Physicochemical Behavior and Supramolecular Organization of Polymers

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Springer

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ISBN 978-1-4020-9371-5 e-ISBN 978-1-4020-9372-2

DOI 10.1007/978-1-4020-9372-2

Library of Congress Control Number: 2008942790

Printed on acid-free paper

9 8 7 6 5 4 3 2 1

springer.com

Preface

This book is concerned mainly with the physicochemical behavior and supramolecular organization of polymers. The book is split in four chapters dealing with solution properties, viscoelastic behavior, physicochemical aspects at interfaces and supramolecular structures of polymeric systems. The classical treatment of the physicochemical behavior of polymers is presented in such a way that the book will meet the requirements of a beginner in the study of polymeric systems in solution and in some aspects of the solid state, as well as those of the experienced worker in other type of material. Indeed the book is a contribution to the chemistry of materials. Taken into account these aspects, Chapter 1 is an introduction to the classical conformational and thermodynamic analysis of polymeric solutions where the different theories that describe these behaviors of polymers are analyzed. Owing to the importance of the basic knowledge of the solution properties of polymers, the description of the conformational and thermodynamic behavior of polymers is presented in a classical way. The basic concepts like theta condition, excluded volume, good and poor solvents, critical phenomena, concentration regime, cosolvent effect of polymers in binary solvents, preferential adsorption are presented in an intelligible way. The thermodynamic theory of association equilibria which is capable to describe quantitatively the preferential adsorption of polymers by polar binary solvents is also analyzed. Chapter 2 is a discussion of the viscoelastic properties of polymeric material where the different concept dealing with the fact that polymers above glass-transition temperature exhibit high entropic elasticity. Polymers exhibit both viscous and elastic characteristics what is present in systems when undergoing deformation. In this Chapter the basic concepts of viscoelasticity are described at beginner level. The analysis of stress-strain in polymeric materials is of great practical interest and several examples of some familiar behavior of polymeric materials are shortly described. The Chapter is splitted in four parts the first dealing with basic concepts of viscoelasticity. The second with dielectric and dynamic mechanical behavior of aliphatic, cyclic saturated and aromatic substituted poly(methacrylate)s with different kind of substituents in the side rings. The discussion in terms of the theories that can describe the viscoelastic behavior of polymers is well explained. The analysis of the different relaxations that take place in these systems allow to understand the molecular origin of the different motions. By this way an interesting approach of the relaxational processes is presented under the experience of the authors in these polymeric systems. The third part deals with the dielectric and dynamic mechanical behavior of poly(itaconate)s with mono and disubstitutions. The effect of the substituents and the free carboxylic groups in poly(monitaconate)s and the disubstitution on poly(diitaconate)s is extensively discussed and interesting conclusion are descrived. The fourth part is the analysis of viscolastic behavior of poly(thiocarbonate)s where the difference is that this family of polymers correspond to condensation polymers instead of vinyl polymers like the formers. The effect of the substitution of the polymers is also analyzed. Chapter 3 is a discussion of the behavior of polymers at interfaces where the Langmuir monolayers and Langmuir-Blodget films are studied. Amphiphilic polymers at the air-water interface are studied via the Langmuir technique. The study and discussion of surface pressure-area isotherms for different polymers are performed by using a surface film balance and the results obtained from this technique are analyzed in terms of the shape of the isotherms. The collapse pressure for different systems are discussed in terms of the chemical structure of the polymer. The adsorption of polymers by spreading and from solution is also discussed. Wetting of solids by a liquid described in terms of the equilibrium contact angle θ and the appropriate interfacial tensions. At equilibrium the forces acting are analyzed using the Young's equation. Chapter 4 deals with the analysis of supramolecular structures containing polymers. Specifically in this chapter the discussion about the effect of polymeric materials with different chemical structures that form inclusion complexes is extensively studied. The effect of the inclusion complexes at the air-water interface is discussed in terms on the nature of the interaction i.e. if the interaction is on entropic or enthalpic nature. The description of these inclusion complexes on different cyclodextrines with poly(ethylene) oxide, poly(ε-caprolactone) and related polymers is an interesting way to understand some non-covalent interaction in these systems. The discussion about the generation and effect of supramolecular structures on molecular assembly and auto-organization processes is also presented in a single form. Finally the use of block copolymers and dendronized polymers at interfaces is new aspect to be taken into account from both basic and technological interest. The effect of the chemical structure on the self-assembled systems is discussed in terms of the different kinds of interaction that can be detected. This book should be a powerful tool for students and scientists working both in polymer chemistry and physic and in material science.

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Abbreviations

a	activity
a.c	alternating current
α	thermal expansion coefficient
α	relaxation associated to Tg
$A_i, i = 2, 3, \ldots$	ith virial coefficient
A	area
$\mathring{A}_o$	surface limiting area
$\mathring{A}_c$	surface critical area
AFM	atomic force microscopy
BAM	Brewster Angle Microscopy
C	concentration
c^*	concentration at which entanglements set in
c^*	overlap concentration
C_k	Kuhmian concentration
C_s	two dimensional compressibility
C_∞	characteristic ratio
CMC	critical micelle concentration
CD	cyclodextrin
D	docility
D	diffusion coefficient
Φ	density
Φ'	universal Flory constant
DLS	dynamic light scattering
DMA	dynamic mechanical analysis
DMF	N,N-dimethylformamide
DMSO	dimethylsulfoxide
ρ	density
DSC	differential scanning calorimeter
$d\varepsilon/dw$	parameter proportional to the total polarization of the chains
δ	solubility parameter of Hildebrand
δ	the lag in the phase angle. G:dynamic modulus
$d\varepsilon/dt$	the time derivative of strain.
ε	static comprensibility modulus

