Physicochemical Behavior and Supramolecular Organization of Polymers

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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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Contents

Abbreviations

a	activity
a.c	alternating current
α	thermal expansion coefficient
α	relaxation associated to Tg
A_i, i = 2, 3, ...	ith virial coefficient
A	area
$Å_o$	surface limiting area
$Å_c$	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