

Mesophase polymers in the coming decade: problems and trends

N.A. Platé, V.G. Kulichikhin and R.V. Talroze

Institute of Petrochemical Synthesis, Academy of Sciences of USSR, Leninsky Prospect, 29, Moscow, USSR

Abstract - Polymers containing mesogenic groups in side and main chains of macromolecules represent liquid crystalline (LC) polymers as a special class of polymeric materials. Peculiarities of electrooptical behaviour of side-chain polymers as ferroelectric materials and optically-recording media as well as the future of LC engineering plastics based on main-chain polymers are discussed.

INTRODUCTION

One of the salient features of polymer science today is the rise and establishment of a new area for this branch of chemistry and physics - synthesis, structure and properties of so-called mesophase polymers.

This class of polymers embraces everything from completely amorphous glassy or elastic materials and up to three-dimensionally ordered crystalline polymers. These are liquid crystalline polymers having mesogenic groups in the main or side chains, mesophase polymers without mesogenes, condis-crystals and condis-mesophase polymers, para-crystals and so on. Liquid crystalline polymers have become very popular since 1970's when it was found that they can generate new types of high-modulus, high-tenacity aromatic fibers and serve as matrices for optoelectronic applications.

To build this new area of fundamental polymer science and its applied variations, valuable contributions from many researchers in different countries should be given due credit. Table 1 shows some milestones in the history of this branch of science.

More than one thousand liquid crystalline polymers have been synthesized and every month 5-10 new mesophase polymers are described in the literature. Over 15 monographs have been published and approximately 10 international and national conferences and symposia are being held every year where this branch of polymer science is intensively discussed. No less than 60 chemical and physical laboratories all over the world are studying various aspects of chemistry, structure, properties and applications of mesophase polymers.

All this shows that LC or mesophase state in polymers is a stable physical state of matter which is very widespread in polymer materials. Now these ideas are entering into the textbooks although even fifteen years ago practically nobody could predict such rapid development of this part of chemistry and physics of macromolecules. Two main features are typical for mesophase polymers:

- the combination of properties typical for low molar mass LC and mesophases (optical properties, sensitivity to the external electrical field) with engineering and foremost of all mechanical properties of polymer materials - plastics, films and fibers.
- the possibility to fix and to freeze any LC structure and texture by cooling the material below glass point.

In this lecture an attempt will be made to illustrate what mesophase polymers can bring to the fundamental polymer science, to the solid state physics, to the modern technology and processing of polymers and finally for consumers. Illustrations will be taken mainly from the experimental results obtained in our groups at the Institute of Petrochemical Synthesis and in the University of Moscow.

Table 1 Milestones in the history of LC and mesophase polymers

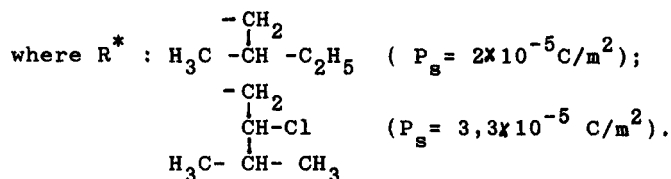
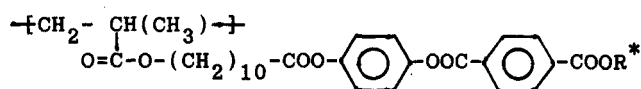
1941	V.A.Kargin (USSR)	-idea about LC state in polymers as wide- spread state
1949	L.Onsager (USA)	- molecular theory of nematic ordering
1950	A.Elliot, E.Ambrose (UK)	- LC lyotropic structure in poly- γ -benzyl-L-glutamate solutions
1956	P.F.Flory (USA)	- Rigid rod theory of LC ordering in polymers
1965	S.Kwolek, P.Morgan (USA)	- High tenacity aramide fiber from LC solutions
1968	A.Nakajima (Japan)	- experimental phase diagram of lyotropic LC polymer system
1970	G.Allen, C.Lewis (UK)	-mesomorphic state in flexible chain polymers -polyphosphazenes
1971	Yu.Amerik, B.Krenzel (USSR)	- synthesis of side-chain polymers with mesogenic moieties
1973	J.Economy (USA)	- synthesis of main chain thermotropic polyester
1974	N.Platé, V.Shibaev (USSR)	- synthesis of thermotropic side-chain LC polymers
1975	P.de Gennes (France)	- theory of LC ordering in main chain mesogenic polymers
1975	A.Roviello, A.Sirigu -(Italy)	- synthesis of thermotropic main chain LC polymers
1984	B.Wunderlich (USA)	- "condis"-state idea brought up to mesophase polymers
1986	H.Ringsdorf (FRG)	- synthesis of combined side chain - main chain , discotic and cross-shaped LC polymers

