CHAPTER 1

INTRODUCTION

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Water-soluble polymers are those, which can either dissolve or swell in water to form either solution or hydrogel. The key to water solubility of water-soluble polymers lies in positioning sufficient number of hydrophilic functional groups along the backbone or side chains of polymers.[1] Some of the major functional groups that possess sufficient polarity, charge or hydrogen bonding capability for hydration are

—COOH, $\text{—COO}^-\text{M}^+$, —CONH_2, $\text{—SO}^-{}_3\text{M}^+$, $\text{—SO}_3\text{H}$, $\text{—NH}_2\text{OH}$, —NH_2, —SH, —NHR, and $\text{—N R}_3^-\text{ X}^+$, where M, R and X stand for metal, alkyl and halogen respectively.

These functional groups not only impart solubility but also bring many useful properties like chelating, dispersing, absorption, flocculation, thickening, drag reduction etc. to the polymers. Water-soluble polymers may be used as materials (e.g. super absorbent, soluble packaging, soft contact lens etc.), but most applications arise from their properties in solution, especially from their ability to modify the rheology of an aqueous medium and to adsorb from solution onto particles or surfaces. Moreover, some of these groups can further react to form other kinds of functional groups. The water-soluble polymers, therefore, find extensive applications in areas including water treatment, cosmetics, personal care product, pharmaceutical, oil recovery, pulp and paper production, mineral processing, agriculture etc.

Water-soluble polymers can be divided into three categories, viz., naturally occurring polymers (e.g. polypeptides, albumin, gelatin, agar, etc.), semi synthetic polymers (e.g. cellular ethers and starch derivatives) and synthetic water-soluble polymers. Among these, synthetic water-soluble polymers have experienced the most rapid development and represent a major business with estimated world market around $6 billion per year. Its diversity and quantity far exceeds those of the natural and semi-synthetic water-soluble polymers and receives greater interest with the development of the petrochemical industry. Some important examples of synthetic water-soluble polymers are listed below:

Nonionic: polyacrylamide, polyvinyl alcohol, polyvinyl pyrrolidone,

Anionic: polyacrylic acid, polyphosphoric acid, polystyrenesulphonic acid, *Cationic*: polyvinylamine, polydimethyldiallyl ammonium chloride, poly (4-vinyl-N-alkyl-pyridinium) salts.