ε	strain that occur under the given stress
ε^*	complex permittivity
ε'	dielectric permittivity
ε_1	dielectric permittivity
ε''	dielectric loss
ε_o	relaxed permittivity
ε_∞	unrelaxed permittivity
E_a	activation energy
E	electrostatic modulus (Young’s modulus)
ε	strain that occur under the given stress.
E’	real part of viscoelastic spectra
E”	imaginary part of viscoelastic spectra.
$E^{\mp}$	the apparent activation energy
Eg	glassy modulus
ΔE	internal energy
ΔE_V	change in the molar internal energy
g	phenomenological interaction parameter
g_T	ternary parameter
G	free energy
G	generation
G’	dynamic stress modulus, storage modulus
G”	dynamic strain modulus, loss modulus.
ΔG	change in free energy
ΔG_M	change in free energy by mixing
ΔG^0	change in standard free energy
GPC	gel permeation chromatography (SEC)
f	fugacity
H	heat
ΔH	change in enthalpy
ΔH_V	change in the molar enthalpy
F(t)	relaxation function
F_{max}	frequency at the maximum of the isotherm
f_{ax}	axial conformation
f_{eq}	equatorial conformation.
F	strength
FEM	transmission electron microscopy
IC	inclusion complex
I	second momento of area of the cross section.
I	intensity of scattering radiation
I_0	intensity of incident radiation
IR	infrared
J	compliance
h	Plank’s constant
k'	Huggins viscosity constant
K	Mark-Houwink pre-exponent coefficient

K_i	equilibrium constants
K_θ	Mark-Houwink coefficient at θ conditions
K(t)	creep
ΔL	difference in the length
l	Debye length
LB	Langmuir-Blodgett
LCST	lower critical solution temperature
m’	parameter of the VFTH equation
m	parameter dealing with the broadness of a relaxation
MMX	force field
MM2P	force field
MD	molecular dynamic
MKS	Mark-Houwink-Sakurada
MDS	molecular Dynamic Simulation
M	mass, molecular weight
M^*	modulus
M_0	molecular weight of polymer repeating unit
M_n	number-average molecular weight
M_v	viscosity-average molecular weight
M_w	weight-average molecular weight
n	critical exponent of the excluded volume
$\Delta\mu_1$	change in chemical potential
n	refractive index of solution
n_0	refractive index of solvent
dn/dc	limiting value of the specific refractive index increment at zero concentration
N	Avogadro’s number
N	crosslink density
HN	Havriliak-Negami
NMR	nuclear magnetic resonance
P2CEM	poly(2-chloroethyl methacrylate)
P3CEM	poly(3-propyl methacrylate)
P2ClCHA	poly(2-chlorocyclohexyl acrylate)
PCHM	poly(cyclohexyl methacrylate)
PCHMM	poly(cyclohexylmethyl methacrylate)
PCHPM	poly(cyclohexylpropyl methacrylate)
PCHBM	poly(cyclohexylbutyl methacrylate)
P2CEM	poly(2-chloroethyl methacrylate)
P2tMCHM	poly(2-tert-butycyclohexyl methacrylate)
P4tMCHM	poly(4-tert-buycyclohexyl methacrylate)
PCHpM	poly(cyclohepthyl methacrylate)
PCHpMM	poly(cycloheptylmethy methacrylate)
PCOcM	poly(cyclooctyl methacrylate)
PCBuM	poly(cyclobutyl methacrylate)
PCBMM	poly(cyclobutylmethyl methacrylate)

P2NBM	poly(2-norbornyl methacrylate)
P3M2NBM	poly(3-methyl-2-norbornyl methacrylate)
P4THPMA	poly(tetrahydropyranyl methacrylate)
PDMA	poly(1,3-dioxan-5-yl-methacrylate)
PTHFM	poly(tetrahydrofurfuryl methacrylate)
P3MTHFMA	poly(3-methyl-tetrahydrofurfuryl methacrylate)
PPHM	poly(phenyl methacrylate)
P2,6DMPM	poly(2,6-dimethylphenyl methacrylate)
P2,4DMPM	poly(2,4-dimethylphenyl methacrylate)
P2,5DMPM	poly(2,5-dimethylphenyl methacrylate)
P3,5DMPM	poly(3,5-dimethylphenyl methacrylate)
P2,4DFBM	poly(2,4-difluorobenzyl methacrylate)
P2,5DFBM	poly(2,5-difluorobenzyl methacrylate)
P2,6DFBM	poly(2,6-difluorobenzyl methacrylate)
P2MClBM	poly(2-monochlorobenzyl methacrylate)
P3MClBM	poly(3-monochlorobenzyl methacrylate)
P4MClBM	poly(4-monochlorobenzyl methacrylate)
P2,3DClBM	poly(2,3-dichlorobenzyl methacrylate)
P2,4DClBM	poly(2,4-dichlorobenzyl methacrylate)
P2,5DClBM	poly(2,5-dichlorobenzyl methacrylate)
P2,6DClBM	poly(2,6-dichlorobenzyl methacrylate)
P3,4DClBM	poly(3,4-dichlorobenzyl methacrylate)
P3,5DClBM	poly(3,5 -dichlorobenzyl methacrylate)
PMOI	poly(monooctyl itaconate)
PMDI	poly(monodecyl itaconate)
PDMI	poly(dimethyl itaconate)
PDEI	poly(diethyl itaconate)
PDPI	poly(dipropyl itaconate)
PDBI	poly(dibutyl itaconate)
PDIPI	poly(diisopropyl itaconate)
PDIBI	poly(diisobutyl itaconate)
PMMA	poly(methyl methacrylate)
PMCHI	poly(monocyclohexyl itaconate)
PDCHI	poly(dicyclohexyl itaconate)
PDCHpI	poly(dicycloheptyl itaconate)
PDCOcI	poly(dicyclooctyl itaconate)
PDCBI	poly(dicyclobutylitaconate)
POS	poly(octamethylene sebacamide)
POT	poly(octamethylene terephthalamide)
POTCl	poly(octamethylene tetrachloroterephthalamide)
PTC	poly(thiocarbonate)
PVP	poly(N-vinil-2-pyrrolidone)
PS	poly(styrene)
PIB	poly(isobutylene)
PEC	poly(ε-caprolactone)