THERMOTROPIC SIDE-CHAIN LIQUID CRYSTALLINE (LC) POLYMERS

I would like to start with cholesteric thermotropic polymers which have been described more than 10 years ago and now are widely studied in various centers in USA, USSR, FRG, Japan. The possibility to change selective reflection wave length varying chemical composition of particular polymer and the temperature permitted already to prepare spectrozonal filters and coloured polaroids. One of the most interesting possibilities to regulate optical properties of cholesteric polymers is the action of external electrical field with subsequent change of colours (ref. 1).

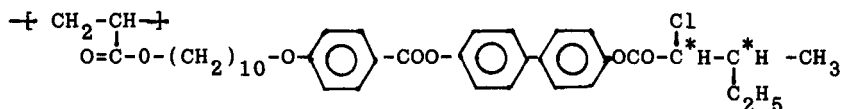
Synthesis of ferroelectric systems resulted in an essential progress in chemistry and physics of LC polymers. Based on the idea suggested by Meyer (ref. 2) and experimentally realized in low molar mass smectics C (S_C)

we were the first who synthesized tilted smectic side chain polymethacryla- with long aliphatic spacers containing different chiral groups and possessing non-vanishing component of polarization (ref. 3,4):

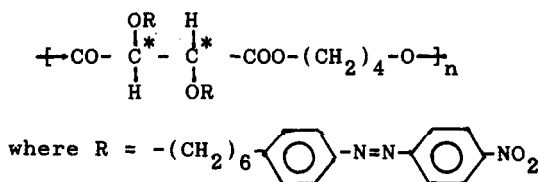


The initial structure of the polymer film is electrically neutral as the dipole moments in different layers are compensated. Application of d.c. field induces the macroscopic alignment of dipoles providing thus the spontaneous polarization of the sample as a whole. Poling fields in the case of polymers are 3 orders of magnitude lower than those for the well known ferroelectric -poly(vinylidene fluoride) (PVF₂) whereas the magnitude of spontaneous polarization of PVF₂ is two orders higher than that that for polymers mentioned above ($\sim 2-3 \times 10^{-5} \text{ C/m}^2$).

The further development of this area shows that this approach permits to achieve P_s coefficients having higher magnitudes. For example Sherowsky, Coles and coworkers (ref. 5) succeeded in the increase of P_s up to $(2-5) \times 10^{-4} \text{ C/m}^2$ with the incorporation of two chiral centres into the mesogenic fragment:



Japanese scientists (ref. 6) introduced chiral centres into the polymer backbone:



and this resulted in extremely high magnitudes of $P_s \times 5 \cdot 10^{-3} \text{ C/m}^2$ comparable with that for PVF₂. The possible upper limit for P_s seems not to be already attained and this makes us to expect new LC polymers which will be not less attractive than true ferroelectrics such as PVF₂ and P(VF₂/F₃).

The other problem that will be pointed out is the role of LC polymers for optical storage applications. I will dwell upon two of possible mechanisms of the recording with the aid of polymer LC materials.

The first one is thermo-optical recording based on the principle schema for the first time described in (ref. 7). In Fig. 1 an example for the thermorecording on the homeotropically oriented polymer film is given (ref. 8).

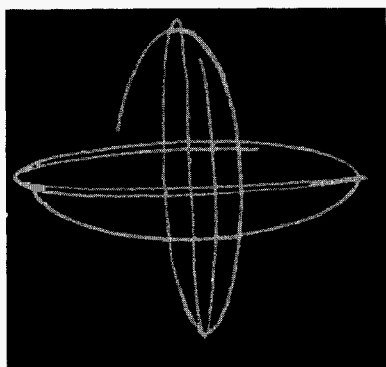


Fig. 1 Photograph of thermally recorded data on the homeotropically oriented dye-containing polymer film (1 mol.%), obtained under elimination with a laser beam of 2 mWt ($\lambda=628\text{nm}$)

This phenomena was subsequently demonstrated and discussed by McArdle (ref. 9), Coles (ref. 10) and other researchers.

