

STRUCTURES OF POLYMERS

PRIMARY STRUCTURE

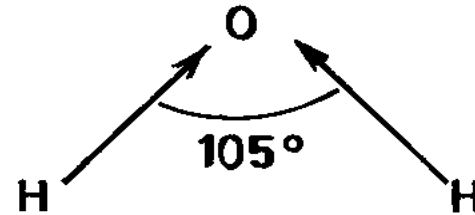
Primary structure refers to the atomic composition and chemical structure of the monomer.

- The nature of bonds in monomers (chemical bonding)
- The type of monomers that are capable of forming polymers (functionality of monomers)
- The mode of linking of monomers (polymerization mechanisms)
- The chemical composition of monomers and the properties conferred on monomers as a result of their chemical composition

A. POLARITY OF MONOMERS



Non-polar; dipoles from polar bonds cancel due to symmetry



Polar; dipoles from polar bonds do not cancel

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- Polarity affects the intermolecular attraction between chain molecules, and thus the regularity and symmetry of polymer structure.
- Properties such as the solubility and electrical nature of polymers, which depend on polymer structure, are intimately related to polarity.

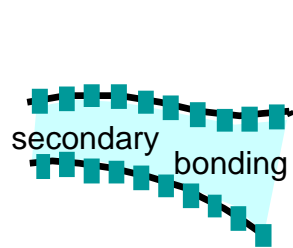
SECONDARY STRUCTURE

A physical picture of what these long molecules are really like referred to as the secondary structure of a polymer molecule the size and shape of an isolated single molecule.

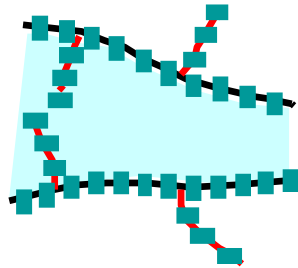
- ❖ The size of the polymer is best discussed in terms of molecular weight.
- ❖ The shape of the polymer molecule (molecular architecture) will be influenced naturally by the nature of the repeating unit and the manner in which these units are linked together.
- **Configuration** — Arrangement fixed by primary valence bonds; can be altered only through the breaking or reforming of chemical bonds
- **Conformation** — Arrangement established by rotation about primary valence bonds

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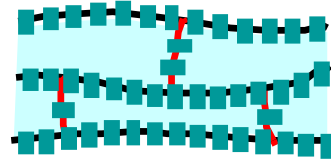
Configuration



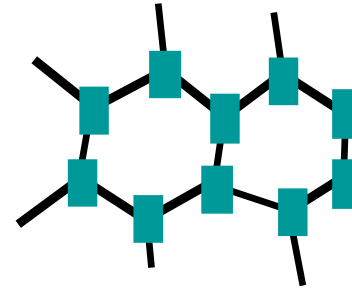
Linear



Branched



Cross-Linked



Network

Recurrence regularity

- Head-to-tail configuration
- Head-to-head configuration
- Tail-to-tail configuration