PEO	poly (ethylene oxide)
Q	first moment of area
r_o^2	unperturbed mean square dimension.
r_{of}^2	free rotation unperurbed mean square dimension
R	gas constant
R_H	hydrodynamic radius
R_η	hydrodynamic radius
R_g	radius of gyration
σ	rigidity factor
σ	applied stress, shear strain. sinusoidal stress response
SDS	sodium dodecyl sulfate
STM	scanning tunneling microscopy
SANS	small- angle neutron scattering
π_C	critical surface pressure
S, ΔS	entropy, change in entropy
ΔS^*_M	change in configurational entropy
ΔS^E_M	change in entropy by mixing
SEC	size-exclusion chromatofraphy (GPC)
$<S^2>$	mean-square radius of gyration
η_{coil}	average density of segments
T_g	glass transition temperature
t	time
T_{max}	temperature where E" has the maximum value.
T_∞	parameter of the VFTH equation
T_0	intial temperature
Γ	surface concentration
T_f	final temperature
T_p	polarization temperature
T_a	anneal temperature
$\tau\ (T)$	relaxation time related with the depolarization current iT
THF	tetrahydrofuran
τ	shear stress
Θ	theta temperature
τ	shear stress
t	thickness in the material perpendicular to the shear
i.T	depolarization current
tanδ:	$G''/G' = \gamma/\sigma$
UCST	upper critical solution temperature
V	molar volume
Vsp	specific volume
V	shear force
ν	rate of conformational change
v	Mark-Houwink power coefficient
v_i	volume fraction
VFTH	Vogel, Fulcher, Tamman, Hesse equation

ω	frequency
dW	work (fdX)
Wd	adhesion work
Ψ	entropic contribution to χ
γ	monolayer surface tension
γ°	water surface tension
χ_{crit}	critical interaction parameter
χ	phenomenological interaction parameter for noncombinatorial part
χ	phenomenological interaction parameter
λ	preferential adsorption coefficient
ξ	screening length
Ø	segment fraction
π	surface pressure
π	osmotic pressure
π/c	reduced osmotic pressure
η_S	surface viscosity
η	solution or melt viscosity
η_0	viscosity at zero shear rate
η_{sp}	specific viscosity
$[\eta]$	intrinsic viscosity
γ	surface tension
$\gamma_{S/V}$	interfacial tension at the solid/vapour
$\gamma_{S/L}$	interfacial tension at the solid/liquid
$\gamma_{L/V}$	interfacial tension at the liquid/vapour
γ	sinusoidal oscillatory shear strain
γ	surface tension
γ	activity coefficient
γ_o	initial sinusoidal oscillatory strain
λ	extension ratio $= L/L_0$
γ	subglass relaxation
β	subglass relaxation
δ	subglass relaxation
$\frac{\phi}{B}$	free volume
$\frac{\langle \mu^2 \rangle}{x}$	mean square dipole moment per polymer repeating unit
π/c	reduced osmotic pressure

Chapter 1
Polymer Solution Behavior: Polymer in Pure Solvent and in Mixed Solvent

Summary The classical treatment of the physicochemical behavior of polymers is presented in such a way that the chapter will meet the requirements of a beginner in the study of polymeric systems in solution. This chapter is an introduction to the classical conformational and thermodynamic analysis of polymeric solutions where the different theories that describe these behaviors of polymers are analyzed. Owing to the importance of the basic knowledge of the solution properties of polymers, the description of the conformational and thermodynamic behavior of polymers is presented in a classical way. The basic concepts like theta condition, excluded volume, good and poor solvents, critical phenomena, concentration regime, cosolvent effect of polymers in binary solvents, preferential adsorption are analyzed in an intelligible way. The thermodynamic theory of association equilibria which is capable to describe quantitatively the preferential adsorption of polymers by polar binary solvents is also analyzed.

Keywords Solution properties · Conformational analysis · Theta condition · Excluded volume · Good and poor solvent · Thermodynamic theories · Preferential adsorption · Cosolvent effect

1.1 Introduction: Solution Properties

Polymer solutions represent the most convinient systems for studying the properties of the macromolecules. In effect, almost the all information that we have now about the properties of macromolecules comes from the characterization realized in solution. This is the state in which linear chains are characterized. Osmotic pressure measurements in polymer solutions revealed for the first time the existence of high molecular masses and this result confirmed the macromolecular hypothesis. The development of our knowledge of the polymer solutions reflects to some extention the development of the Polymer Chemistry itself.

In a limited sense solutions are homogeneous liquid phases consisting of more than one substance in variable ratios, when for convenience one of the substances, which is called the solvent and may itself be a mixture, is treated differently from

L. Gargallo, D. Radić, *Physicochemical Behavior and Supramolecular Organization of Polymers*, DOI 10.1007/978-1-4020-9372-2_1,

the other substances, which are called solutes [1]. Normally, the component which is in excess is called the solvent and the minor component(s) is the solute. When the sum of the mole fractions of the solutes is small compared to unity, the solution is called a dilute solution. A solution of solute substances in a solvent is treated as an ideal dilute solution when the solute activity coefficients γ are close to unity ($\gamma = 1$) [1,2].

The deviations from ideal solution behavior are generally associated with a finite heat of solution. However, the properties of systems containing high molecular weight components, have shown extremely large deviations from the behavior to be expected of ideal solutions, even in cases where the heat of mixing was negligible.

To understand the thermodynamic behavior of a binary system containing a polymeric component and a low molecular weight component, it is necessary to consider that the most polymer molecules may be represented as flexible chains. If such chains are sufficiently long, the shape or conformation of their backbones may be likened to the random flight path of a particle undergoing Brownian motion and is then commonly refered to as a "random coil". The problem now is to analyze what happens with the shapes or conformations under different situations. At extreme dilutions, each one of these chains can assume a large number of conformations. The probability that any one chain exists at a given time in a given conformation will be independent of the conformations assumed by all the other chains. In the pure amorphous polymer the chain molecules are just as flexible as in solution. At the same time, it is possible to assume that they can be able to exist in a similar number of conformations. But, now these molecular conformations are not independent of each other. The shape of each molecular chain must be correlated with the shape assumed by its neighbors so as to fill the available space. When a molecular chain is transferred from the pure polymer phase to a dilute solution, this restraint is eliminated, and this accounts for the characteristic positive of the entropy mixing ΔS_M^E values of solutions of chain molecules. We can distinguish two ranges of concentration in systems containing chain molecules. In dilute solution, the polymer coils will only occasionally interpenetrate. At higher concentrations the total available volume is much less than the sum of the volumes enclosed by the twisting chain molecules. Then, in this range, the shape of a given chain, due to the presence of other polymer chains, will depend on the fraction of the volume occupied by these chains.

A quantitative theory of the change in conformational entropy produced by the mixing of flexible chain polymers with a solvent of low molecular weight was formulated by Flory [3] and Huggins [4].