The second way was suggested by Wendorff et al. (ref. 11,12). It is based on the photochromic materials as holographic storage medium. Photogenerated trans-cis transition in side fragments perturbs the local LC ordering resulting in the change of the local refractive index (Fig. 2).

This permits to realize erasable optical storage. Such materials possess high information capacity up to 10^9 bit/mm² with resolution as high as 3000 lines/mm². Fig. 3 shows some examples of holographically recorded phase gratings (ref. 11). More detailed information on this subject is given in the publications of V. Shibaev (ref. 13,14).

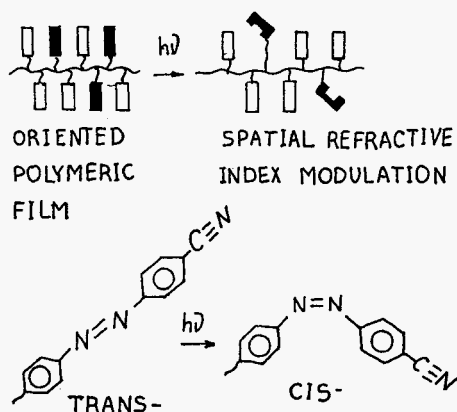


Fig. 2 Principle schema for photochemical recording.

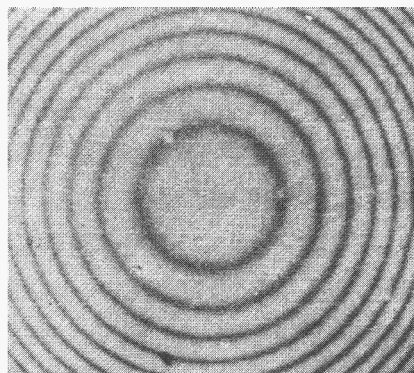


Fig. 3 Centre of Frenel zone phase plate stored by holographic techniques in $7\mu\text{m}$ film of LC polymer (ref. 11)

Besides the orientational field effects the electrodynamical instability phenomena are observed in side-chain polymers under the influence of an electric field. They induce the formation of domain structure manifested in the system of alternating dark and light strips. This system of domains act as a diffraction grating with a period coinciding with the distance between strips (ref. 15).

The combination of different structural units in side-chain macromolecules — backbones and side mesogenic groups — determines the macroscopic behaviour of LC polymers. There exists two different possibilities to affect the structure and orientation of such polymers by acting upon the backbones and side-chains of macromolecules according to the mesophase structure-type and to the method of influence. Uniaxial deformation of side-chain polymer fibers and films induces the orientation of mesogenic groups parallel to the strain axis for the nematic phase and tilted to the latter for different smectics (ref. 16)

In electric and magnetic fields the orientation behaviour of a polymer depends on the dielectric or diamagnetic anisotropy sign (ref. 17). Nevertheless the mutual influence of backbones and chemically binded mesogenes manifests in the dynamics of LC director reorientation.

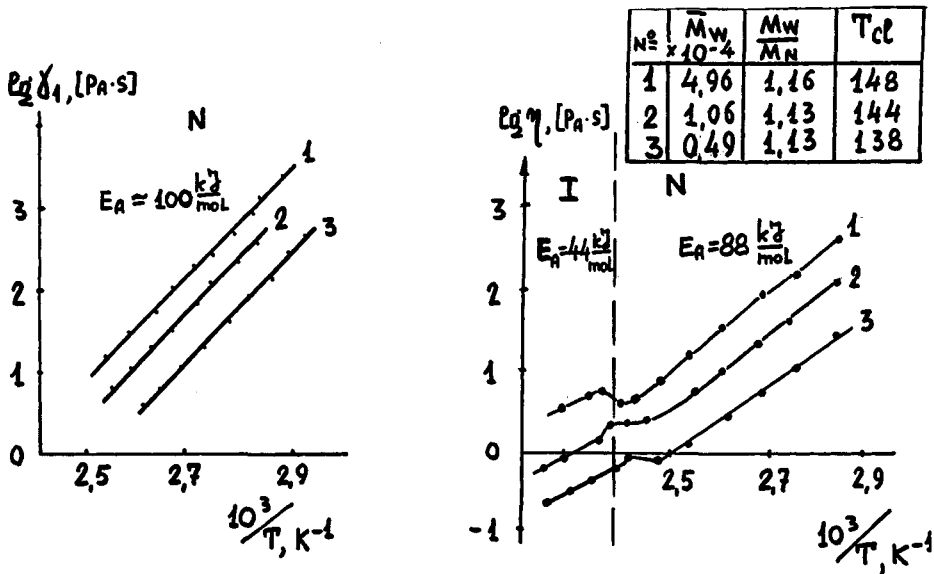
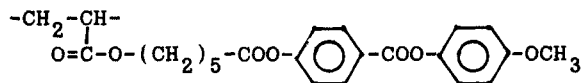