Water-soluble polymers are commonly synthesized from water-soluble monomers, e.g.,: acrylic acid (AA) and its sodium salt, acrylamide (AM), hydroxyethyl methacrylate (HEMA), hydroxyethyl acrylate (HEA), vinylyyrolidone (VP) and quaternary ammonium salts like, dimethyldiallyl ammonium chloride (DMDAAC) etc. Various processes including aqueous solution polymerization, inverse suspension polymerization and inverse emulsion polymerization are generally applied for commercial synthesis. Solution polymerization is commonly used in the synthesis of linear, low molecular weight water-soluble polymers. In the solution polymerization process, the water-soluble monomers are polymerized in a homogenous aqueous solution in the presence of free-radical initiators mostly by redox couples. The polymerization is a very exothermic reaction (ΔH=55-95 kJ/mol) in the solution process. As the conversion of the monomer and molecular weight of the polymer increase, the viscosity of the system increases sharply; this makes heat removal very difficult. This could cause explosive polymerization and is detrimental to the production. Therefore, in such a process the monomer content in the solution must be controlled. Linear, high molecule weight, polyacrylamide-based polymers are often commercially synthesized through inverse emulsion (W/O, 0.05-1 μm) polymerization[2-7], whereas the production of lightly crosslinked polyacrylic acid based super absorbent polymers are generally manufactured by inverse suspension (W/O, 0.05-2 mm) polymerization. In both cases the water and monomer mixture (i.e. water phase) is emulsified/suspended in an aliphatic or aromatic hydrocarbon phase (i.e. oil phase), where the size of the particles strongly depends on the chemical and physical properties of the emulsifiers or dispersing agents used. The existence of the oil phase overcomes some of the problems associated in solution process, since it lowers solution viscosities and can dissipate the heat of polymerization. Moreover, it is also an attractive method because the oil phase permits relatively higher monomer content. However, the biggest disadvantage in these processes is the separation and/or recycling of the oil phase after the polymerization, which drives up the cost and causes environmental pollution. A clean, low cost process with good productivity is highly desired in the industry. Usually, redox polymerization of acrylamide in aqueous medium yields polymer having not so high molecular weights primarily because of fast termination process via transfer of electron to the oxidant of the redox couple (e.g. metal ions at higher oxidation state) from the growing polymer chain. However, it has been shown recently that if the polymerization is carried out in a constrained space of a reactor (e.g. interlayer space of a clay mineral) such that the growing polymer chain may not be able to transfer the electrons to the metal ions, high molecular weight polymers are formed.[8] The effect of microenvironment of a phyllosilicate in the polymerization process is not usually confined to delayed termination only; it also affects the mechanism of formation and sometimes the structure of the polymer. The role of charged groups on factors that govern the efficiency of polyacrylamide (PAM) in its use as discussed above especially its recent application as water soluble viscofier and displacement fluid in secondary oil recovery in the salt rich waters, a complete molecular characterization is required. In the case of charged PAM the relative dissociation of the ionic groups and the distribution and alignment of the charged dipoles along the chain are expected to play a decisive role on the final state of conformation of the polymer chain. The effect of hydrodynamic field on the viscosity of partially hydrolyzed PAM has been discussed in the literature. The effect of various salt ions on the characteristic of polyelectrolyte in the aqueous solution and the site-binding interaction of salt ions with the polymer is also important.

1.1 VERMICULITE

Vermiculite occurs in nature in the form of macroscopic crystals. Vermiculites, the geological name given to a group of hydrated laminar minerals, aluminium iron magnesium silicates, are similar in appearance to mica. Biotite and phlogopite are common parent minerals of vemiculite and mixed-layer mica/vermiculite (hydrobiotite or hydrophlogopite).Due to its structural features, vermiculite clays play an important role in many natural processes and industrial applications. These include oil and gas production,[9] and the removal of organic contaminants from water etc.[10-12] Recently, these clays have also been used to produce new nanoporous materials.[13] Vermiculite crystals are constituted of stacking negatively charged sheets, which are held together by charge balancing interlayer counter ions.[14] The sizeable interlayer spacing of the clay plays an important role in the transport processes of natural and contaminant species in the soil. Modeling of clay minerals is therefore of significant interest for understanding the underlying physico-chemical processes in these phenomena, particularly clay swelling and the behavior of metallic ions and organic compounds in the interlamellar space. This behavior may well depend on the dynamics of the clay structure that is generally probed by the methods of vibrational spectroscopy.

CHEMICAL COMPOSITION & STRUCTURE

Vermiculite is a trioctahedral 2:1 layered silicate. Its empirical formula is: $Mg_{1.8}Fe^{2+}_{0.9}Al_{4.3}SiO_{10}(OH)_2 \cdot 4(H_2O)$