In dilute solutions, the polymer chains behave, to a first approximation, as a gas. Indeed, the expression for the osmotic pressure is similar to the ideal gas law.

The "osmotic pressure of a solute" is the hydrostatic pressure that must be applied to a solution in order to increase the activity, a. (or fugacity, designated f, introduced by G. N. Lewis as a measure of thermodynamic "escaping tendency". It is an effective gas pressure corrected for deviations from the perfect gas laws) of the solvent sufficiently to balance its decrease caused by the presence of the solute. Equilibrium is established through a membrane permeable only to the solvent. This pressure is, by integrating

$$(\mathrm{dG}/\mathrm{d}\pi)_{\mathrm{T}} = \mathrm{V} \tag{1.1}$$

under the assumption of constant v_1 (negligible compressibility) and combining with (1.2)

$$\mathrm{G}_1 - G_1^0 = \mathrm{RT}\ \ln(\mathrm{f}_1/\mathrm{f}_1{}^0) \tag{1.2}$$

for the free energy of transfer of a mole of, for example, component 1 from pure liquid to solution. Whenever gas pressure obeys the ideal gas law with what is considered desired accuracy, fugacity can be replaced by gas pressure:

$$\pi = -\mathrm{RT}/\mathrm{V}_1 \ln \mathrm{f}_1/\mathrm{f}_1{}^0 = -\mathrm{RT}/\mathrm{V}_1 \ln \mathrm{a}_1 \tag{1.3}$$

The osmotic pressure is a convenient variable for experiments, especially for high – polymer solutions.

There are, however, several intriguing facts that have aroused theoretical interest.

(i) the chain swells in good solvents, but does not in poor solvents (in the vecinity of a "Boyle" temperature.)
(ii) the chains overlap the total solution volume, while the polymer concentration is still low.

Thermodynamic predictions based on the liquid lattice theory do not fit osmotic experimental data [5].

For binary polymer-solvent, the Gibbs mixing function, ΔG_M, can be written, without approximation, as the sum of a combinatorial term plus an interactional term

$$\Delta \mathrm{G}_{\mathrm{M}}/\mathrm{RT} = \mathrm{n}_1 \ln \upsilon_1 + \mathrm{n}_2 \ln\ \upsilon_2 + \mathrm{n}_1\ \upsilon_2\ \mathrm{g}_\upsilon \tag{1.4}$$

Here, n_i is amount of substance and υ_i the volume fraction, this last magnitude being defined by $\upsilon_i = w_i \nu_{sp,i}/(w_1 \nu_{sp,1} + w_2 \nu_{sp,2})$, where w_i is the weight fraction and $v_{sp,i}$ the specific volume ($i = 1, 2$). Index 1 refers to solvent and index 2 to polymer. g is a phenomenological interaction parameter that takes into account deviations of ΔG_M from its combinatorial value. Subscript υ in g_υ denotes that g is defined on a volume fraction basis.

Differentiating equation (1.4) gives the chemical potentials of the components: $\Delta\mu_1$ and $\Delta\mu_2$. For the solvent

$$\Delta\mu_1/\mathrm{RT} = \ln \nu_1 + (1 - \mathrm{V}_1/\mathrm{V}_2)\upsilon_2 + \upsilon_2^2 \chi_\mathrm{v} \tag{1.5}$$

Where

$$\chi_\mathrm{v} = \mathrm{g}_\mathrm{v} + \nu_1(\mathrm{dg}_\mathrm{v}/\mathrm{d}\nu_1) \tag{1.6}$$

V_i being molar volume and χ a phenomenological interaction parameter taking into account the deviations of $\Delta\mu_1$ from its purely combinatorial value. Subscript v in

χ_v denotes that χ is also defined on a volume fraction basis, the same as g_v. The equation (1.6) would be not strictly applicable to the dilute solution limit, but it can be interpreted as the definition of χ for the whole range of concentrations [6].

If instead of volume fractions, segment fractions, Φ_i, are used, then

$$\Delta G_M/RT = n_1 \ln \Phi_1 + n_2 \ln \Phi_2 + n_1 \Phi_2 g_\Phi \tag{1.7}$$

With $\Phi_i = w_i v^*_{sp,i} / \left(w_1 v^*_{sp,1} + w_2 v^*_{sp,2}\right)$, where $v^*_{sp,i}$ is the characteristic (hard – core) specific volume ($i = 1, 2$).

Differentiating equation (1.7) gives

$$\Delta u_1/RT = \ln \Phi_1 + (1 - V^*_1/V^*_2)\Phi_2 + \chi_\Phi \Phi_2^2 \tag{1.8}$$

Where

$$\chi_\Phi = g_\Phi + \Phi_1(dg_\Phi/d\Phi_1) \tag{1.9}$$

Subscript Φ on interaction parameters g_Φ and χ_Φ means that g_Φ and χ_Φ are defined on a segment fraction basis, and v^*_i is the characteristic molar volume. These $v_i^{*,5}$ are obtained from the reduced volumes, V_i

$$V_i = V_i/v^*_i \tag{1.10}$$

To obtain the reduced volumes, it is usual to use the equation of state due to Flory [7], from which is derived [7]

$$Vi = [1 + \alpha_i T/3(1 + \alpha_i T)]^3 \tag{1.11}$$

α_i being the thermal expansion coefficient.

For the polymer component, differentiation of equation (1.4) gives a result similar to equation (1.5)

$$\Delta\mu_2/RT = \ln \nu_2 + (1 - V_2/V_1)\nu_1 + (V_2/V_1)v_1^2 \chi'_v$$

Where

$$\chi'_v = g_v + \nu_2(dg_v/d\nu_2) \tag{1.12}$$

χ'_v being a phenomenological interaction parameter for the noncombinatorial part of the solute (polymer) chemical potential, defined on a volume fraction basis. Equations similar to equation (1.9) and (1.12) serve to define χ' on a segment fraction basis, χ'_Φ.

