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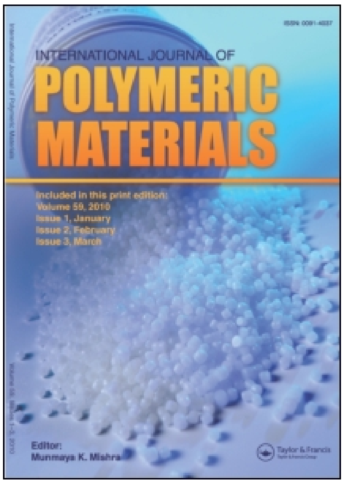

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Macromolecules in Ordered Media: Synthesis and Transformations

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Macromolecules in Ordered Media: Synthesis and Transformations

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A review of synthesis and transformations of macromolecules in ordered media is presented.

KEY WORDS Macromolecules, ordered media, synthesis transformations.

The processes of initiation, growth and transformation in liquid isotropic medium demonstrates on average one in 10^6 collisions is successful.

Polymerization in ordered media, solid monomers, crystallizing complexes of polymerizable monomers with other substances, adsorption layers on the surface of solid sorbents, micelles, channel complexes, and liquid-crystalline (or mesophase) media are able to exhibit unique forms of ordering the reaction medium.

V. A. Kargin and V. A. Kabanov[1] have reviewed publications on the solid-phase polymerization of monomers; trioxane and acetaldehyde, and proved the unsuitability of the quantitative description of similar processes taking place in the liquid phase.

The most favourable conditions for the formation and growth of macromolecular chains in structured systems are determined by a combination of mobility of the monomers and their ordered alignment with respect to each other. Polymerization in crystallizing media leads to the generation of labile "half-finished products" at the boundary of the crystalline and isotropic medium. They emerge for a short period of time and are quickly transformed into appropriate polymer chains.

The hypothesis of labile "half-finished products" explains satisfactorily the specific features of polymerization processes in structured media and can be justifiably adopted for the qualitative explanation of the specific features of reactions in ordered media.[2] The favourable orientation of monomer ensures an increase in the effective number of collisions and growth of the chain. At the moment of phase transitions, one should however take into account the space and time limitation on the existence of labile monomer layers. These will hinder the synchronous growth of chains, which leads to a low degree of monomer conversion.

The liquid-crystalline state combines orientation and also translational order with high molecular mobility. Such systems are interested in complex biochemical processes.

Several types of liquid-crystalline state are shown in Figure 1.[3-14] Most of the studies have been carried out with nematic liquid crystals, although other forms of ordering have been studied. Cholesteric liquid crystals are of particular importance in biological studies. Structures and textures discovered in the liquid-crystalline solutions of biological systems are similar to these that exist in low-molecular thermotropic liquid-crystalline systems.

Polymerization of vinyloleate with the formation of liquid-crystalline thermotropic polyvinyloleate was studied in 1965.[15] The monomer passes from the isotropic state to the liquid-crystalline state at −18°. At −40° vinyloleate is transformed into a crystal, and the thermal effect of the transition is 5 to 7 times higher than the thermal effect which accompanies the emergence of the liquid-crystalline state. It was established by X-ray analysis that radiation initiation of polymerization of mesomorphous vinyloleate produces a crystalline polymer, whilst the amorphous polymer was formed in the isotropic phase.

Kinetic control of the polymerization of vinyloleate and some other monomers in mesomorphous and isotropic media behave similarly. The molecular mass of polymers obtained in the mesomorphous state is higher than that of the corresponding polymers formed in the isotropic medium.[16-26]

Monomers used in these papers were obtained by functionalizing appropriate mesogene compounds containing polymerizable groups and generated nematic, smectic and cholesteric forms of liquid-crystalline polymers.

Three groups of liquid-crystalline polymer systems can be differentiated[27]:

1. On the basis of polymers containing mesogene groups in the main chain alternated with flexible fragments or in side branches where these groups are connected with the main chain by flexible "decouplings."

2. Polymers in which the mesomorphous state manifests itself in the presence of a low-molecular liquid such as water and include soaps, lipids and some proteins.