The negatively charged layer of its structure is formed from a sheet of edge-connected XO_6 octahedra, where X is an octahedral atom (Mg, Al, Fe), which are symmetrically bound to two sheets of corner-connected TO_4 tetrahedra, where T is a tetrahedral atom (Si, Al), forming six-membered silicate rings.[15] The vermiculite structure, which is shown in Fig.1.1, contains three types of oxygen atoms. Oxygen atoms of the first type (O_I) link two Si atoms and are located at the corners of the SiO_4 tetrahadra. Oxygen atoms of the second type (O_{II}) are tetra-coordinated oxygen bound to a silicon atom and three magnesium atoms. Oxygen atoms of the third type (O_{III}) are tetra-coordinated oxygen coordinated to one hydrogen atom and three magnesium atoms. The external surfaces of the layer are built from oxygen of the first kind (O_I). The structure of vermiculite has a monoclinic unit cell and the unit cell is characterized by the following values of the lattice parameters: a = 5.33 A^{0}, b = 9.18 A^0, c = 28.90 A^0, and β= 97^0(ref. 15). The interlamellar spaces are large enough (Fig.1.1) to accommodate both inorganic and organic counter ions compensating the eventual charge of the layer. The amount of isomorphous substitution in vermiculite, however, is greater than in montmorillonite and much of this occurs in tetrahedral sheet but as Walker has pointed out, it seems probable that highly charged members of smectite group grade into the low-charged vermiculites. Only in the fully hydrated phase (d (001) = 1.48 nm) are all the available sites occupied by water molecules. As dehydration progresses, some of the unbound water are removed before the bound water. The interlayer expansion and collapse of vermiculite layers are influenced by the nature of the exchangeable cation as well as by that of the interlayer liquid.[16] In this respect and its ability to form complexes with organic compound vermiculite bear a striking resemblance to montmorillonite.[17-19] However, Mg-saturated vermiculite fails to expand beyond a basal spacing of ~1.45 nm with glycerol whereas all Mg montmorillonite appear to give double layer complex with glycerol (d (001)~1.78nm). Weiss has reported that the basal spacing of vermiculite containing n-alkyl

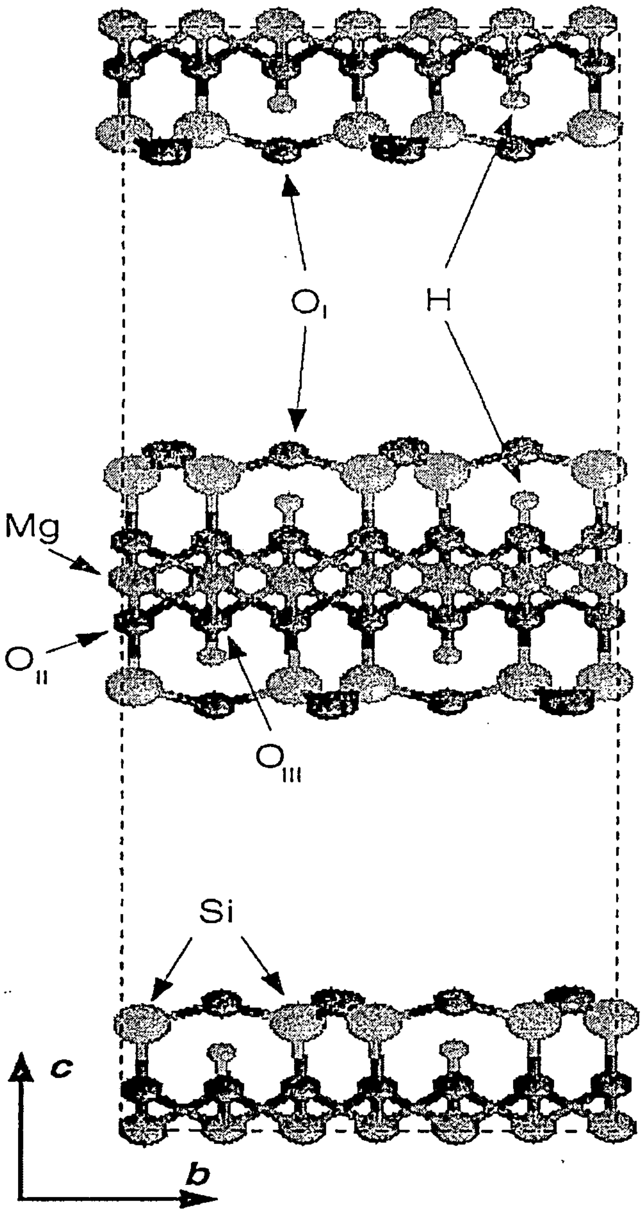

Figure 1.1. The layered structure of vermiculite.

