; the latter case is referred to as the bond-fluctuation algorithm.38

As before, the beads interact through an appropriate potential interaction. Once an initial configuration is created, a randomly chosen bead is allowed to move to a new position without destroying the chain connectivity. The energy of the chain in its new configuration is computed, and the move is accepted or rejected using the Metropolis algorithm.39 Instead of making local moves, so-called pivot algorithms can be used to execute cooperative rearrangements.40,41

The use of molecular dynamics,42 in which Newton's law is solved for the classical equation of motion of every monomer, has been restricted to rather short chains.43,44 Such atomistic simulations are difficult for polymers since even a single chain exhibits structure from a single chemical bond (*ca*. 1 Å) up to *R*g (*ca*. 10-103 Å), and the separation in time scale between segmental and global dynamics is huge. Brownian dynamics is an alternative method,45 wherein

Newton's equation of motion is supplemented with a friction term and a random force, which satisfy a fluctuation-dissipation theorem at a given *T*. Since the friction coefficient is in general phenomenological, this Langevin equation is usually written for an effective segment. All of the above methodologies are in current use.

Experimental Techniques. Polymers require a variety of techniques to probe their multifarious structures, dynamics, and interactions. Polymer structure may be probed in real space, by microscopy, and in Fourier space, by scattering.

Both approaches are important, but scattering has been more central to the testing of molecular theory. Classical light scattering (LS) and small-angle X-ray scattering (SAXS) have been used for over 50 years, but small-angle neutron scattering (SANS) has, in the past 25 years, become an essential tool.46-49 The factor, *S*(*q*):

$$S(q) \,\boldsymbol{)}\, \frac{1}{N^2} \overset{N}{\underset{j}{}} \; \overset{N}{\underset{k}{}} \; \hat{a}_j \hat{a}_k{}^* \exp[-i b_q .(b_j - b_k)] \qquad (1.4)$$

where bq is the scattering vector ()(4π/λ) sin(θ/2), with λ the wavelength and θ the scattering angle). *S*(*q*) generally contains both intramolecular ("form factor") and intermolecular ("structure factor") correlations and in the thermodynamic limit (*q* f 0) measures the osmotic compressibility of the mixture. Consequently, scattering techniques provide valuable information on molecular interactions, and not just structure. The accessible length scales depend on *q* and are typically 30-104 nm for light, 0.5-50 nm for SANS, and 0.1-100 nm for SAXS.

This combined range exactly matches that associated with macromolecular dimensions monomer sizes on the order of 1 nm, molecular sizes up to 0.5 μm, and aggregates or multi- molecular assemblies from 0.01 to 10 μm. The scattering power of individual monomers is embodied in the factor *âj*, which depends on refractive index for LS, electron density for SAXS, and nuclear properties for SANS.

Polymers exhibit dynamics over many decades of time scale, ranging from segmental rearrangements in the nanosecond regime to long-range chain reorganizations that can take minutes or even days. Two classes of technique have proven particularly revealing in recent years: measurements of rheological proper- ties and translational diffusion. The former concerns the response of a fluid to an imposed deformation; in the dynamic mode, the deformation is sinusoidal in time, and frequency variation permits investigation of different time scales of motion. Significant progress in commercial instrumentation has made these techniques accessible to a wide variety of researchers. The centrality of chain diffusion to the reptation model of entangled chain dynamics (V*ide infra*) spurred an explosion of technique development and application in the late 1970s and 1980s, methods which are now being profitably applied to a much broader range of issues. Examples include forced Rayleigh scattering (FRS)50 and forward recoil spectrometry (FRES);51 more established methods, such as pulsed-field gradient NMR52 and fluorescence photobleaching recovery,53 also found many new adherents. Dynamic light scattering (DLS) has proven to be a particularly versatile and fruitful technique. It provides information on the dynamic structure factor, $S(q,t)$ (see eq 2.10 and associated discussion). Although most often applied to monitor mutual diffusion processes in solutions and blends, it can also reflect viscoelastic properties and conformational relaxation.54-56

The importance of the surface, interfacial, and thin film properties of polymers has encouraged application of surface- sensitive or depth-profiling techniques. Some of these are familiar to the analytical chemistry communitysESCA, SIMS, reflection infrared, and ellipsometry. Others, particularly X-ray and neutron reflectivity,57,58 and the aforementioned FRES, are less familiar. As with SANS, neutron reflectivity exploits the scattering contrast between 1H and 2H to probe composition profiles normal to an interface, with spatial resolution below 1 nm. The wavevector dependence of the specular reflectance is sensitive to gradients of scattering cross section, even of buried interfaces, and for appropriate samples can provide a uniquely detailed picture of molecular organization. As with scattering methods in general, reflectivity suffers from the inversion problem: the absence of phase information means that one can never obtain a unique real-space transform from the data.