3. Rigid-chain and semi-rigid polymers of linear structure.

Some liquid-crystalline (mesophase) polymers do not contain mesogene groups, poly-4-methylpentene-1, as well as linear polyethylene containing the regulated amount of branches.[28,29]

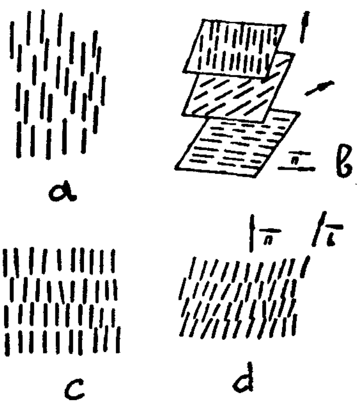


FIGURE 1 Types of the liquid-crystalline order, a—nematic; b—cholesteric; c—normal smectic; d—inclined smectic.

Experimental investigations of polymerization in liquid-crystalline media are subdivided into two groups: 1) the monomer is not a liquid crystal, but in its mixture with another compound the liquid crystal phase emerges and 2) the monomer is a liquid crystal.

Amidst liquid-crystalline polymers cholesteric structures occupy a special place. Mesophases of the cholesteric type are formed only by chiral molecules which usually possess a shape resembling a rod. A large number of biopolymers, including RNA, DNA and their complexes with other molecules belong to cholesteric polymers.[8]

A considerable difference in kinetic control was shown by radical polymerization of cholesterylacrylate in liquid-crystalline and isotropic media. Degrees of transformation of the monomer do not differ and are approximately 20%.[30,31]

Copolymerization of small amounts of chiral monomer with nematic structure leads to a cholesteric mesophase.

French authors have studied the polymerization of vinylaromatic acids salts in lyotropic liquid crystals medium. The monomer also acts as an emulsifier and the process differs from ordinary emulsion polymerization due to the high concentration of emulsifier.[32] Such ordered medium behave like micelles.

The kinetic of polymerization of a number of monomers of methacryl series have been studied.[33–35] Monomers are characterized by their anisotropy-cetylmethacrylate, cetyl ether of *p*-methacryloxybenzoic acid, etc. in Figure 2. The polymerization rate in liquid-crystalline media is higher than in the isotropic medium. Monomers having voluminous substituents exhibit a higher polymerization rate than for simpler homologues.

The presence of aliphatic along chain branches linked to give crest-shaped polymers,[6,14,36] higher homologues of poly-n-alkylacrylates, poly-n-alkylmetacrylates, poly-n-alkylvinyl ethers and esters, poly-n-alkylstyrenes, etc.

Polymerization rates of some monomers: para-acrylo-oxybenzylydene, para-methoxyaniline, ortho-(hydroxybenzylydene)-para-aminostyrene or -(paracyano-benzylydene)-para-aminostyrene in liquid-crystalline and isotropic media indicates that the effects observed can be explained[38,39] by destruction of the mesophase. This hypothesis is not correlated with other experimental studies in isotropic medium.[40–42]

Paleos puts forward two possibilities of formation of liquid-crystalline polymers.[13]

1. The interaction of molecules containing mesogene groups, and forms liquid-crystalline structures in Figure 3.
2. Synthesis of liquid-crystalline polymer due to the interaction between reactive polymer and liquid-crystalline monomer.

Some of the apparently controversial results of studying the kinetics of polymerization of a number of mono- and bi-functional monomers synthesized using acrylic and methacrylic acids and Schiff bases[43] in liquid-crystalline and isotropic states have not been explained.

Polymerization was carried out at 100 to 110° (nematic phase), 120 to 130° (isotropic phase). Unexpectedly the polymerization rate in the isotropic medium turned out to be higher.