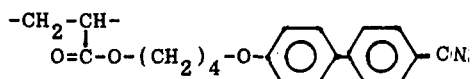
Fig. 4 Rotational (γ) and shear (η) viscosities as a function of temperature

The comparison of the rotational viscosity of the nematic polymer having the following structure



with the usual shift viscosity of the polymer melt (Fig. 4) shows that both coefficients are of the same order of magnitude. The same correlation is truly seen for apparent activation energies of the rotational viscosity and viscous flow. Thus the rotation of the LC director in side-chains of macromolecules induces the rearrangement of backbones (ref. 18,19)

On the other hand the opposite situation can be realized—backbones may control the orientation of side-chain mesogenes. Let us show this on an example that will be discussed more in details by R. Talroze at this Symposium (ref. 19). Let's consider a side-chain nematic polymer of the structure (Fig. 5)



Above the clearing point the system as a whole is isotropic both for mesogenic groups and backbone segments distribution. Below T_g the polydomain structure is formed but within each domain mesogenes and segments should be anisotropically distributed. The external magnetic field induces the macroscopic alignment of mesogenes along the field direction. Orientation of segments across the director is stronger in complete agreement with Gaussian distribution function. This situation can be represented as relevant ellipsoid formation (Fig. 5).

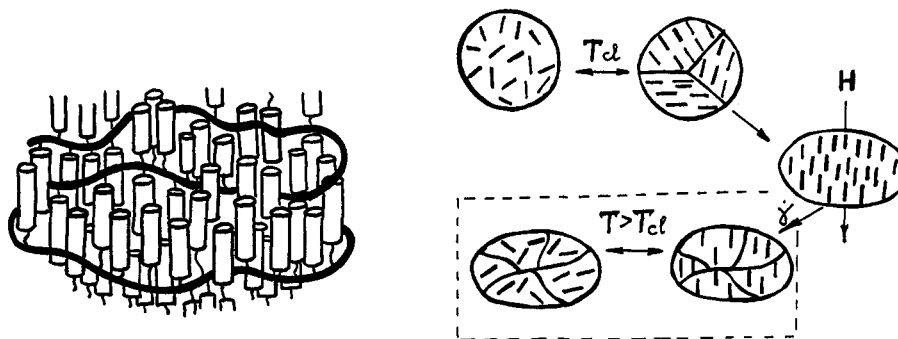


Fig. 5 Orientation memory in cross-linked LC polymer

When an LC polymer is γ -irradiated in an oriented state the cross-linking of the spatial structure of macromolecule takes place. That is we fix by chemical bond formation the spatial distribution of chains equilibrium for the field direction, which determines the orientational structure before irradiation. The cross-links are scarce, less than 0,1%. They virtually have no effect, either on the order parameter or on clearing temperature. At the same time the spatial distribution of coils is completely responsible for the orientational behaviour of the LC network.

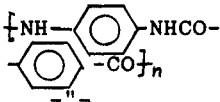

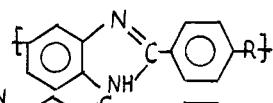
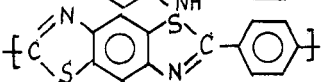
When the temperature is raised above that of clearing the LC structure disappears and the PMR spectra of the sample coincide with those of the polymer in the isotropic melt. But a complete isotropic state can't be achieved as the anisotropic coil conformation is cross-linked by irradiation. As a result of it on cooling below clearing temperature the oriented LC structure with orientation prefixed by the network and coinciding with the field applied before the irradiation is realized irrespective of any external influences.

On the contrary to the classical organic low molar mass liquid crystals side chain LC polymers are able to keep their structure when being cooled below glass-point transition. This permits to prepare solid state devices (gratings) and fix in the frozen state any desirable structure and morphology of LC polymer which is manifested in the elastic state or in the melt.

ENGINEERING MATERIALS BASED ON MAIN-CHAIN LC POLYMERS

The forming of thermostable super high-modulus and super high-tenacity aramide fibres from LC solutions was the only single example for the practical application of the LC state up to 1980's (Table 2).