The relationship between the g parameter and the χ or χ' parameters is given by equations (1.4), (1.7), and (1.11). Integration of these equations up to the concentration $\nu_2(= 1 - \nu_1)$ or $\Phi_2(= 1 - \Phi_1)$ yields the value of g: g_v as function of ν_2 or

g_Φ as a function of Φ_2. With the common symbol x to represent either ν or Φ, the results are

$$g_x = 1/x_1 \int_0^{x_1} \chi dx_1 = 1/x_2 \int_0^{x_2} \chi' dx_2 \tag{1.13}$$

($x = \nu$ or Φ). In the limit of zero concentration of polymer ($\nu_2 = \Phi_2 = 0$) and in the limit of pure polymer ($\nu_2 = \Phi_2 = 1$) we have

$$g_x^0 = \chi x^0 = \int_0^1 \chi dx_1 \tag{1.14}$$

$$g_x^1 = \chi x^1 = \int_0^1 \chi' dx_2 \tag{1.15}$$

where the superscripts 0 and 1 mean respectively $\nu_2 = \Phi_2 = 0$ and $\nu_2 = \Phi_2 = 1$.

Equations (1.13) and (1.14) show that the g interaction parameter is the reduced residual chemical potential (a) of the polymer, in the limit $\Phi_2 = 0$, and (b) of the solvent, in the limit $\Phi_2 = 1$ [6].

Theoretical g^0: The theoretical expression for the g^0 parameter, using the theory of polymer solutions developed by Flory and by Patterson based on the ideas of Prigogine and his school, has been given by Horta [8].

To calculate g^0, Masegosa et al. [6] have taken from the literature data of χ as a function of concentration. They have calculated g^0 for 41 polymer – solvent systems. The values of g^0 calculated are collected in Table 1.1.

In those cases in which $\tilde{V}_2/\tilde{V}_1$ is known, both $g_v{}^0$ and $g_\Phi{}^0$ are given. For the rest of the systems, only $g_v{}^0$ is given. Prediction of thermodynamic properties on ternary systems formed by a polymer and two solvents or two polymers and a solvent requires the knowledge of the parameter g^0, characteristic of the interaction of the corresponding binary pairs [9]. However, due to the variety of sources for the several systems studied, the data correspond to different polymer molecular weights, m, and to different temperatures. Since the variation of χ with concentration may depend on M for low M′s, it has selected data only for $M > 2 \times 10^9$, where no M dependence is detected.

Using the concept of a regular solution, it is possible to treat the free energy of mixing as being made up additively from contributions due to configurational probability and a free energy arising from nearest – neighbor interactions. The latter are characterized by the "Flory – Huggins interaction parameter", χ, which specifies, in units of RT, the excess free energy for the transfer of a mole of solvent molecules from the pure solvent to the pure polymer phase. With the initial state involving a solvent and a disordered polymer phase, the Flory – Huggins treatment leads to

$$\Delta G_M = RT(n_1 \ln \Phi_1 + n_2 \ln \Phi_2 + n_1 \chi \Phi_2) \tag{1.16}$$

Table 1.1 Empirical values of the g° interaction parameters at infinite dilution calculated from the experimental data of χ vs. polymer concentration. (From ref. [6])

System^a	T, °C	$\bar{V}_2/\bar{V}_1$	$g_\phi{}^o$	$g_v{}^o$
PDMS–benzene	20, 25	0.9509^b	0.65	0.63
PDMS–toluene†	20	0.9722	0.61	0.60
PDMS–cyclohexane†	20, 25	0.9517^b	0.51	0.49
PDMS–*n*-pentane	20	0.9099	0.47	0.42
PDMS–*n*-hexane	20	0.9324	0.42	0.38
PDMS–*n*-heptane	20	0.9509	0.46	0.43
PDMS–*n*-octane†	20	0.9619	0.49	0.47
PDMS–*n*-nonane	20	0.9712	0.45	0.43
PDMS–2-2-4-trimethyl-pentane	20	0.9595	0.44	0.42
PDMS–3-methylpentane	20	0.9996	0.48	0.48
PDMS–p-xylene	20	0.9823	0.55	0.54
PDMS–ethylbenzene	20	0.9828	0.58	0.57
PDMS–hexamethyl-disiloxane	20	0.9303	0.34	0.29
PDMS–octamethyl-trisiloxane	20	0.9487	0.26	0.22
PS–cyclohexane†	20–30	0.8932^b	0.84	0.82
	25		0.74	0.71^c
PS–methyl ethyl ketone†	10, 25, 50	0.8817^b	0.70	0.65
PS–ethylbenzene	10, 35	0.9211^b	0.56	0.53
PS–diethyl ketone	20	0.8995	0.78	0.75
PS–acetone	25	0.8705	0.82	0.79
PS–*n*-propyl acetate	25	0.8813	0.71	0.67
PS–*n*-butyl acetate	20	0.9036	0.71	0.68
PS–benzene	15–45	0.8719^d	0.42	0.34
			0.46	0.38
PS–toluene	25, 30	0.9221^b	0.35	0.29
			0.42	0.37
PS–*n*-propyl ether	20	0.8904	0.82	0.80
PS–carbon tetrachloride	20	0.8891	0.45	0.38
PS–dioxane	20	0.9131	0.56	0.52
PIB–benzene†	25	0.8894	0.73	0.70
PIB–*n*-pentane†	25	0.8443	0.66	0.60
PIB–*n*-octane	25	0.8980	0.54	0.49
PIB–cyclohexane†	25	0.8901	0.48	0.42
NR–benzene†	25	0.9075	0.46	0.40
NR–methyl ethyl ketone	25	0.8965	0.83	0.81
NR–ethyl acetate	25	0.8924	0.84	0.82
PPO–carbon tetrachloride†	5.6	0.9391	−0.05	−0.12
PPO–chloroform†	5.6	0.9272	−0.86	−1.01
POCS–benzene	25, 40			0.55
POCS–methyl ethyl ketone	25			0.73
PP–diethyl ketone	25		0.85	
PP–diisobutyl ketone	25		0.70	
PBD–chloroform†	25		0.15	

[a] Dagger indicates data available on the whole concentration range. [b] At 25°C. [c] Reference [26]. [d] At 30°C.

The concept of "regular solution" was introduced by Hildebrand (1929) [10] and defined as a solution in which the partial molar entropies of the components are those to be expected from the ideal solution law. From this definition it follows that any deviation from ideal solution behavior in a regular solution is entirely accounted for by the heat of mixing. When Hildebrand first formulated the concept of regular solutions, he assumed that athermal solutions would necessarily follow the ideal solution law. Much later, when the physical chemistry of solutions of high molecular weight substances was subjected to detailed investigation, it became obvious that differences in molecular size of solute and solvent may lead to a very large deviation from solution ideality even if no heat effect accompanies the formation of the solution.