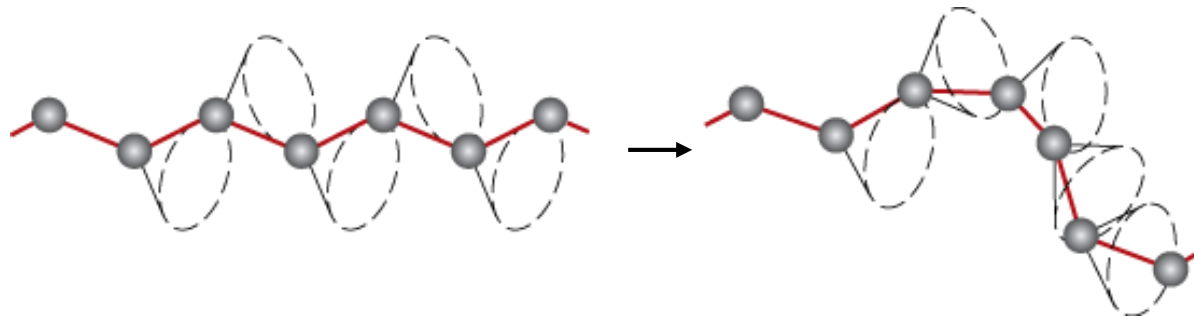
Stereoregularity

- Cis, Trans isomerism
- Tacticity: Isotactic, Syndiotactic, Atactic

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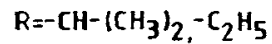
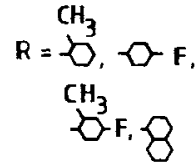
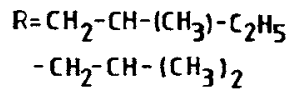
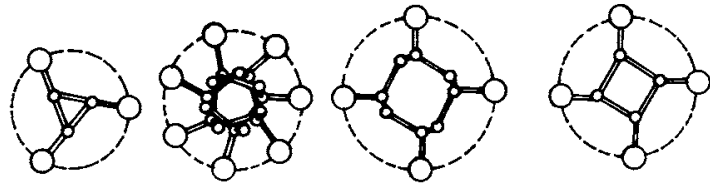
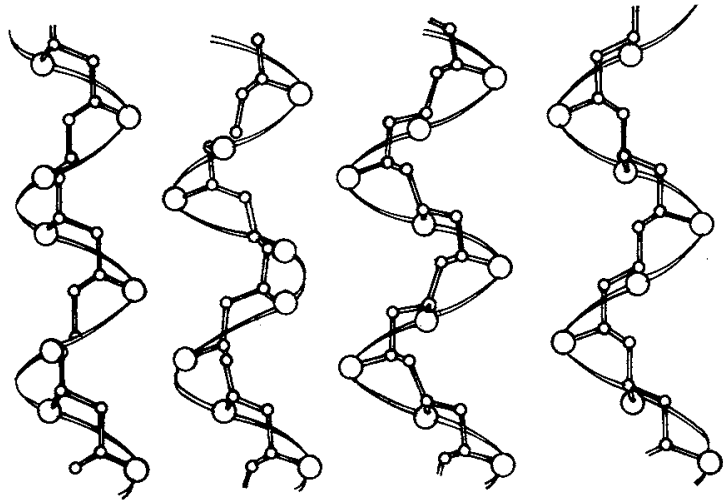
Conformation – Molecular orientation can be changed by rotation around the bonds

- note: no bond breaking needed
- Steric factors
- Whether the polymer is amorphous or crystalline
- Whether the polymer is in a solution state, molten state, or solid state

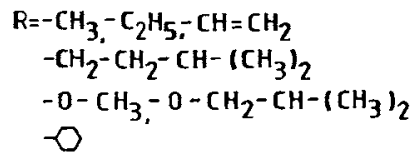


A segment of polymer chain showing four successive chain atoms; the first three of these define a plane, and the fourth can lie anywhere on the indicated circle which is perpendicular to and dissected by the plane.

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OR



(a)

(b)

(c)

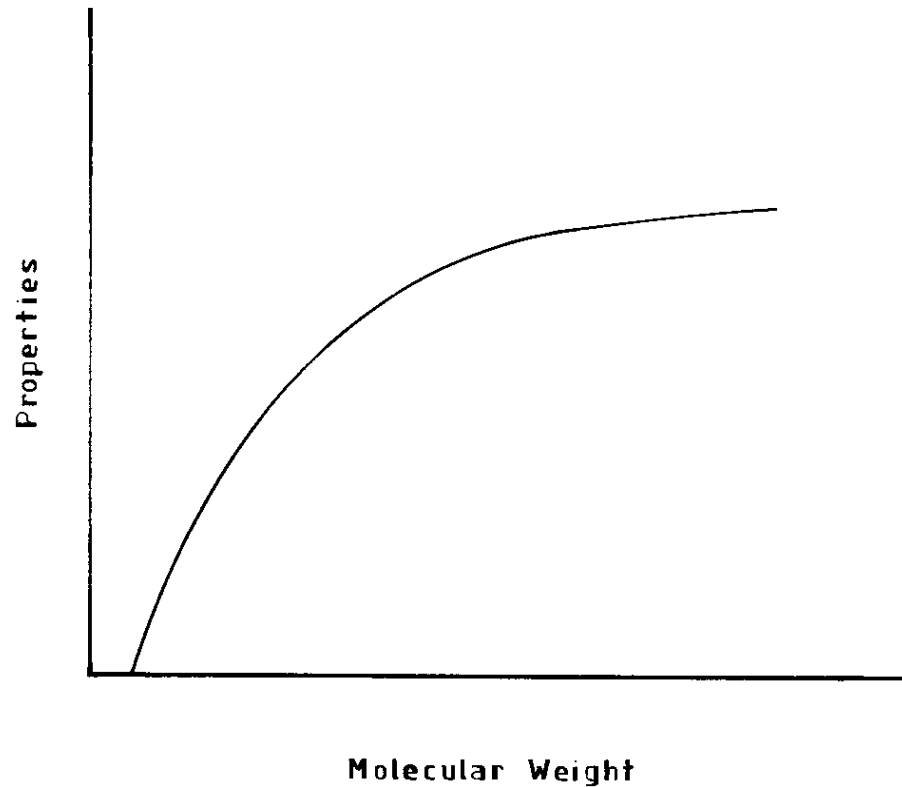
(d)