Table 2. Mechanical properties of fibers obtained from lyotropic LC systems (ref. 20)

Trade mark	Chemical formulae	Country	Tenacity, sN/tex	Modulus, GPa	Elongation at break, %
Kevlar		USA	180	127	2.4
Terlon		USSR	190	150	2.5
Vniivlon		USSR	270	140	4.0
PBT		USA	200	490	2.8

Due to the formation of ordered domains with parallel packing of macromolecules long axes viscosity as well as elasticity are anisotropic properties in LC state. Even shear deformation is enough to transform the polydomain system having disclination network to a highly oriented monodomain system without defects (ref. 21)

Such transformation may be registered with the aid of flow curve for LC polymer (Fig. 6). It consists of four parts: flow with an undestroyed structure (creep regime) I, sharp decrease of viscosity resulting from the orientation process (transition from polydomain to monodomain structure) II, quasi-Newtonian (monodomain) flow III and anomalous viscous flow (coexistence of viscous-elastic effects and instabilities) (ref. 22,23).

During spinning process, the regimes III or IV take place resulting in the extreme molecular orientation of liquid jets. This orientation should be fixed after shear or elongation flow either with the rapid evaporation of the solvent or by using coagulation baths.

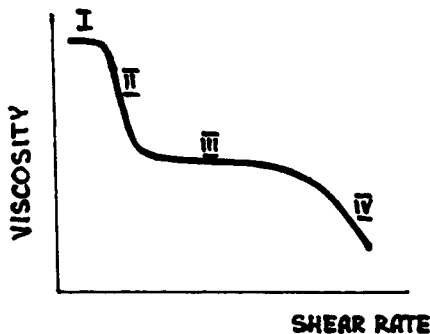


Fig. 6 Schematic flow curve of LC system

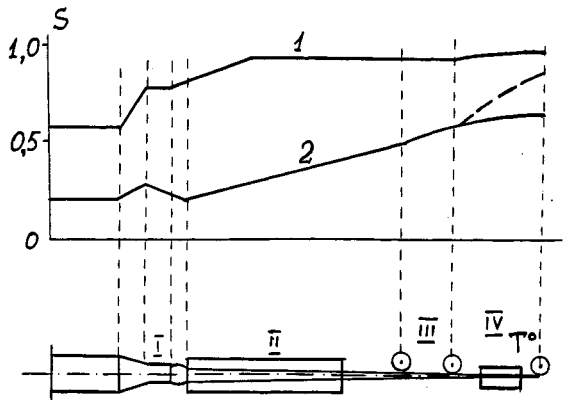


Fig. 7 Scheme for changing the factor of orientation along spinline for LC (1) and isotropic (2) solutions (or melts)

From the scheme for changing the factor of orientation along the spinline for LC (I) and isotropic (2) solutions (Fig. 7) one can see that high orientation of LC system is already achieved at the moment the solution flows out the spinneret channel. It is reinforced in the extension zone and further orientation remains practically constant.

Mechanical characteristics of fibers from thermotropic LC polymers practically do not yield to the aramides fibers besides initial modulus.

Table 3. Fibers tensile properties for different thermotropic polymers (ref. 20)

Structure of monomer unit	Tenacity sN/tex	Initial modulus, GPa	Elongation at break, %
$\left[\text{CH}=\text{N}-\text{C}_6\text{H}_3(\text{CH}_3)-\text{N}=\text{CH}-\text{C}_6\text{H}_5 \right]$	340	136	4.4
$\left[\text{O}-\text{C}_6\text{H}_3(\text{C}_6\text{H}_5)-\text{O}-\text{CO}-\text{C}_6\text{H}_4-\text{CO} \right]$	290	115	4.3
$\left[\text{CO}-\text{C}_6\text{H}_4-\text{CO} \right]_{0.7} \dots \left[\text{O}-\text{C}_6\text{H}_3(\text{Cl})-\text{O} \right] \dots$			
$\dots \left[\text{CO}-\text{C}_{10}\text{H}_6-\text{CO} \right]_{0.3}$	314	70	4.7

For the flexible chain polymers the orientation is increased monotonically and mainly in gel state or as-spun fibers. The orientation processes in liquid anisotropic state lead to practically defectless fibers.

Nevertheless fibers don't cover all the necessities in high strength materials for modern technique. If you deal with plastics it makes the usage of solutions practically impossible because it is not possible to remove the solvent traces from the bulky material. Different types of thermotropic main-chain LC polymers based on polyesters, poly(azomethynes) and etc. appeared in 1970's and 1980's.