The kinetics of the polymerization of *p*-methacryloyloxy-benzoic acid was stud-

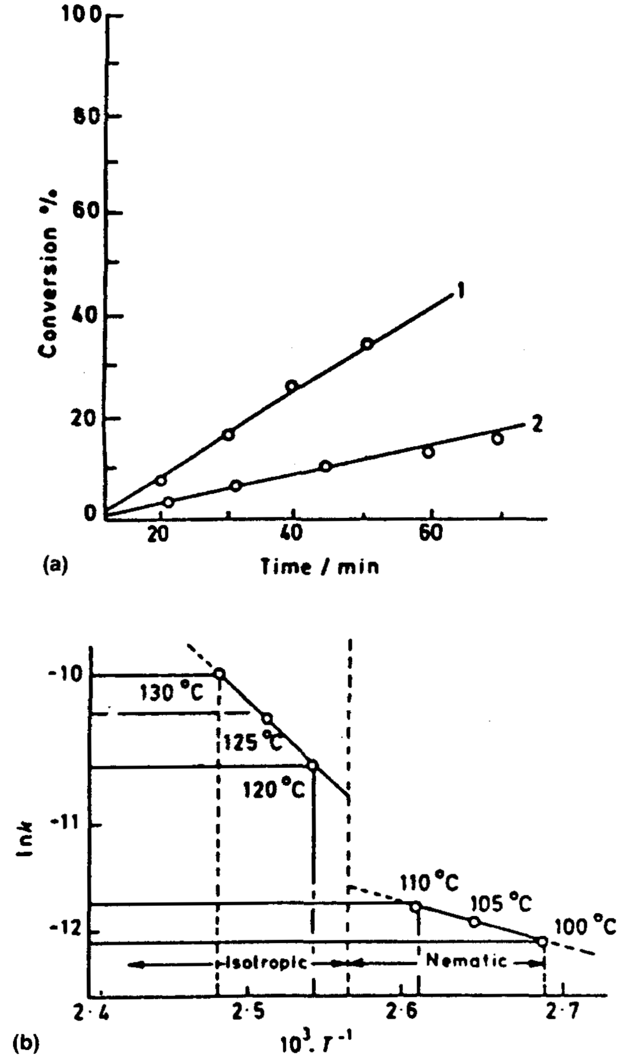


FIGURE 2 Kinetic regularities of some monomers radical polymerization in isotropic and liquid-crystalline media, a—conversion-time curves of the thermal polymerization of *p*-methacryloyloxybenzoic acid in liquid-crystalline medium (curve 1) and in DMF (curve 2); b—Arrhenius plot of the polymerization of N-(*p*-acryloyloxybenzylidene)-*p*-methoxyaniline in the nematic and isotropic phases.

ied,[44,45] and it is supposed that a dimeric complex is formed in Figure 4. During mixing of the monomer with *p*-cetyloxybenzoic acid, the complexes exhibits smectic ordering, while nonyloxybenzoic acid displays nematics structure. Polymerization rates in smectic and nematic states have proved to be 5 to 6 times higher than the rate in the isotropic liquid.

In the absence of specific interactions the monomer with the liquid-crystalline medium does not lead to formation of dimeric complex. In radical polymerization of non-mesogene monomers which do not interact with the reaction medium, e.g. methylmethacrylate, styrene, methacrylic acid, etc. the rate of the process are

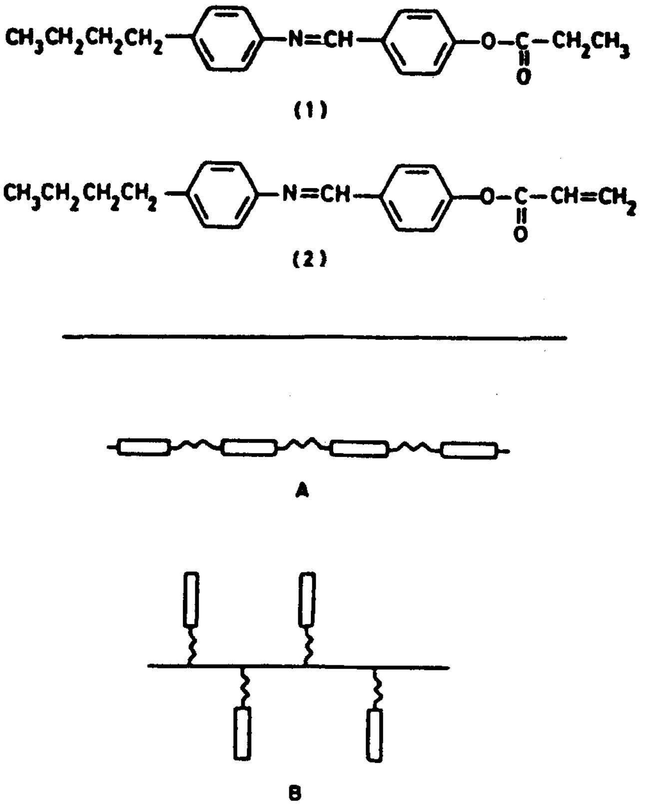


FIGURE 3 Mesogenic groups (1, 2) in the main (A) and side (B) polymer chains.

