Sperling: Dilute Solutions

3.1 INTRODUCTION

3.1.1 Polymer size and shape

-Size and shape of polymer =

heart of polymer science and engineering

i.e., MW+MWD+Chain conformation → Mechanical and rheological properties are predicted

-Mark-Houwink-Sakurada eq for intrinsic viscosity:

$[\eta] = KM_v^{\alpha}$

K and α are constants specific to the solvent and temperature used in the measurements.

Linear vs planar (globular) molecules

-Linear chains:

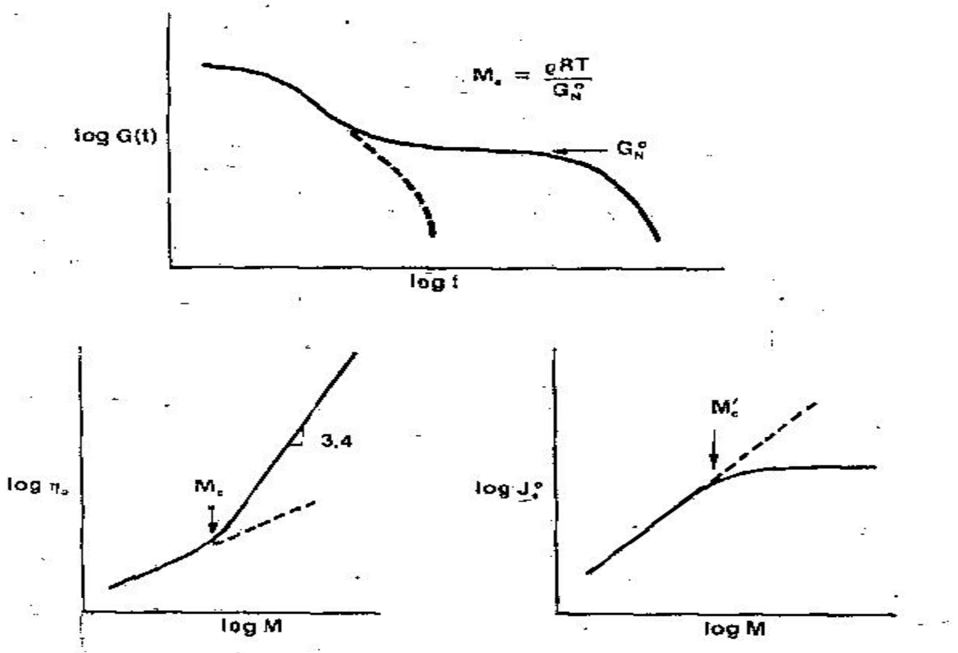
PE, PEO, PP, PS, PMMA, PVAC, polybutadiene.....→ Easy to recoil and entangle (Physical cross-linking)→Large viscosity increase w/ MW

-Planar or globular structured chains:

Hyperbranched polymer (HBP), graphene (2D), allyl isocyanurate as compared with allyl ether..... (See Supplementary)→ Hard to recoil and entangle→Reduce the mixture viscosity significantly at low contents.

Scan JE Mark Figure 24 and Table (Rouse model)

(*Physical Properties of Polymers, ACS, Washington, D.C.,1984*)



CHARACTERISTIC MOLECULAR WEIGHTS FOR
UNDILUTED LINEAR POLYMERS

	M_e	M_c	M_c'
Polystyrene	19,000	36,000	130,000
Poly (α-methyl styrene)	13,500	28,000	104,000
1,4 Polybutadiene	1,700	5,000	11,900
Poly (vinyl acetate)	6,900	24,500	86,000
Poly (dimethyl siloxane)	8,100	24,400	56,000
Polyethylene	1,250	3,800	14,400
cis-Polyisoprene	6,300	10,000	28,000
Poly (methyl methacrylate)	5900 (10,000)	27,500	> 150,000
Polyisobutylene	8,900	15,200	—

Figure 24. Characteristic molecular weights.

Notes 1) Rubbery plateau is defined and extended to longer time (higher temperature) with higher MW. 2) flexible chains are entangled at smaller molecular weights than rigid ones (Table 2.4).

Classical problems related to MW

1. Typical MW of polymer: 25,000<MW<1,000,000

-Below this is oligomer

-Telemor: Oligomers formed by chain transfer reaction

-Telechelic oligomer or telemors with functional groups on both ends→Intended for further chemical reactions particularly for block copolymers or network formation.

-Macromer (macromonomer): Polymer having reactive group at only one end group

-Ultra high MW: MW>10^6 (UHMWPE)

-Pleistomer:MW>10^7

-As MW↑---Mechanical strength↑(asymptotically), Viscosity↑(two steps), Processability↓(Extrusion, injection not possible, Needs gel spinning)

2. MW depends on preparation methods, and shows MWD.

3. Chain conformation = Spatial arrangement

▶Determined by light scattering (dilute solution), small angle neutron scatterings (SANS) (bulk state)

▶Size (shape) is estimated using the structure and MW of polymers

($<r^2>=cnl^2$, freely jointed, rotating, hindered rotation models)

4. Chain conformation depends on temperature, solvent structure, crystallization, orientation, presence of other polymers.

Molecular weight determination

◆Gaseous molecules: By IG law

Molecules must be separated (diluted→ideal gas law)

PV=nRT → n → MW= weight/n

◆Polymer: By dilute solution law (Solution thermodynamics)

Polymer chains must be separated in solvent

<*Sperling Ch 4: Concentrated solution, phase separation, diffusion*>

3.1.2 How does a polymer dissolve?

▶Amorphous polymer at T>Tg (Polymer melts);

Follow Fick's law of diffusion, 4.4)

$J_A= -CD\nabla x_A=-D\nabla C_A$ <Flux is directly proportional to the gradient>

$C=C_A + C_B$, D=Dffusivity

▶ T<Tg = Non-Fickian <Diffusion depends on (relaxation) time>

Slow diffusion of solvent into the polymer→ Plasticizes polymers→Lowers the Tg below ambient temperature→ Swelling occurs rapidly in rubbery state→ Swollen-unswollen boundary moves inward (Stress at the swelling boundary causes craze or fracture: ESCR)→ Polymers diffuse out of swollen mass into solvent to follow Fickian diffusion.

▶Cross-linked polymer only swells to equilibrium, not dissolved.

▶Also, polymers with high T_m, or strong secondary bonds (PAN) are not dissolved without degradation→ MW cannot be determined directly.

3.2 The solubility parameter

Solubility of A in B is governed by the free energy of mixing

$$\Delta G_M = \Delta H_M - T\Delta S_M \qquad (3.1)$$

$\Delta G_M < 0$: Solution occurs spontaneously.

$\Delta G_M > 0$: Separation occurs spontaneously.

$T\Delta S > 0$: ∵ Entropy increases upon mixing→ Entropy drives mixing.

▶$\Delta H_M > 0$ (Endothermic) for nonpolar organic compounds.

▶Exception is found when the two species attract one another by having opposite polarities (acid and base), or hydrogen bonding.