The copolyester of p-hydroxybenzoic and terephthalic acids with dihydroxydiphenyl (precursor of Xydar) was prepared by Economy in

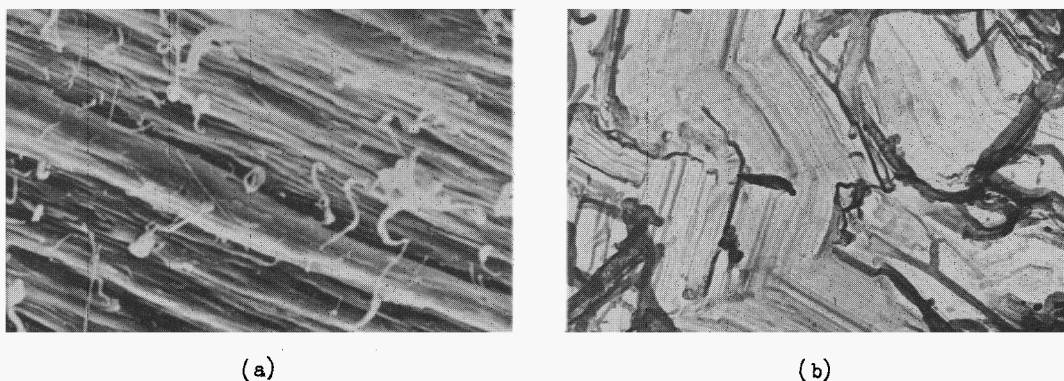


Fig. 8 The skin (a) and core (b) morphologies in the mesophase polymer rod.

1972-1973 (ref. 24). Transitions from the systems containing intermolecular hydrogen bonds (polyamides) to those having slightly interacted ester-groups induced the appearance of LC-thermoplasts having the same properties in melts as those known for anisotropic solutions.

Excellent ability to orientation of LC systems and the domain character of flow lead to unusual morphology of bulky materials (Fig. 8) (ref. 25,26). Polyfibrillar structure as well as flat anisodiametric elements are seen. The latter can consist of fibrils and microfibrils. In this case the skin-core effect manifests itself when the fibrillization of the skin is much higher than of the core (ref. 27).

The skin consists of highly oriented fibrillized external layer and slightly oriented sublayers. The schema of the hierarchy model is given in Fig. 9 according to E.Baer (ref. 26).

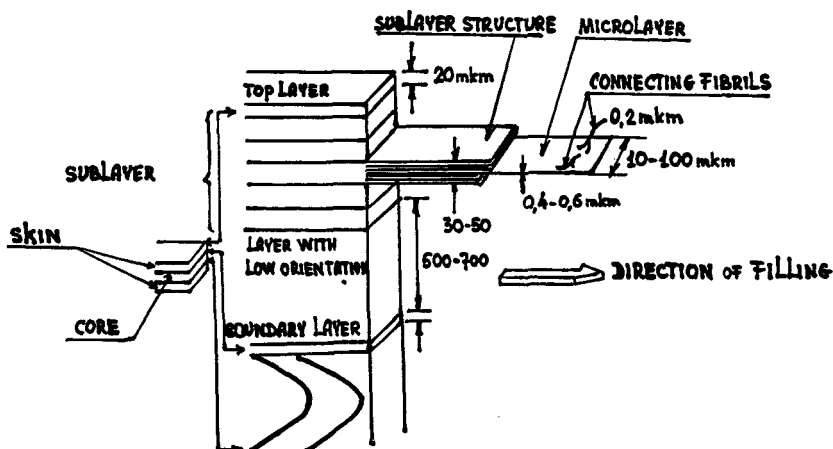


Fig. 9 Morphological hierarchy in injection molded plate of LC copolyester

For LC-thermoplastic fibers today the mechanical characteristics comparable with those of aramides can be attained. Super-high magnitudes of strength and modulus are obtained for fully aromatic polymers whereas alkylene-aromatic polyesters forming LC melts don't have high mechanical properties. Such polymers need probably special processing conditions that are different from traditional ones. For such polymers the effect of preservation of orientation at $T > T_m$ was observed (ref. 28) and this opens possibilities of practical applications of these fibers for making composite materials by fiber technology. It deals with preparation of composites from blends of fusible and nonfusible fibers with subsequent melting of the fusible component and its transformation into the matrix having high orientational ordering.

An interesting schema for the scale of levels of ordering in mesophase polymers was given by Wunderlich (Fig. 10) (ref. 29).