practically the same as in isotropic media. In this case the reacting monomers are chaotically distributed in the liquid-crystalline medium, and orientation effects are not observed.[46]

The polymerization of acetylene in nematic liquid crystals of derivatives of phenylcyclohexane, RC_6H_{10}—C_6H_5R' (R-radical-alkyl, and R'-also alkyl- or alkoxy-group) have been investigated.[47–51] The Ziegler-Natta catalyst system—$Ti(OBu)_4$ + AlR_3 0.05 moles/l; $AlR_3/Ti(OBu)_4$ = 4.0 was used as catalyst.

Only in the case of polymerization of acetylene in liquid-crystalline medium was highly oriented polyacetylene formed with a 85–94% of cis-configuration.

Scanning electron microscope indicates a high degree of orientation. Oriented linear polyacetylene formed is characterized by excellent electrophysical properties—electrical conductivity (after doping) of $1.6 \cdot 10^4$ s/cm, electrical anisotropy of 7.0 with the polyacetylene film 4 to 15 μm thick.

The concept of a pretransitional state has been advanced by Ya. I. Frenkel in his general theory of liquid.[52] An increase in the polymerization rate of *p*-methacryloyloxybenzoic acid which is not subjected to Arrhenius dependence was observed.[53,54]

According to Ya. I. Frenkel embryos of the "conjugate" mesomorphous phase called heterophase fluctuations must exist. In the liquid crystal these emerge as

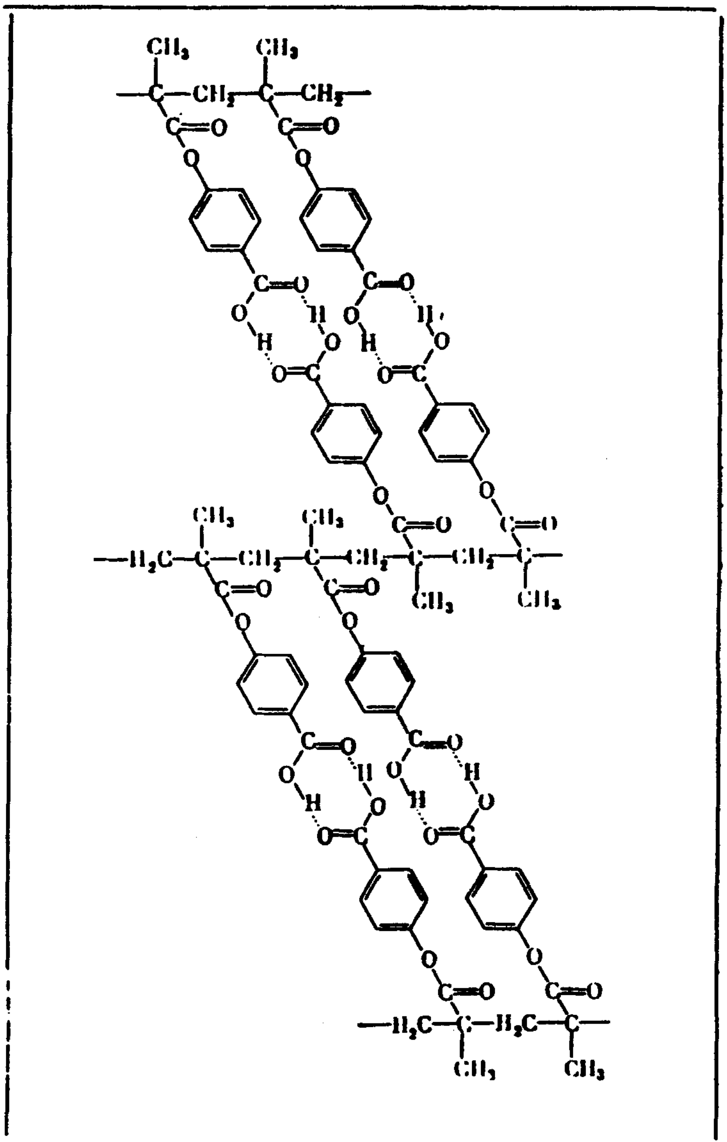


FIGURE 4 Schematic structure of poly-(*p*-methacryloyloxybenzoic) acid dimeric complexes.