- ❖ The shape (flexibility) of a polymer molecule is temperature dependent. At sufficiently high temperatures, the polymer chain constantly wiggles, assuming a myriad of random coil conformations. The flexibility of polymer molecules, which is a function of substituents on the backbone, has a strong influence on polymer properties.

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Molecular Weight

The unique properties exhibited by polymers and the difference in behavior between polymers and their low-molecular-weight analogs are attributable to their large size and flexible nature.



*Change of physical properties
with molecular weight.*

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The molecular weight of polymers can be determined by a number of physical and chemical methods.

These include

- (1) end group analysis, (M_n)
- (2) measurement of colligative properties, (M_n)
- (3) light scattering, (M_w)
- (4) ultracentrifugation, (M_w)
- (5) dilute solution viscosity, (M_w), (M_v)
- (6) gel permeation chromatography (GPC) (M_n), (M_z)

Colligative properties are determined by the following measurements on dilute polymer solutions:

- Vapor pressure lowering
- Boiling point elevation (ebulliometry)
- Freezing point depression (cryoscopy)
- Osmotic pressure (osmometry)

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TERTIARY STRUCTURE

- Tertiary structure is concerned with the nature of the intermolecular secondary bonding forces and with structural order of the resulting polymer.
- The process of molecular aggregation occurs essentially by either of two possible arrangements of molecules, leading to either a crystalline or amorphous material.

A. SECONDARY BONDING FORCES (COHESIVE ENERGY DENSITY)

A quantitative measure of the magnitude of secondary bonding forces is the cohesive energy density (CED), which is the total energy per unit volume needed to separate all intermolecular contacts and is given by:

$$\text{CED} = \frac{\Delta E_v}{V_L}$$

where ΔE_v = molar energy of vaporization
 V_L = molar volume of the liquid

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B. CRYSTALLINE AND AMORPHOUS STRUCTURE OF POLYMERS

When a polymer is cooled from the melt or concentrated from a dilute solution, molecules are attracted to each other forming a solid mass. In doing so, two arrangements are essentially possible:

- In the first case, the molecules vitrify, with the polymer chains randomly coiled and entangled. The resulting solid is amorphous and is hard and glassy.
- In the second case, the individual chains are folded and packed in a regular manner characterized by three-dimensional long-range order. The polymer thus formed is said to be crystalline.

1. Crystallization Tendency

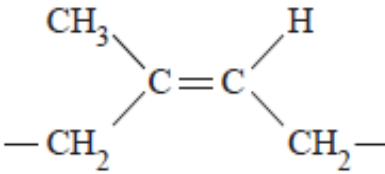
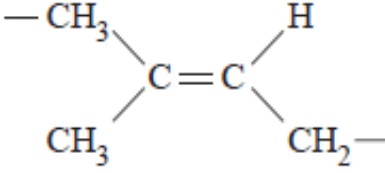
The tendency for a polymer to crystallize, therefore, depends on the magnitude of the inherent intermolecular bonding forces as well as its structural features.

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2. Structural Regularity

Regularity is not sufficient to ensure crystallizability in polymers. The spatial regularity and packing are important.