1.A. Brief Outline. For an article of this length, and a topic of this breadth, a good deal of selectivity is necessary. We have employed several criteria in this selection. First, we highlight areas that are of great current interest and in which substantial progress has been made in recent years. Some of these are "classical" issues (*e.g.*, excluded volume, chain entanglement) which have been examined for over 50 years, whereas others (*e.g.*, polymer brushes, copolymer phase dia- grams) are of more recent vintage. Second, we emphasize phenomena which illustrate the concepts identified in section
1.B; some important problems which are not inherently poly- meric (*e.g.*, the glass transition) are omitted. Third, and most important, we feature problem areas in which the interplay of theory and experiment has proven to be particularly fruitful.

Necessarily there is a great deal of personal taste, some might say arbitrariness, to the selection. Certainly there are serious omissions, both in topical coverage and in thorough referencing. For example, liquid crystalline polymers, polymer crystallization, polymers with interesting electrical and optical properties, polymer gels, and networks are all neglected. In the interests of clarity and simplicity, there are many issues for which the discussion is overly simplified. For all these sins and more, we can only apologize in advance.

In the next section, we consider the equilibrium and dynamic properties of isolated chains and then proceed to concentrated solutions, melts, and mixtures in section 3. In section 4 interfacial polymer systems are considered: polymer brushes, block copolymers, and micelles. We conclude with a brief summary and a discussion of possible future directions.

2. Dilute Solutions

2.A. Equilibrium. The probability distribution function G(RB,L) of the end-to-end vector RB of an isolated chain with interactions can be expressed by the path integral13

$$G(\mathbf{R},L) = \int_{\mathbf{b}(0)}^{\mathbf{b}(L)} \mathrm{d}[\mathbf{b}] \exp\left[-\frac{d}{2b^2}\int_0^L \mathrm{d}s \left(\frac{\mathrm{d}\mathbf{b}}{\mathrm{d}s}\right)^2 - \frac{1}{2}\int_0^L \mathrm{d}s' \int_0^L \mathrm{d}s \; V[\mathbf{b}(s) - \mathbf{b}(s)] \right] \qquad (2.1)$$

where $\mathbf{r}(s)$ is the position vector of the sth monomer in d-dimensional space; d[$\mathbf{r}$] implies summation over all possible paths between the ends of the chain $\mathbf{r}(0)$ and $\mathbf{r}(L)$, and V is the potential interaction between the sth and s th monomers. The argument of the exponential is referred to as the Edwards Hamiltonian; the first term, the “kinetic energy”, reflects the chain conformation, while the second, the “potential energy”, accounts for the energetics of monomer—monomer interactions. Usually it suffices to assume that V is short-ranged and is represented by a pseudopotential of strength w, $V = w\delta^d[\mathbf{r}(s) - \mathbf{r}(s)]$, where δ^d is the d-dimensional delta function. The excluded volume parameter, w, can be viewed as the angular- averaged binary cluster integral for a pair of segments:5,7

$$wb^2 = \int \mathrm{d}[\mathbf{b}(s) - \mathbf{b}(s)]\; 1 - \exp(-V) \qquad (2.2)$$

Clearly w depends on T and on the (nonuniversal) specifics of the polymer and solvent. It is possible to define a special temperature, Θ, in the vicinity of which

$$w \sim (T - \Theta)/T \qquad (2.3)$$

This Flory theta temperature2 is somewhat analogous to the Boyle point of the van der Waals gas, in that it represents the temperature at which excluded volume repulsions and monomer-monomer attractions cancel, and the osmotic second virial coefficient vanishes. It is also the critical temperature for liquid-liquid phase separation in the infinite *N* limit. Conse- quently, both "upper" (*i.e.*, UCST) and "lower" (*i.e.*, LCST) theta temperatures are possible, although the former is much more common. At *T*) Θ, *w*) 0 and *G*(RB,*L*) reduces to a Gaussian distribution. For this case, the mean-square segment- to-segment distance between segments *i* and *j* is proportional to |*i* - *j*|, so that *R*g ∼ *N*1/2.59 If *w* > 0, monomer-monomer interactions are effectively repulsive, and the chain expands. Dimensional analysis of the Edwards Hamiltonian shows that the free energy is of the form6

$$\frac{F}{kT} \sim \frac{R_g^{2}}{L} + \frac{wL^{2}}{R_g^{d}} \qquad (2.4)$$

with the first term reflecting the conformational entropy and the second the interactions. Since in the absence of excluded volume effects *R*g ∼ *L*1/2, the appropriate dimensionless coupling constant is *z*) *wL*(4-*d*)/2.5,8 Therefore, *R*g may be written as *L*1/2R(*z*), where the expansion factor, R(*z*), needs to be deter- mined. By minimizing *F* with respect to *R*g, one obtains *R*g ∼ *Lv*, with *v*) 3/(*d* + 2). More rigorous derivation shows this exponent to be correct, in the asymptotic limit of *z* f , except for *d*) 3, where *v* ≈ 0.588, not 3/5.8,60,61