ammonium ions of increasing chain length (C_5 to C_{12}) increases in a stepwise fashion.[20] This behavior was thought to arise from the fact that on passing from an odd to next even number of carbon atoms the interlayer distance increases by 0.20-0.21 nm, but that on passing from an even to next higher odd number of carbon atoms – there is virtually no increase in this distance. Walker and co-workers demonstrated the presence of two distinct types of interlayer water in vermiculite crystal.[23,26] The existence of both types of water in vermiculite has since been substantiated by IR spectroscopy. Horward and coworkers observed that montmorillonite intercalated two layers of ethylene glycol or glycerol from their respective vapor phase whereas vermiculite did not yield regular double layer complexes with either ethylene glycol or glycerol, irrespective of the saturated cation and the pre-exposure to water vapor.[21] Rather, a series of complexes formed with basal spacing of about 1.36, 1.40, 1.43, 1.50, and 1.53 nm; two or more complexes may be present in the sample. Brindley has drawn the attention to the fact that about 1/6 of the diagonal sites are associated with monovalent cations in montmorillonite and with divalent cation in vermiculite.[22] In a double layer complex of extended amine molecules, 5/6 of the total sites are therefore available on each oxygen surface. This means that the amount of organic molecules, which can accommodate in a complex of this type far exceeds that which is present in the corresponding one-layer complex. With vermiculite, interlayer swelling is usually less pronounced, probably because the silicate layers are more strongly held compared to montmorillonite. The amide molecules tend to link to the cation by means of water bridges. Some vermiculite samples, however, may expand to a basal spacing of 6.3 nm after prolonged immersion in liquid N-ethylacetamide. This behavior is reminiscent of that shown by n-butyl ammonium-vermiculite in water producing large interlayer separation. Extensive crystalline swelling of this type is attributed to the operation of osmotic repulsive forces giving rise to the formation of diffuse double layers when vermiculite crystals are immersed in strong amino acid solutions.[23,24] The effect of adsorbent charge and the kind of exchangeable cation present on the adsorption and retention of diquat and paraquat by 2:1 type layer silicates have been investigated by Weaver.[25] Maximum uptake by montmorillonite was close to the exchange capacity of the sample, being little influenced by nature of the saturating organic cations. On the other hand vermiculite adsorbed appreciably less than its exchange capacity and the extent of adsorption depended on the saturating organic cation decreasing in the order $Na^+ > Ca+^2 > Mg^{+2}$.Vermiculite can also intercalate various amino acids. The relative lack of experimental data on vermiculite-amino acid complexes is perhaps explained by the fact that the interlayer sorption of the organic species is usually less readily achieved with vermiculite than with montmorillonite because of greater charge and hence greater electrostatic attraction between the vermiculite layers. Extensive interlayer expansion can occur in vermiculite complexes with amino acid cations.[26] Thus single crystal of vermiculite of which the inorganic cations initially present have been replaced by ornithine, lysine, and Ɣ-amino butyric acid cations, swell in the respective amino acid solutions, when its concentration is below a critical value. Following Norrish, this type of swelling is initiated by the hydration of the interlayer amino acid cation, which dissociate from the clay surface.[27] This is followed by the development of diffuse double layer on interlayer surfaces so that subsequent interlayer expansion is controlled by osmotic repulsive interactions.