microdrops of isotropic liquid. The heterophase fluctuations consist in continuously forming and self-destroying aggregates of the monomer.

The same molecular dimeric complexes can take part in the formation of heterophase fluctuations.

Polymerization processes occurring in the pretransitional states are worthy of further study. The existence of heterophase fluctuations has been proved experimentally.[55]

Ordering of the reaction medium must exert an influence on the microstructure of the polymer which is being formed.

TABLE I

Configurational composition of poly-(*p*-methacryloyloxybenzoic) acid prepared in isotropic and liquid-crystalline media

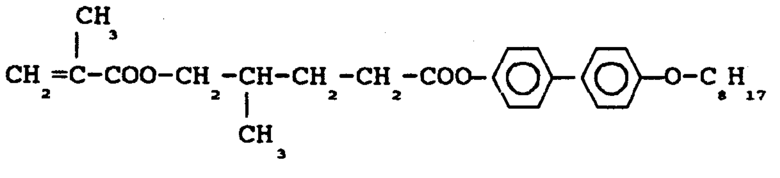
C, mole/l	t, °C	Content of triads, %			$\mu = H^2/4IS$
		I	H	S	
		In dimethylformamide solution			
0,7	110	11	44	45	1,00
1,3	110	9	42	49	1,00
		In nematic form			
0,8	110	7	38	55	0,94
0,8	130	8	34	58	0,64
1,7	110	8	36	56	0,72
1,7	120	7	37	56	0,87
1,7	130	9	35	56	0,61
3,4	110	7	38	55	0,93
3,4	120	6	36	58	0,98
3,4	130	5	34	61	0,91
		In smectic form			
1,7	110	8	40	52	0,99
1,7	130	8	39	53	0,90

Table I presents data characterizing the configuration of the model compound—the polymer of methacryloyloxibenzoic acid in different media from the results of NMRH′ spectrometry.[4,45,56] The microstructure of the liquid-crystalline polymer is characterized by an enhancement of the syndiotactic triads content. Similar results have been obtained for cholesterylacrylate. The high content of syndiotactic triads is the result of the interaction of cholesterol groups.

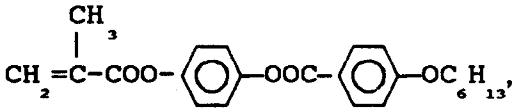
Analysis of the data on the microstructure of polymethacryloyloxybenzoic acid indicates that there is a trend towards stereoblock structures.

Mesogene compounds[57] containing asymmetric carbon atoms are usually employed as chiral nematic phases, segmetoelectric liquid crystals and as dopants for inducing the spiral structure in nematics and inclined smectics. Chiral mesogenes with groups capable of polymerization are of great interest because their polymerization as an oriented thin layer can lead to new polymer materials with unique properties.

The new chiral monomer (s)-4-(5-methacryloyloxy-4-methylpentaneoyloxy)-4′-octyloxybiphenyl



was used as a dopant for 4-methacryloyloxypheny-4′-hexyloyloxybenzoate



$$CH_2{=}\overset{\overset{CH_3}{|}}{C}{-}COO{-}C_6H_4{-}OOC{-}C_6H_4{-}OC_6H_{13},$$

forming the monotropic nematic phase.

These compounds form a "finger-print" texture typical of chiral nematics. The length of the helix is determined by the distance between neighbouring bands and is equal to 6 μm, which corresponds to selective reflection of light in the IR region. Assuming that the average distance between neighbouring pseudo-nematic layers is equal to 5 Å the twist angle of the helix which makes up 0.03° was calculated.