The entropy of mixing disoriented polymer and solvent may be obtained:

$$\Delta S_M{}^* = -k(n_1 \ln \Phi_1 + n_2 \ln \Phi_2) \tag{1.17}$$

An asterisk is appended to the symbol ΔS_M^* as a reminder that it represents only the configurational entropy computed by considering the external arrangement of the molecules and their segments. Contributions to the entropy resulting from specific interactions between neighbords will be considered later.

If the configurational entropy $\Delta S_M{}^*$ is assumed to represent the total entropy change ΔS_M on mixing, the free energy of mixing is obtained by combining equations

$$\begin{aligned}\Delta G_M &= \Delta H_M - T\Delta S_M = \Delta H_M - T\Delta S_M{}^* \\ &= kT[n_1 \ln \Phi_1 + n_2 \ln \Phi_2 + \chi n_1 \Phi_2]\end{aligned} \tag{1.18}$$

The chemical potential μ_1 of the solvent in the solution relative to its chemical potential μ_1^0 in the pure liquid is obtained by differentiating the free energy of mixing, ΔG_M, with respect to the number n_1 of solvent molecules. Differentiation of equation for ΔG_M with respect to n_1 and multiplication of the result by Avogadro's number N in order to obtain the chemical potential per mole gives

$$\begin{aligned}&\mu_1 - \mu_1^0 = RT[\ln(1 - \Phi_2) + (1 - 1/r)\Phi_2 + \chi\Phi_2^2] \\ &r = V_2/V_1\end{aligned} \tag{1.19}$$

This equation may be written

$$\mu_1 - \mu_1^0 = -TdS_1^* + RT\,\chi\,\Phi_2^2 \tag{1.20}$$

$$\mu_1 - \mu_1^0 = -TdS_1^* + \Delta H_1 \tag{1.21}$$

Where

$$dS_1^* = -R[\ln(1 - \Phi_2) + (1 - 1/r)\Phi_2] \tag{1.22}$$

is the relative partial molar configurational entropy of the solvent in the solution. It may be obtained directly by differentiation of equation (1.17). If x varies inversely with T, the first two terms in equation (1.22) represent the relative partial molar entropy.

$$\Delta S^i_M = -R(n_1 \ln x_1 + n_2 \ln x_2) \tag{1.23}$$

And the ideal partial molar entropy is obtained by differentiation with respect to n_1 or n_2

[with $x_1 = n_1/(n_1 + n_2)$ and $x_2 = n_2/(n_1 + n_2)$] as

$$\Delta S^i_1 = -R \ln x_1;\ \Delta S^i_2 = -R \ln x_2 \tag{1.24}$$

And if the solution is athermal, so that $\Delta H_1 = \Delta H_2 = 0$, the ideal free energy of mixing is

$$\Delta G^i_M = -T\Delta\Delta^i_M = RT(n_1 \ln x_1 + n_2 \ln x_2) \tag{1.25}$$

The solvent activity would then be given by

$$\ln a_1 = -\Phi_2 V_1/V_2 - 1/2(\Phi_2 V_1/V_2)^2 - 1/3(\Phi_2 V_1/V_2)^3 - \cdots + \chi\Phi_2^2 \tag{1.26}$$

In this case a large value of V_2/V_1 would make mixing impossible if χ had an appreciable positive value. Thus, endothermic mixing of high molecular weight polymers with solvents is possible only because of the conformational entropy gained by flexible chain molecules in the process of dilution.

Whatever the detailed interpretation of the thermodynamic behavior of polymer solutions, the term

$$(1/2 - \chi)\Phi_2^2 \tag{1.27}$$

in equation (1.28) arises from contributions to $\Delta G^E_1/RT$ due to binary interactions of the chain segments of the solute. These may have their origins in a change in the conformational entropy of the polymer, in changes in intermolecular contact energy in the mixing process, in a change in the randomness of orientation of solvent molecules when they are displaced from contact with the macromolecular solute, in volume changes . . . etc. Expressing by asterisks quantities resulting from such binary interactions, gives the relation:

$$1/2 - \chi = -(\Delta H^*_1 - T\Delta S^*_1)/RT\ \Phi_2^2 \tag{1.28}$$

If we denote by Θ a temperature at which the coefficient of Φ_2^2 vanishes, then $\Delta H_1{}^* = \Theta\Delta S^*_1$, and this equation may be rewritten as

$$1/2 - \chi = \Psi(1 - \Theta/T) \tag{1.29}$$

where Ψ is

$$\Psi = T\Delta S_1^*/R\Phi_2^2 \tag{1.30}$$

The use of the parameters Θ and Ψ has supplanted the interaction parameter χ, as suggested by Flory [11] which describes the behavior of a given polymer - solvent at a single temperature.

The assumption of forces of interaction between solvent and solute led to the century old principle that “like dissolves like”. In many cases the presence of similar functional groups in the molecules suffices. This rule of thumb has only limited validity since there are many examples of solutions of chemically dissimilar compounds. For example, for small molecules methanol and benzene, water and N,N-dimethylformamide, aniline and diethyl ether, and for macromolecules, polystyrene and chloroform, are completely miscible at room temperature. On the other hand, insolubility can occur in spite of similarity of the two partners. Thus, polyvinylalcohol does not dissolve in ethanol, acetyl cellulose is insoluble in ethyl acetate, and polyacrylonitrile in acrylonitrile [12]. Between these two extremes there is a whole range of possibilities where the two materials dissolve each other to a limited extent.

Rather than the “like dissolves like” rule, it is the intermolecular interaction, between solvent and solute molecules, which determines the mutual solubility. A compound A dissolves in a solvent B only when the intermolecular forces of attraction K_{AA} and K_{BB} for the pure compounds can be overcome by the forces K_{AB} in solution [13].