1.2 CLAY CATALYZED POLYMERIZATION

Clay is the key inorganic substance with applications ranging from pollution prevention and remediation to enhanced oil recovery, the treatment of petroleum liquids to the manufacture of cosmetics and pharmaceuticals to the synthesis of polymer nanocomposite materials. An understanding of clay-organic interactions and the effects of these interactions on the structure of clay complexes is a key issue for future development in all of these applications. Synthetic and naturally occurring clay minerals due to their favorable structures, are used in a number of widely diversified roles in the chemical industry as catalyst for cracking or depolymerization,[28] alkylation,[29] isomerization[30] polymerization[31] etc. In 1960's and earlier clay initiated polymerizations of vinyl monomers emphasized on the use of dry clay minerals and non-polar solvents.[16,32,33] Although the carbocationic polymerizations of vinyl monomers have been investigated extensively with Lewis acid such as $AlCl_3$, $TiCl_4$, Et_2O, BCl_3, alkyl aluminiums etc.[34-40] the first report on such polymerization of styrene with acid clays[32] came in 1964. Almost 100% yield of polystyrene of molecular weights 500-2000 was achieved. The catalytic activity of the clay has been shown to be due to active protons associated with tetrahedral (due to dehydration of mineral) aluminium.[41,42] The formation of carbonium ion following surface adsorption of olefins on acid sites caused subsequent polymerization. Proton accepting contaminants such as water, amines etc., being preferentially adsorbed over styrene suppressed the polymerization. Styrene polymerized on the surface of homoionic clays.[43] It is argued that an electron transfer from adsorbed styrene to the aluminium produces radical cations, which dimerize rapidly. Both radical cation and dimers are involved in the initiation step but the propagation being cationic. Using activated clay minerals, however, styrene did not polymerize in the presence of ethanol, dioxane, ethyl acetate and methyl methacrylate (MMA) within 30 minutes of the reaction. All these data lead to postulate that the active sites are the octahedral aluminium at the crystal edges. The aluminium acts as electron acceptors. Matsumoto, Sakai and Arihara preferred the concept of BrÖnsted acidity rather than Lewis acidity to be responsible for the initiation of the polymerization of styrene by montmorillonite, a smectite clay mineral.[44] The inconsistency of their experiments, however, is in the reduction of polymer yield in the presence of trityl chloride, which selectively adsorbs on Lewis acid sites. They argued in favor of the BrÖnsted acidity on the ground that the replacement of exchangeable hydrogen ions by sodium or ammonium ions almost completely inhibited the polymerization. On reacidifying the mineral, however, the activity to polymerize styrene was restored. Since the degree of polymerization increased with the dielectric constant of the medium and was almost independent of the initial concentration, cationic mechanism for the initiation process was favored.[45] This would apply equally well to the propagating process and therefore, the initiation by a radical ion mechanism cannot be ruled out.[43] The possibility of proton transfer to monomer leading to decreased average degree of polymerization, as in conventional cationic mechanism, has also been discussed.[41] The work of Matsumoto and co-workers along with Solomon and Rosser lead one to the conclusion that acidity of the clay cannot be solely ascribed to either BrÖnsted acidity or Lewis acidity.[43,44]It is understood that dry mineral surface is very acidic due to the polarization of residual water molecules by the exchangeable cations. Such acidity is influenced by the solvent as evident from the blue colorations of aqueous benzidine in the presence of oxidized montmorillonite [43,46]. Solomon and Rosser failed to find evidence of styrene interacting with the clay mineral which lead them to assume that styrene is either incapable of moving into the interlayer space or capable of doing so with difficulty. Blumstein and co-worker have studied the polymerization of MMA and methyl acrylate in montmorillonite interlayer induced by γ-radiation.[47-50] The interlayer polymer was difficult to isolate by the usual solvent extraction and could only be isolated by treating the clay polymer complex with hydrofluoric acid, which damaged most polymers.[51] Glavati and co-workers found that the polymerization of acrylonitrile/montmorillonite complex by γ-radiation produced stereospecific polymers.[51]