Polymerization initiated by UV-radiation is accompanied by preservation of "finger-print" texture and, consequently, preserves the parameters of the helical structure. Such a material acts as a diffraction grating with a sinusoidal distribution of the optical density.

These "frozen" structures can produce promising film segmetoelectrics, materials for non-linear optics, etc.

Recently the theoretical and practical aspects of the high-temperature transformations of the mesophase into "carbonized" macromolecules[58] have been explored.

The transition of polymer non-mesogene substance into liquid-crystalline (or meso-) phase have been explored and are termed chemotropic[59] and can result from polycondensation. In this case rigid mesogene fragments of macromolecules

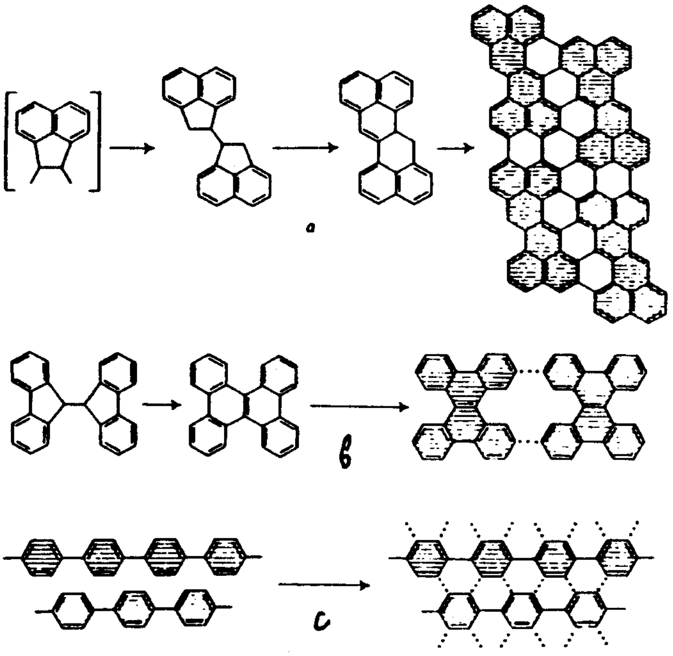


FIGURE 5 Scheme of mesophase formation from hydrocarbons of different structure. a—rapidly; b—slowly; c—slowly.

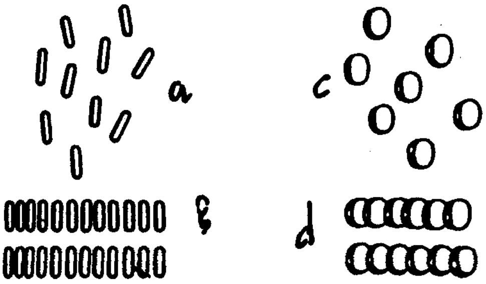


FIGURE 6 Disk-like mesophases: a—nematic; b—smectic; c—nematic; d—colonnar discotic.

are formed in the course of the thermal treatment directly in the initial amorphous polymeric matrix.

Liquid-crystalline states emerge in the course of thermal treatment of heavy petroleum residues and individual organic substances (polyvinylchloride, polyacenaphthylene, anthracene, phenanthrene, etc.). In the process of formation of mesomorphous states the thermolysis of complex aromatic hydrocarbons takes place (Figure 5).

Dehydropolycondensation taking place at high temperatures lead to the formation of a mesophase which is similar to a nematic liquid crystal. Polycyclic compounds with molecular mass higher than 600–700 shape the mesophase. The melting point of each of these compounds exceed the temperature for development of mesophase structure. The mechanism of shaping has been studied in greatest detail in the thermolysis of polyacenaphthylene.[60-62]

Mass-spectroscopy product analysis of the products of the thermal transformations of acenaphthylene, dimer- and polyacenaphthylene, as well as petroleum resins containing acenaphthylene and decacyclene have been studied. Analysis of the data leads to the conclusion that oligomers of acenaphthylene formed in the process of thermolysis are the main products responsible for the generation of the mesophases. The dehydropolycondensation of acenaphthylene links occurs and acenaphthylene is detected in all the products of thermal treatment.[63]

A new type of mesophase with a disk-shaped structure (Figure 6), has been detected for some condensed polyhydrocarbons and their heteroderivatives.