The solubility parameter δ of Hildebrand [14] as defined in equation (1.31), can often be used in estimating the solubility of non-electrolytes solutes in organic solvents.

$$\delta = (\Delta E_v/Vm)^{1/2} = (\Delta H_v - RT/Vm)^{1/2} \tag{1.31}$$

In this equation Vm is the molar volume of the solvent, and ΔE_v and ΔH_v are the molar energy and the molar enthalpy (heat) of vaporization for a gas of zero pressure, respectively. δ is a solvent property which measures the work necessary to separate the solvent molecules (i.e. disruption and reorganization of solvent/solvent interactions) to create a suitably sized cavity, large enough to accommodate the solute. Accordingly, highly ordered self-associated solvents exhibit relatively large δ-values. As a rule, it has been found that a good solvent for a certain non-electrolyte has a δ –value close to that of the solute [15].

When a polymer in solid state is in contact with a liquid solvent, we observe first a swelling phenomenon because the penetration of the small molecules of the solvent inside of the polymer structure. This behavior is different to that of the solutes non-macromolecules where the molecular identities are separated progressively to pass to the bulk of the solvent. In the case of the polymers this process is more complicated.

The mutual solubilities of components whose molecular sizes are drastically different is the case of the binary polymer-solvent systems, the molecules of the solute (polymer) are many order of magnitude larger than those of the solvent (monomer). In the solubility of the components whose molecular sizes are not significative different, the molar volume ratio is perhaps 2 or even 5, but always less than 10 [10].

The thermodynamic properties of polymers solutions have been reviewed by several authors [11, 17–19], we confine our attention here to the most common and perhaps also the most useful relation proposed by Flory [3] and Huggins [4] a generation ago.

The quantitative theory of the change in conformational entropy produced by the mixing of flexible chain polymers with a solvent of low molecular weight was formulated by Flory [3] and Huggins [4] who evaluated the number of distinguishable ways in which N_1 solvent molecules with a molar volume V_1 and N_2 polymers chains with a molar volume V_2 can be placed on a lattice so they each lattice site is occupy by either a solvent molecule or one of the V_2/V_1 segments of a polymer chain. In the calculation there is an assumption that, in placing a given chain segment on the lattice, which already contains previously placed chains, the probability of occupancy of a lattice site may be approximated by the overall fraction of occupied sites. This approximation is not real in very dilute solutions, where molecular coils, with a high local concentrations of chain segments, are separated by regions of pure solvent. The assumption of the Flory – Huggins theory is reasonable in the concentration range in which the chains interpenetrate each other, so that the density of chain segments is uniform, on the molecular scale, and it is in this range that the theory has been successful.

The Free energy change, ΔG, which results when we mix n_2 moles of polymer with n_1 moles of solvent at constant temperature and pressure is given by

$$\Delta G/RT = n_1 \ln \Phi_1 + n_2 \ln \Phi_2 + \chi \Phi_1 \Phi_2 (n_1 + V_2/V_1 n_2) \tag{1.32}$$

Where V_2/V_1 (r) is the ratio of the molar volume of the polymer to that of the solvent and χ is the Flory parameter which depends primarily on the intermolecular forces between solute and solvent. According to the original formulation, this parameter is zero for athermal mixtures. However, subsequent work has shown that both the excess entropy and the excess enthalpy contribute to χ:

$$\chi = \chi_s + \chi_h \tag{1.33}$$

where χ_s is the contribution from the excess entropy and χ_h is that from the excess enthalpy.

Knowledge of the magnitude of polymer – solvent interactions, and particularly of the “goodness” of a solvent for a given polymer, is very important for the investigation of the properties of polymers and the solutions and also for technological applications [20]. The goodness of solvents has hitherto been determined by either the Hildebrand solubility parameter δ [10] or the Flory – Huggins interaction parameter χ [21–25].

In the first case it is necessary to know solubility parameters of both the solvent, δ_1, and the polymer, δ_2. A general rule for non – polar systems is that the solvent is better when its δ_1 values is closer to δ_2. In polar systems, contributions of dispersive forces, dipole moments and hydrogen bonds to the total χ value [26–29] should be taken into account. The solubility parameter can thus be used only for a rough estimation of the goodness of a solvent, without claiming particular reliability of the conclusions drawn.

Another possible variable for the characterization of the goodness of solvents is the interaction parameter χ values, expressing the measure of deviations of actual solutions from ideal ones. This value can be determined by several methods, which are, mostly experimentally demanding and time-consuming. χ is dependent on both the polymer concentration and molecular weight and information provided about the specific interactions in the solution is of no particular interest [11, 30, 31]. Solvents, obviously different in quality, yield quite close values and thus the resolving capability is low. Comparison of results obtained by various methods and/or experimenters is thus fairly difficult [30, 32–34].

Once the second virial coefficient has been obtained for a given polymer – solvent system one can calculate the corresponding Flory – Huggins interaction parameter, χ, from the equation:

$$A_2 = (1/2 - \chi)/\rho_2^2 V_1 \tag{1.34}$$

Where ρ_2 is the density of the polymer ($\mathrm{g\,cm^{-3}}$) and V_1 is molar volume of the solvent ($\mathrm{cm^3 mol^{-1}}$).

We can also summarized a method for calculating the Flory – Huggins interaction parameter, χ, for a given polymer and solvent using the solubility parameters δ.

The solubility parameter of the polymer, δ_2, can be related to χ by: [35, 36]

$$\chi = V_1/RT(\delta_1 - \delta_2)^2 \tag{1.35}$$

where δ_1 is the solubility parameter of the solvent. (Units of solubility parameter are $(\mathrm{energy/volume})^{1/2}$, generally $\mathrm{cal}^{1/2}\ \mathrm{cm}^{-3/2}$). The last equation can be rewritten as

$$\delta_1^2/RT - \chi/V_1 = [2\delta_2/RT]\delta_1 = \delta_2^2/RT \tag{1.36}$$

This is the equation of a straight line. Hence, when the left – hand side is plotted as a function of δ_1 one can estimate δ_2.

Figure 1.1 is an example of a plot obtained from equation (1.34). The δ_2 value estimated is $10.2\,\mathrm{cal}^{1/2}\ \mathrm{cm}^{-3/2}$ [37]. The values of R and T used were 1.99 cal/mol K and 298 K, respectively.