Table 3.8 *Properties of Polyisoprene Isomers*

| Isomer | Structure | Properties |
|---|---|--|
| 1,4- <i>cis</i> -polyisoprene (heavea rubber) |  | Soft, pliable, easily soluble rubber; has a high retractive force; used for making vehicle tires |
| 1,4- <i>trans</i> -polyisoprene (gutta-percha) |  | Tough, hard; used as golf ball covers |

- The stereoregular *trans* form is more readily packed and crystallizable and has properties of crystalline polymers.
- Isotactic and syndiotactic polymers possess stereoregular structures. Generally these polymers are rigid, crystallizable, high melting, and relatively insoluble. On the other hand, atactic polymers are soft, low melting, easily soluble, and amorphous.

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3. Chain Flexibility

The flexibility of chain molecules arises from rotation around saturated chain bonds. With a chain of $-\text{CH}_2-$ units as a basis, variations on this unit will affect rotation of adjacent units and, hence, chain flexibility. Studies of this type have led to the following general conclusions:

- Rapid conformational change due to ease of rotation around single bonds occurs if such groups as $(-\text{CO}-\text{O}-)$, $(-\text{O}-\text{CO}-\text{O}-)$, and $(-\text{C}-\text{N}-)$ are introduced into the main chain. If they are regular and/or if there exist considerable intermolecular forces, the materials are crystallizable, relatively high melting, rigid, and soluble with difficulty. However, if they occur irregularly along the polymer chain, they are amorphous, soft, and rubbery materials.
- Ether and imine bonds and double bonds in the *cis* form reduce the energy barrier for rotation of the adjacent bonds and “soften” the chain by making polymers less rigid, more rubbery, and more readily soluble than the corresponding chain of consecutive carbon-carbon atoms. If such “plasticizing” bonds are irregularly distributed along the polymer chain length, crystallization is inhibited.
- Cyclic structures in the backbone and polar group such as $-\text{SO}_2-$, and $-\text{CONH}-$ drastically reduce flexibility and enhance crystallizability.

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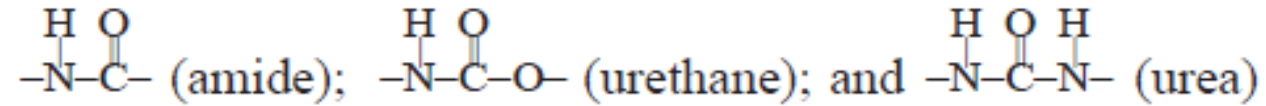
Table 3.9 *Effect of Chain Flexibility of Crystalline Melting Point*

| Polymer | Repeating Unit | T _m (°C) |
|--------------------------|--|---------------------|
| Polyethylene | $-\text{CH}_2-\text{CH}_2-$ | 135 |
| Polyoxyethylene | $-\text{CH}_2-\text{CH}_2-\text{O}-$ | 65 |
| Poly(ethylene suberate) | $-\text{O}(\text{CH}_2)_2-\text{OCO}-(\text{CH}_2)_6\text{CO}-$ | 45 |
| Nylon 6,8 | $-\text{NH}(\text{CH}_2)_6\text{NHCO}(\text{CH}_2)_6\text{CO}-$ | 235 |
| Poly (<i>p</i> -xylene) | $-\text{CH}_2-$  $-\text{CH}_2-$ | 400 |

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4. Polarity

Polymer molecules with specific groups that are capable of forming strong intermolecular bonding, particularly if these groups occur regularly without imposing valence strains on the chains, are crystallizable.



Molecules whose backbone contains $-\text{O}-$ units or with polar side groups ($-\text{CN}$, $-\text{Cl}$, $-\text{F}$, or $-\text{NO}_2$) exhibit polar bonding. If these groups occur regularly along the chain (isotactic and syndiotactic), the resulting polymers are usually crystalline and have higher melting points.

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Table 3.10 *Effect of Polarity on Crystallizability*

| Polymer | Repeat Unit | T _{em} (°C) |
|----------------------|--|----------------------|
| Polyethylene | $-\text{CH}_2-\text{CH}_2-$ | 135 |
| Nylon 6 | $\begin{array}{c} \text{H} \quad \text{O} \\ \quad \\ -\text{N}-\text{C}-(\text{CH}_2)_5- \end{array}$ | 223 |
| Nylon 6,6 | $\begin{array}{c} \text{H} \quad \quad \quad \text{H} \quad \text{O} \quad \quad \quad \text{O} \\ \quad \quad \quad \quad \quad \quad \quad \\ -\text{N}- (\text{CH}_2)_6 - \text{N}-\text{C}- (\text{CH}_2)_4 - \text{C}- \end{array}$ | 265 |
| Polyoxymethylene | $-\text{CH}_2-\text{O}-$ | 180 |
| Poly(vinyl chloride) | $\begin{array}{c} -\text{CH}_2-\text{CH}- \\ \\ \text{Cl} \end{array}$ | 273 |
| Polyacrylonitrile | $\begin{array}{c} -\text{CH}_2-\text{CH}- \\ \\ \text{CN} \end{array}$ | 317 |