Formations and transformation of macromolecules into liquid-crystalline or mesomorphous states have been described by Yu. B. Amerik and N. A. Plate for carbonized petroleum pitches.[59] High-quality needle-shaped coke for the manufacture of electrodes is obtained on this basis. Pitches are also used as binders for electrodes. Recently mesomorphous pitches have been used in the production of metallurgical coke.

Carbon fibres with strengths reaching 500 to 600 kg/mm^2 are obtained on the basic mesophase petroleum pitches.

Reduction in mobility of the polymeric chains is observed in liquid-crystalline media, which influence their reactivity. In the nematic phase disintegration of the pyrogallol of picric acid and related compounds occur slower than usual.[64] The organized medium has displayed a pronounced braking effect on photochemical processes.[53]

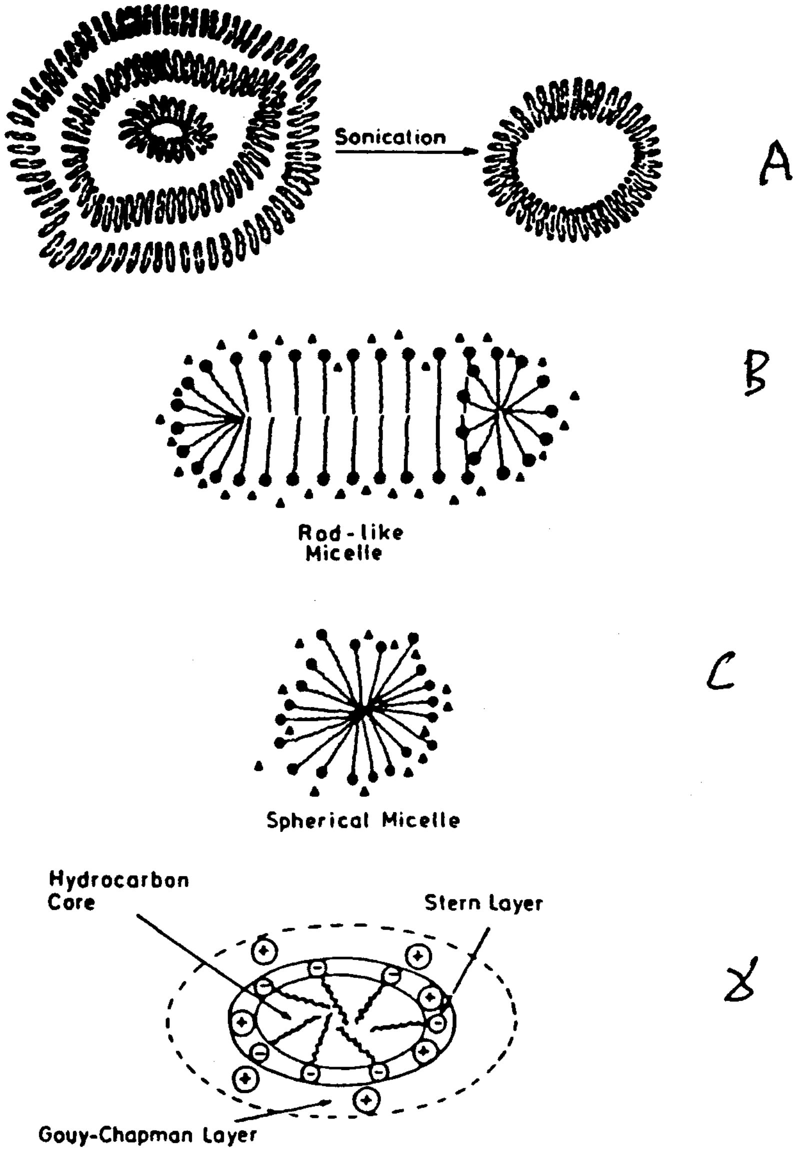


FIGURE 7 Scheme of vesicles (A) and micelles (B, C, D) formation.

Anisotropic medium increases the photostability of polymers, which is usually achieved by the introduction of screening additives or acceptors.