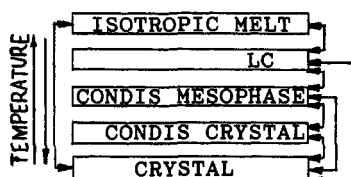
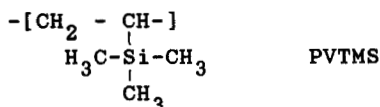


Fig. 10 Structure evolution for different polymers and scheme of probable transitions

Between crystalline and isotropic states one can find the set of different mesophase structures losing different kinds of order with an increasing temperature.

After destroying conformational order in initial three-dimensional crystal the condis-crystal is formed while the partial disappearance of positional order leads to condis-mesophase structure and the consideration of only orientational order gives rise to LC-phase (ref. 30).

Few words on linear mesophase polymers without mesogenic groups. One can find such representatives among organo-element polymers. One example is the best membrane active (oxygen-nitrogen separation) polymer-poly(vinyl trimethylsilane) :



Its structure coincides with that known for condis-crystals (Fig. 11).

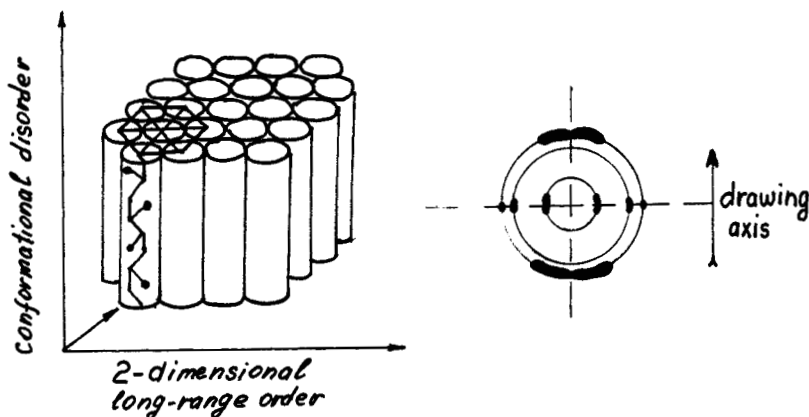


Fig. 11 Structure model of PVTMS. Pseudo-hexagonal lattice with $a = 1.13$ nm and $c = 2.54$ nm; conformation: helix (average) $15/4$.

This special packing of macromolecules is not excluded to provide the particular membrane activity of PVTMS. The next example - poly {2,2,2-bis-(trifluoro ethoxyphosphazene)}(PPh) . Its structure is given in Fig. 12. (ref. 31).

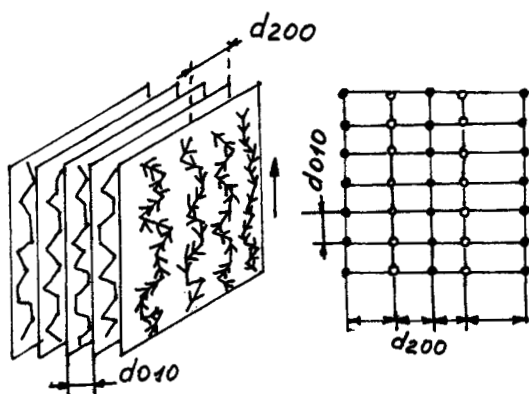


Fig. 12 Schematic view of the layer one-dimensional structure of PPh.

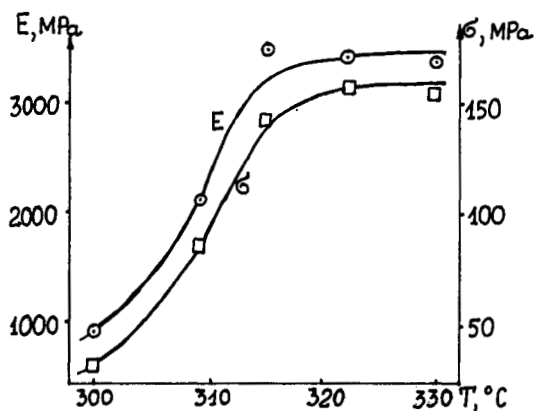


Fig. 13 Temperature dependence of tensile modulus (E) and strength (σ) for LC polymer rods.

PPh spontaneously fibrillizes during the extrusion process and serves also as a suitable modifier in the processing of super-high molar mass polyethylene (ref. 32).