Thermal polymerization of a number of vinyl monomers could be induced by montmorillonite/2-2 azobis-isobutyramidine (AIBA) system if AIBA was previously introduced to the clay mineral.[52] The cationic form of AIBA goes to the exchange sites in montmorillonite to form AIBA-clay complex, which decomposes thermally to generate free radicals. The complex has initiating efficiency. The rate of polymerization with AIBA-montmorillonite complex initiator is greater than for AIBA alone.[53] It has been proposed that free radicals remain attached to the adjacent planes of AIBA-montmorillonite dispersed in water and on heating these planes move away from each other allowing more water to penetrate. The influence of aluminosilicates and magnesium silicates on the free radical polymerization of MMA has been studied in terms of termination reaction and supported by studies of the reaction of stable free radicals with the minerals. In the absence of clay mineral the yield of polymethylmethacrylate (PMMA) was 3.68% (mol. wt. 1.36×10^6) whereas with montmorillonite the yield was 0.68% (mol. wt. 3.05×10^6). That the decreased amount of polymer in presence of mineral is not due to depolymerization has been established by heating PMMA with montmorillonite and determining the viscosity average molecular weight, $M_{V,}$ before and after treatment. In a recent ESR study to assess the state of iron in montmorillonite, signals in the weak field at 'g; values of 7.6, 4.2 and 3.9 were assigned to Fe (III) ions in the octahedral layer of the mineral. The intensities of the wide bands of the spectra remain unchanged when the cations were altered as the exchanging sites. This indicated that the montmorillonite had particularly no iron in the ion exchangeable positions. Studies on structural properties of the polymers from clay catalyzed polymerizations of vinyl monomers have been made by several workers. Blumstein and co-workers studied the dilute solution properties of the polymers prepared in the presence of clay minerals which differed significantly from those obtained using conventional free radical technique and suggested that the interlayer PMMA developed a two-dimensional sheet structure in the presence of a cross linking agent during the polymerization.[47-50] Analyzing the NMR data they concluded that PMMA probably consisted predminantly of isotactic sequences. Small-scale stereo-regularity of this kind could be ascribed to the orientation induced in the intercalated monomer by ion dipole and the ester carbonyl group of the monomer. Earlier, Glavati and co-workers obtained oriented stereo regular polyacrylonitrile and polyacrylic acid using similar procedures.[51] It has been reported that the influence of clay minerals on polymerization reactions extends beyond direct action on monomers.[53-54] The minerals may also modify the chemical compounds used as polymerization initiators. It has been observed that clay minerals could affect both the rate and the rate of decomposition of initiators. Uskov and co-workers reported that polyvinylchloride (PVC) or a vinyl chloride copolymer modified by latex of butylacrylate-methylmethacrylate copolymer, butadiene-styrene copolymer, PMMA or a similar polymer was prepared by adding the latex to the reactor during the suspension polymerization.[55] The addition was made after 30-95% conversion of monomers. If inorganic compounds such as silica, montmorillonite or a calcium phosphate were added before or during the polymerization, the polymer with satisfactory particle size separated out from the aqueous suspension. Recently, Talapatra, Saha and co-workers reported that bentonite in conjunction with alcohols or thiols effectively initiate aqueous polymerization of vinyl monomers on the surface of the minerals.[56-60] A granular soil amendment was formulated from acrylamide polymers, silicic acid or silicate and once or more of phosphates, nitrates and sulfates or free form of urea, guanidine, dicyandiamide and amidinothiourea.[61] The product markedly improved aggregation of clay containing soils. T. Ono and co-workers, however, polymerized MMA in H_2O containing phyllosilicates in presence water and azo initiators.[62]

1.3 POLYMER-SOLVENT INTERACTION

In view of the wide range of use of water-soluble synthetic polymers, the understanding of the role of polar groups on different factors, which govern the efficiency of their use, is important. Attempts at describing solvent, temperature and molecular weight dependence on the conformational characteristics of the polymer have stimulated the development of many fundamental models for polymer structure and dynamics. One of the outstanding problems involves providing a description of the degree to which solvent penetrates through the polymer coils as the chain dimension swell with increased excluded volume interactions. The theory of polymer solution dynamics is associated with establishing the relation between the macroscopic hydrodynamic properties of polymer solution and molecular structure of the polymer and the solvent. The increase in molecular dimension from monomer to oligomer, oligomer to usual length polymer and from the later to the pleistomer is accompanied by the appearance of new properties.[63] Many present and possible industrial applications of high molecular weight polymers arise from the unusual properties they induce to their solutions. The study of their solution properties is prerequisite for the development of this modern domain.