The crossover formulas for *R*g have been derived for arbitrary values of *z* between 0 and ,8,11,60-62 in agreement with many experimental data.63

For *T* e Θ the chain shrinks and eventually undergoes a coil- to-globule transition.8,64-66 It is now necessary to include three- body potential interactions in the Edwards Hamiltonian, where V is the new parameter:

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$$G(\mathbf{R},L)) \int_{\mathbf{b}(0)}^{\mathbf{b}(T)} d[\mathbf{b}] \exp -\frac{d}{2b}\int_0^T ds \left(\frac{\partial \mathbf{b}}{\partial s}\right)^2 -$$

$$\frac{w}{2}\int_0^T ds \int_0^T ds' \, \delta\,[\mathbf{b}(s) - \mathbf{b}(s')] -$$

$$\frac{V}{2}\int_0^T ds \int_0^T ds' \int_0^T ds'' \, \delta\,[\mathbf{b}(s) - \mathbf{b}(s')][\mathbf{b}(s') - \mathbf{b}(s'')] \qquad (2.5)$$

The free energy can be written (*d*) 3)

$$\frac{F}{kT} \sim \frac{R_g^{\,2}}{L} + \frac{wL^2}{R_g^{\,3}} + \frac{VL^3}{R_g^{\,6}} \qquad (2.6)$$

For asymptotically large |*z*|, R is inversely proportional to |*z*|. Thus, a plot of R|1 - Θ/*T*|x*M* versus |1 - Θ/*T*|x*M* should be linear as *T* f Θ and constant for *T*/Θ . 1, as illustrated for polystyrene/cyclohexane in Figure 6.67,68 The stiffness of the polymer backbone may be addressed by calculating explicitly the tensional energies associated with rotations about C-C bonds as functions of torsional angle and by calculating how far chain orientation persists along the chain contour. The rotational isomeric state model,3,4

which is equivalent to a one-dimensional Ising model, permits exact calculations in the absence of any long-range correlations along the backbone. The key result, that the molecule is rod-like if the chain is sufficiently stiff, is physically apparent. Effective size exponents, *v*eff, can be ascribed to semi flexible chains in dilute solutions. As the temperature is lowered, *v*eff changes continuously from about 3/5 to 1. Instead of possessing uniform curvature along the chain contour, there are several polymers where many rod-like regions, interspaced by coil-like regions, are formed. The formation of rod-like regions is a cooperative phenomenon and can appear as an abrupt change from a coil to a “helix” or rod configuration as the temperature is lowered; this is referred to as the helix-coil transition, although it is not a true phase transition.69

Chain stiffness can also arise from charged monomers. The size of a polyelectrolyte chain in solution has been studied extensively, but the experiments are difficult and not yet definitive, as recently reviewed.70 If the charge density on the polyelectrolyte chain is sufficiently high and the electrostatic interaction is unscreened, the chain is rod-like. Questions about the electrostatic persistence length induced by the presence of charges on the chain,71 the extent of counterion condensation on the polyelectrolyte,72 and the structure factor are abundant

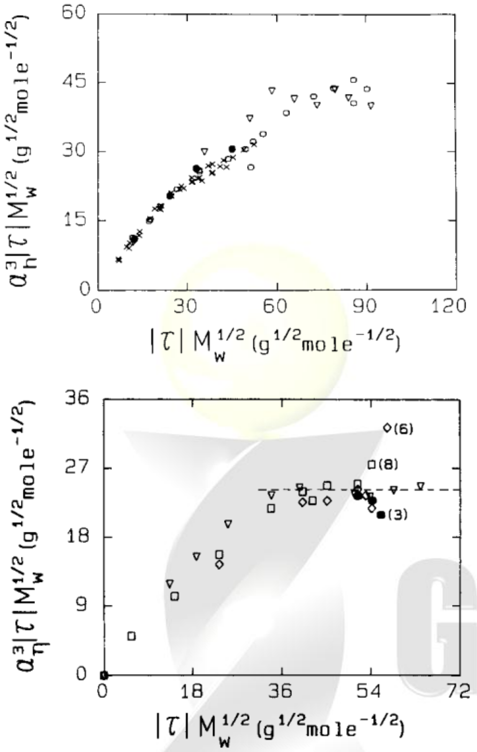

Figure 6. Coil-to-globule transition for polystyrene in cyclohexane; Rh and Rη denote the expansion factors obtained by dynamic light scattering and intrinsic viscosity, respectively, and τ ❩ 1 – Θ/T.[67,68] The different symbols reflect measurements on different molecular weight samples. Reproduced with permission from refs 67 and 68.

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(12) More properly, the local stiffness is characterized by a persistence length, which is closely related to, but logically distinct from, the statistical segment length. However, the latter is more useful in computing flexible chain dimensions and will be used exclusively throughout the paper.

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