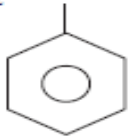
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5. Bulky Substituents

The vibrational and rotational mobility of intrinsically flexible chains can be inhibited by bulky substituents; the degree of stiffening depends on the size, shape, and mutual interaction of the substituents.

Large or bulky substituents, on the other hand, increase the average distance between chains and, as such, prevent the effective and favorable utilization of the intermolecular bonding forces.

Table 3.11 *Stiffening of Polymer Chains by Substituents*

| Polymer | Repeat Unit | T _m (°C) |
|-----------------|--|---------------------|
| Polyethylene | — CH ₂ — CH ₂ — | 135 |
| Polypropylene | — CH ₂ — CH — CH ₃ | 176 |
| Poly(1-butene) | — CH ₂ — CH — CH ₂ CH ₃ | 125 |
| Poly(1-pentene) | — CH ₂ — CH — CH ₂ CH ₂ CH ₃ | 75 |
| Polystyrene | — CH ₂ — CH —  | 240 |

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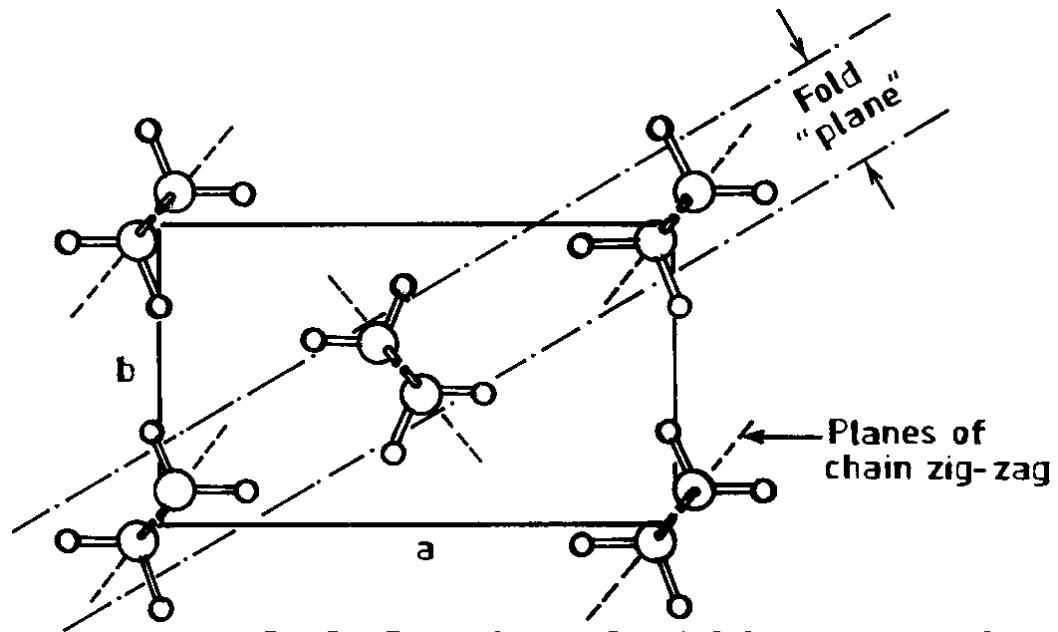
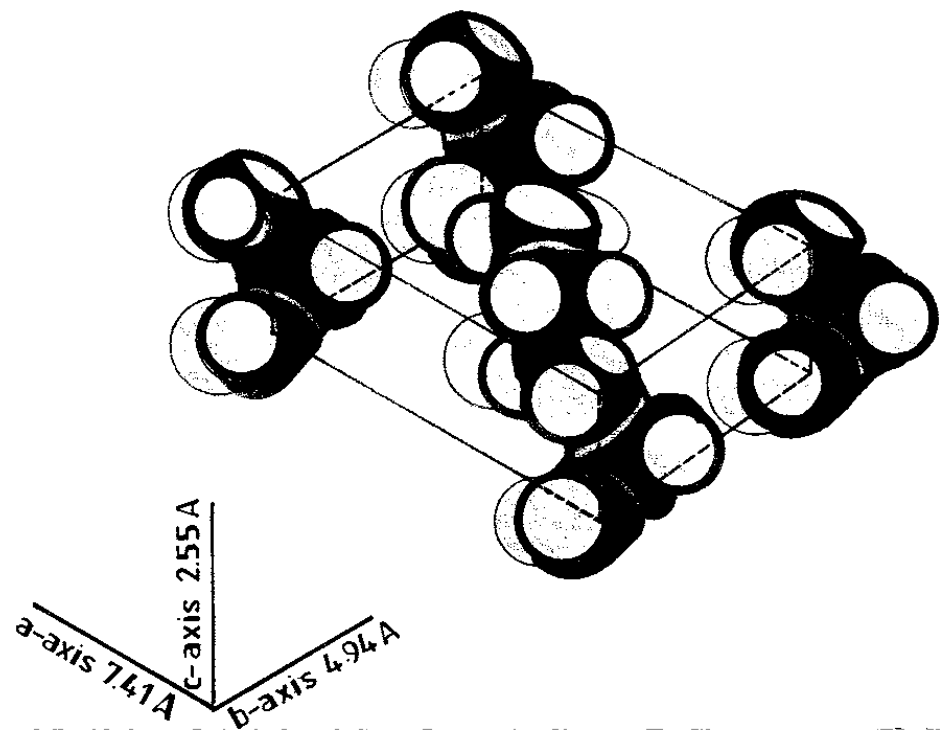
C. MORPHOLOGY OF CRYSTALLINE POLYMERS