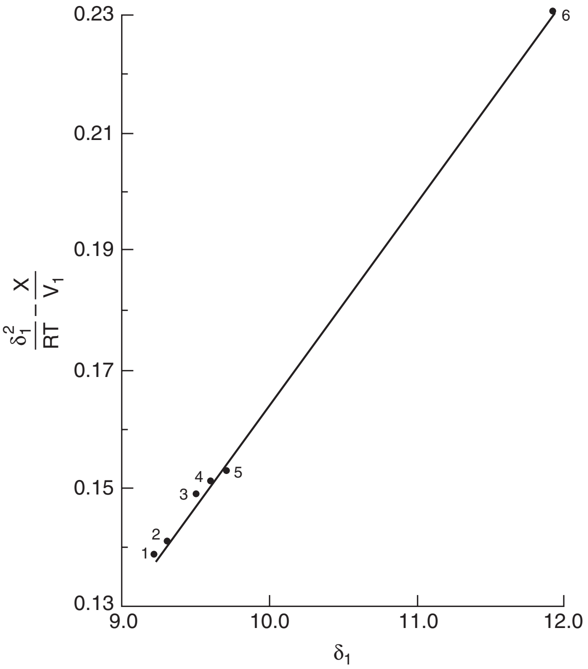
There are also other quantities that are dependent on the goodness of solvents. Among them is the Huggins viscosity constant k', which can be determined quite easily and, because of its interesting properties, seems to be suitable for direct determination of the goodness of a particular solvent [20].

The dependence of viscosity η of dilute polymer solutions on concentration c can be described by a polynomial in the form [31, 38].

$$\eta = \eta_0(1 + a_1 c + a_2 c^2 + \ldots) \tag{1.37}$$

where η_0 is the viscosity of the pure solvent. This equation is generally presented in the form:

Fig. 1.1 Plot of equation (1.36) for poly(vinyl acetate) in benzene (1), Chloroform (2), Chlorobenzene (3), methyl ethyl ketone (4), acetone (5) and acetonitrile (6). (From ref. [37])



$$[\eta] = \eta_0(1 + [\eta]c + k'[\eta]^2c^2 + \ldots) \tag{1.38}$$

where $[\eta]$ is the intrinsic viscosity and k' is the dimensionless Huggins viscosity constant. Neglecting terms with third and higher powers of concentration yields the well known Huggins equation. Figure 1.2 shows a classical plot to obtain $[\eta]$ and k' for several fraction of the poly (monobenzyl itaconate) (PMBzI) [39].

As mentioned in some monographs [31, 38] and confirmed by numerous experimental results [40–43], the Huggins constant is independent of the molecular weight of the polymer. Its value is influenced only by the goodness of the solvent. However, it can be expected that the Huggins constant will be molecular – weight – dependent only in polymers easily associating in solution, either by the effect of specific interactions as strong ionic, or polar interactions or by the effect of hydrogen bonds [20].

One of the most surprising generalities in the world of polymers is that $[\eta]$ values for a series of homologous polymers under a fixed solvent condition (solvent and temperature) follows a simple power law as

$$[\eta] = KM^{\nu} \tag{1.39}$$

over an extended range of M. Here, K and ν are constants for the polymer + solvent considered. This equation (1.39) is referred to as the Mark – Houwink – Sakurada (MHS).

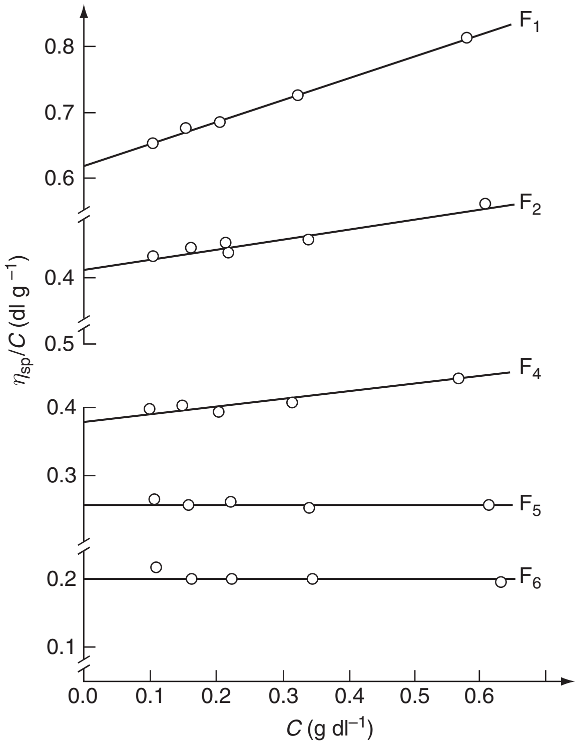


Fig. 1.2 Viscosity data on some fractions of PMBzI, plotted according to the Huggins equation. (From ref. [39])

The relation between number molecular weight, Mn and intrinsic viscosity, $[\eta]$, for poly(pentachlorophenyl methacrylate) (PPClPh) can be represented by the Mark – Houwink – Sakurada equation [44].

Figures 1.3 and 1.4 ilustrate these double logarithmic plots in different solvents.

Becerra et al. [44] have found for PPClPh, the following relations:

o-Dichlorobenzene at 25°C: $[\eta] = 25{,}4 \cdot 10 - 5\,\mathrm{Mn}^{0{,}67}$
o-Xilene at 25°C: $[\eta] = 28{,}6 \cdot 10 - 5\,\mathrm{Mn}^{0{,}63}$
Chlorobenzene at 25°C: $[\eta] = 29{,}1 \cdot 10 - 5\,\mathrm{Mn}^{0{,}63}$
Toluene at 25°C: $[\eta] = 35{,}2 \cdot 10 - 5\,\mathrm{Mn}^{0{,}58}$
Benzene at 40°C: $[\eta] = 53{,}7 \cdot 10 - 5\,\mathrm{Mn}^{0{,}50}$
Ethylbenzene at 25°C: $[\eta] = 61{,}0 \cdot 10 - 5\,\mathrm{Mn}^{0{,}50}$

The results obtained on poly(pentachlorophenyl methacrylate) show that $[\eta]$ is accurately proportional to $\mathrm{Mn}^{0{,}50}$ for the ideal or theta (θ) solvent.

According to Fugita [45] the main experimental facts that have to be explained theoretically are as follows:

1. When $[\eta]$ is plotted against M on a log – log graph paper, it gives a straight line over a wide range of M;