Liquid-crystalline elastomers are of scientific and practical interest since they expand the possibilities of creating and using rubbers.[65]

Micellar systems are another type of organized media and are formed as a result of aggregation of 30 to 150 molecules of surface-active substances when its concentration exceeds the critical concentration[10,66] (Figure 7).

Spontaneous polymerization of protonized salts of 4-vinylpyridyl and 10-sodium

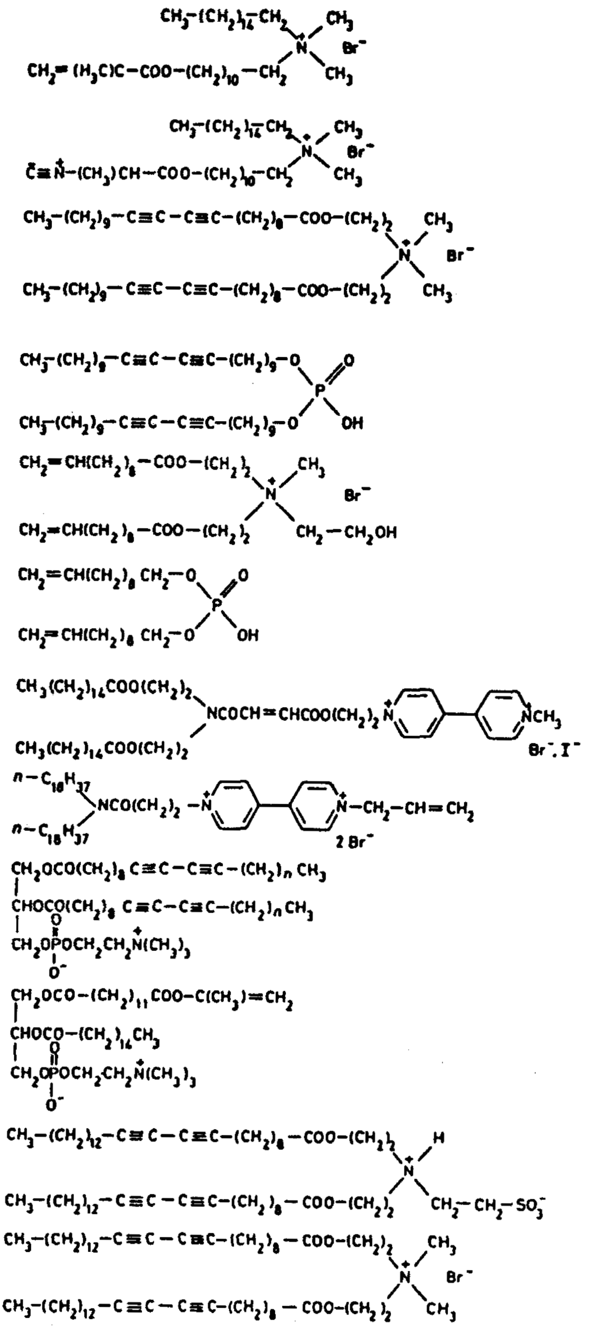


FIGURE 8 Some typical monomers forming micelles or vesicles.

undeonate are typical of polymerization in micellar-organized media.[67,68] Polymerization of the last monomer, initiated by irradiation occurs only in conditions of micellar or lyotropic liquid crystal medium. Initiation of trimethyldodecylammonium bromide in isotropic medium leads predominantly to formation of byproducts of destruction, due to the destructive effect of radiolysis of water.

Polymerization reactions taking place in vesicularly organized media are actually close to micellar polymerization.[10] Liposomes and similar smectic phases formed by lipides are typical medium.

Typical monomers considered in Figure 8 usually have two long alkyl chains linked with polar head part.[69–73] Compounds quaternized by ammonium, carboxylate, sulphate or phosphate groups belong to such monomers.

Photochemical polymerization in organized media exhibit effects similar to those described.

Liposomes are of practical importance in medicine for controlled release of pharmacologically active substances.[74]

Several years ago the photochemical and laser polymerization of derivatives of styrene in vesicular media were published,[75] and show kinetics which differ considerably from those for the usual isotropic media.[75]

The excellent review by Paleos[13] considers a range of specific features associated with polymerization in organized media, specifically vesicular and liposome organization.

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