The fringed micelle concept, which enjoyed popularity for many years, held that, since polymer chains are very long, they passed successively through the crystallites and amorphous regions.

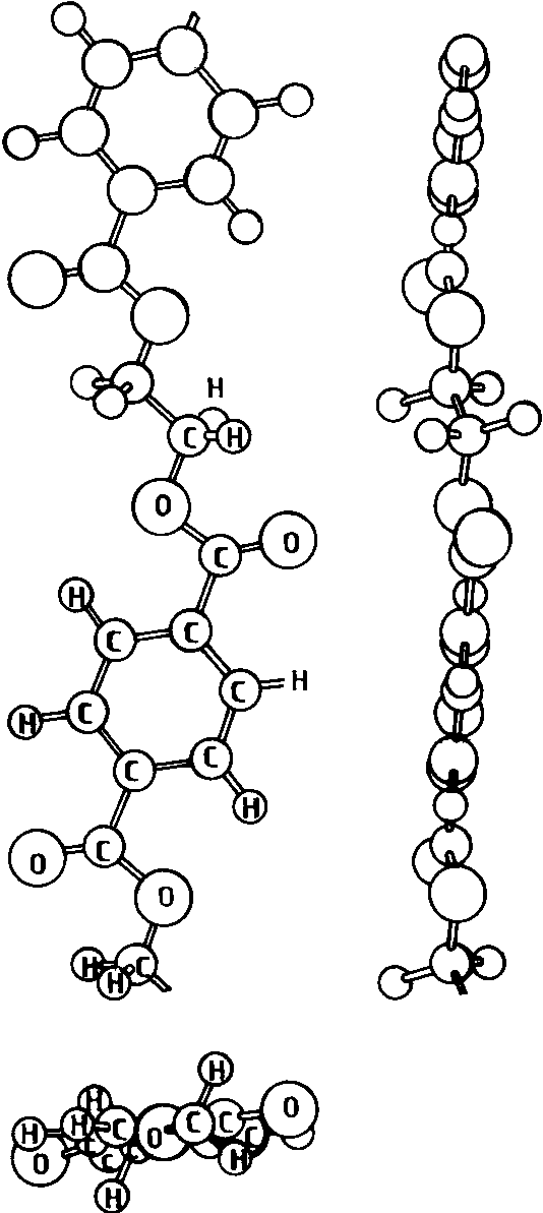


Fringed micelle model.

a. Polyethylene



b. Poly(ethylene terephthalate)



c. Polypropylene

