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Editorial

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EDITORIAL

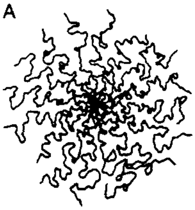
Development of new polymeric materials involves new arrangements of monomers more than it does development of new monomers. New monomer development for linear homopolymers is an expensive and limited endeavor in terms of the new properties that can be generated. Many more new avenues can be reached by permutations and rearrangements of existing monomers. Highly branched polymers, block copolymers and modifications of macromolecules and surfaces by grafting reactions are examples of new arrangements that differ significantly from linear homopolymers. End-functionalized polymers can be used as the "monomers" or building blocks of larger structure or assemblies. All of these structures contain chains that are attached by their ends into the structure. This is what known as "tethered chains". The following figure illustrates some of the possibilities.

The structures in figure all have chains tethered to some grafting site. In star-branched polymers, the grafting site is the central point. In graft polymers, it is the backbone line. End-functionalized polymers can be adsorbed or bound by the ends to a surface. In block copolymers, the tethering site is the interface between blocks of different, usually immiscible, chemical structure. Block copolymers and end-functionalized polymers have amphiphilic character, meaning that they tend to form aggregates or microstructure such as micelles, microemulsions, lamellae and monolayers.

Tethered chain structures become particularly interesting, and distinct in their behavior, when the lateral number density of chains is high. Owing to interactions among the chains, densely tethered chains are strongly stretched along the normal to the grafting site. So, for example, the arms of multibranched star molecules have been shown to be extended, as have chains terminally anchored on a surface or chains in block copolymer melt lamellae. Chain stretching is a unifying characteristic of tethered chains.

Bulk homopolymers

A

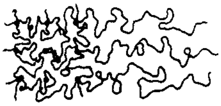


Multi-arm stars

B

Polymers from macromonomers

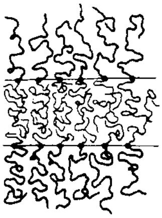
C



Tails in crosslinked networks

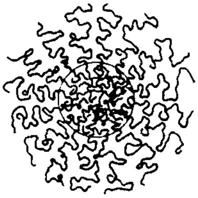
Block copolymer microphases

D



Ordered block copolymer
phases

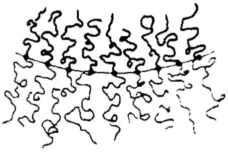
E



Micelles

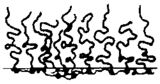
Polymers at interfaces

F



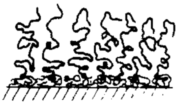
Block copolymers at
fluid - fluid interfaces
(microemulsions, vesicles, etc

G



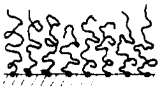
Graft copolymers at
fluid - fluid interfaces

H



Adsorbed block copolymers

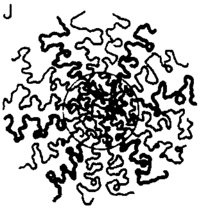
I



Grafted polymers

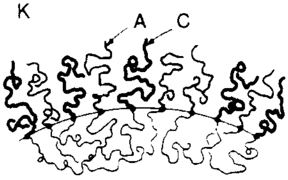
Mixed layers

J



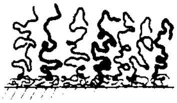
Mixed micelles

K



ABC triblocks at
fluid - fluid interfaces

L



Mixed adsorbed layers

Remarkably, the deformed state obtains under equilibrium conditions, in the absence of geometrical constraints and externally applied forces. Stretching in tethered chains is generated by their "desire" to aggregate and by the resulting interactions among the chains as they balance the energy of this stretching with adsorption energy, osmotic pressure, or interfacial energy.

This equilibrium deformation, in turn, affects many facets of tethered chain behavior. Stretched, tethered chains mix and move differently among their neighbors. Stretching inhibits interdigitation in cicumstances associated with growth of stored deformation energy. Novel dynamic behavior can also be driven by the release of stretching energy.

The systematic study of tethered chains and polymeric surfactants opens of several new avenues of importance to science and technology. Diblock polymers and end-functionalized polymers are the macromolecular counterparts of short chain surfactants. The study of polymeric aggregation and assembly behavior has some distinct advantage over the study of small surfactants. Long polymer chains interact according to fairly universal laws that reflect their general long-chain nature more than their local chemical structure. Their theoretical analysis is accordingly simpler. Macromolecular surfactants can be manipulated structurally in ways impossible for small surfactants. Molecular weight can be varied systematically over wide ranges allowing for study of the ensuing trends and tuning of material properties. The sizes of the structures formed by polymeric surfactants are generally larger making their observation some what easier. Chain architectures can be realized with polymer surfactants that can not be obtained otherwise(star-block copolymers, multi-block copolymers and others). The architectural variety of polymeric surfactants open new avenues for the design of new materials of technological relevance. For example, manipulating chain flexibility in polymeric surfactants opens the possibility for materials exhibiting proper liquid crystalline phases in both melts and solutions. Thus there are important points of contact to be made and exploited with the surfactant science and liquid crystal research communities.