In the treatment of properties of very dilute polymer solutions it is convenient to represent the molecule as a statistical distribution of the chain elements or segments about the center of gravity.[64] For a random chain devoid of intramolecular interactions between segments mean square distance between the ends of polymer chain is proportional to the number of segments in the chain and hence to the molecular weight. This is true regardless of steric restrictions due to interaction between neighboring segments and other restrictions on rotations about bonds of the chain, provided that the chain possesses a degree of flexibility and that it is sufficiently long. Interactions between remotely connected segments separated by many intervening segments along the chain may be considered to alter the linear dimension of the polymer chain. Interactions between remotely connected segments of the given chain arise as consequences of the finite volume of each segments from which all other segments are excluded, and of the net energy of interactions between segments which happen to be in contact. In thermodynamic terms, this implies that the entropy change is important when a macromolecule dissolves. There may also be significant enthalpy change on account of the interaction of the solvent with large number of component monomer units in the polymer. There are both entropic (excluded volume) and enthalpic (attraction and repulsion) contribution to the non-ideality of the polymer solution and for most polymer-solvent system there is a unique temperature where their effects cancel. This temperature is called theta temperature and at this temperature the osmotic virial coefficient is zero. The cancellation of the effects at this temperature means the solutions then behaves ideally even though the concentration is not low and it's thermodynamic and structural properties are easier to describe.[65,66] Systematic studies arising from the coupling of different experimental techniques are required for elucidation of diverse theoretical experimental aspects. The most important parameters characterizing macromolecular chain in dilute solution are the molecular weight, mean square radius of gyration and intrinsic viscosity. Their determination for high molecular weight polymers, on the basis of different theoretical approximations, opens a large area for discussing various aspects such as influence of molecular weight and solvent power on concentration domain, theta condition and the chain flexibility in the perturbed and unperturbed states. A long chain hydrocarbon molecule in a solution takes on somewhat kinked or curled shape, intermediate between tightly rolled up mass and the rigid linear configuration. Presumably all possible degrees of curling are represented owing to internal Brownian movement of the flexible chains but the configuration of intermediate extension predominate statistically. If a continuous energetically indifferent solvent surrounds the long chain molecule, the weight factor for particular configuration is determined only by internal parameters - potential energy for restricted rotation and prohibition of segment interpenetration. The mean value of any internal property in such an indifferent solvent might be called unbiased statistical mean for the property. If the solvent is energetically unfavorable, so that dissolving of the high polymer is an endothermic process, the polymer segments will attract each other in solution and squeeze out the solvent between them. Other conditions being equal, a given high polymeric material made up of flexible molecules will exhibit a high intrinsic viscosity in an energetically favorable solvent and low intrinsic viscosity in an energetically unfavorable solvent. This is of course hold only in very dilute system. At higher concentrations energetically unfavorable solvent will favour polymer-polymer contact and hence lead to danger of gelation while an energetically favorable solvent will stand at higher concentration of the polymer and yet give a stable solution. If a good solvent is mixed with a precipitating agent, the resulting mixture may be expected to be less favorable to long chain molecule than in a pure solvent. There should also be close connection between intrinsic viscosity and intramolecular agglomeration. Exactly the same solvent characteristic, which determines the mean geometrical property of isolated long chain molecule, should determine the amount of association of different solute molecules into aggregate. When a nonsolvent is added to a high polymer solution the point at which precipitate begins represent a certain agglomeration tendency for chain segment of different molecules. To a first approximation, therefore, it should represent a certain definite mean value for any shape dependent internal property. The solvent composition, which is critical from the standpoint of solubility, should correspond to certain intrinsic viscosity no matter what the solvent and what the nonsolvent be.[67] All these should be more pronounced for the polymer molecules of high flexibility than for the rigid chains. In a poor solvent the effective molecular shape is more compact and curled than the unbiased statistical mean. An increase in temperature should increase the relative importance of entropic factor over the energetic factor. In such a solvent increase in temperature should result in an increase in intrinsic viscosity. In a very good solvent, energetic weighting factor favors the most extended configuration of the polymer.

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