Dealing with mesophase structure it becomes possible to realize nontraditional methods for the strength and modulus enhancing. For instance the strength and modulus of LC polyester extrudates on the base of phenylhydroquinone, terephthalic and hydroxybenzoic acids increase with the enhancing of the extrusion temperature. Starting with the temperature corresponding to condic mesophase - LC transition these characteristics grow up. This is accompanied by the change brittle fracture for extrudate obtained at low temperatures to a fibrillar one with highly expressed effect skin-core at high processing temperatures (Fig. 13). These data show the advantage of the processing in the LC state in comparison with the condic one (ref. 33).

Highly oriented domains in LC thermoplast may be considered as reinforcing fibers in composite materials. The strength of individual LC materials calculated using such approach is lower than that for epoxy - carbon composites but it is comparable with that for epoxy - Kevlar composites (ref. 34).

The discrete structure becomes an essential characteristic for blends of non-compatible materials containing LC thermoplasts as one of components. Let's consider the situation with such blends. Under extrusion the formation of reinforcing anisotropic threads of LC phase is accompanied by its migration to the surface of extruded rods (ref. 35).

The exterior of LC phase distribution for polysulfone (PSF)- LC polyester (PES) system is clearly seen from the electron microphotograph of so called "morphological skeleton" of a polyester separated after the removal of the matrix polysulphone with the selective solvent (Fig. 14).

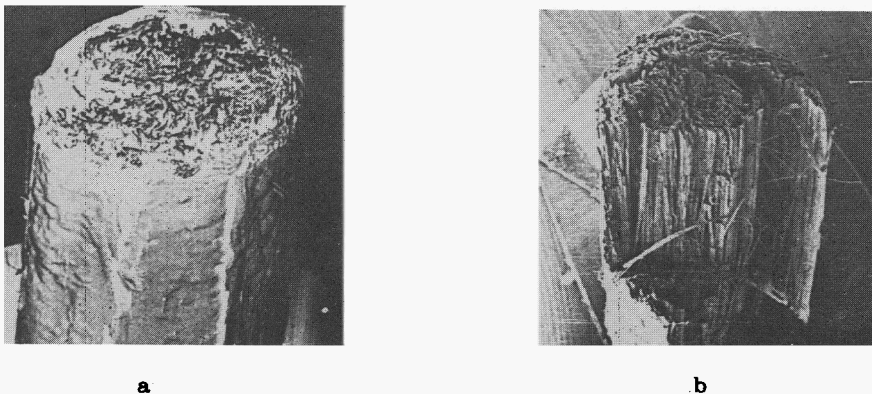


Fig. 14 Composite "in situ" after removal of the commercial thermoplast by selective solvent before (a) and after (b) partial destruction of the skin.

Fibrillar - layered morphology of PES in the core and thin LC skin are clearly seen.

The complicated morphology of the blend melt flow leads to unusual rheological properties of blends. In Fig. 15 typical flow curves for blend PSF/PES obtained with an capillary viscometer at 240°C are given.

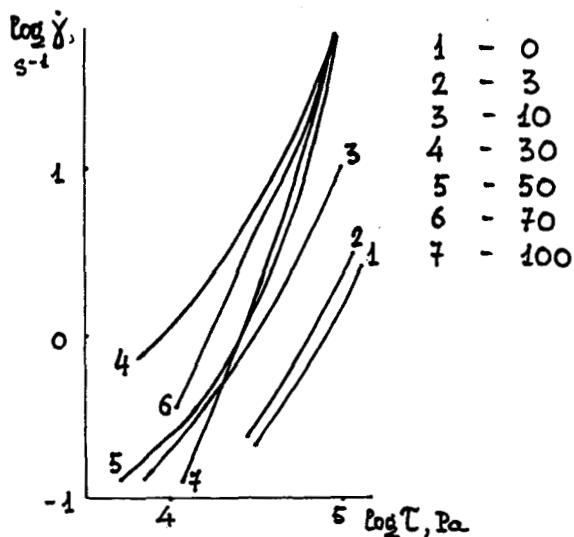


Fig. 15
Flow curves of PSpH/PES blends at 240°C

Activation energies of viscous flow for components are essentially different (for PES higher than for PSpH), that is why the ratio of viscosities of the components in the temperature range 240 - 280°C changes. This results in different curves: viscosity-concentration (Fig. 16). At 240° two arches intersecting in the phase inversion region can be seen, at 260° smooth curve with a minimum in this region and at 280° C dependence becomes practically additive .

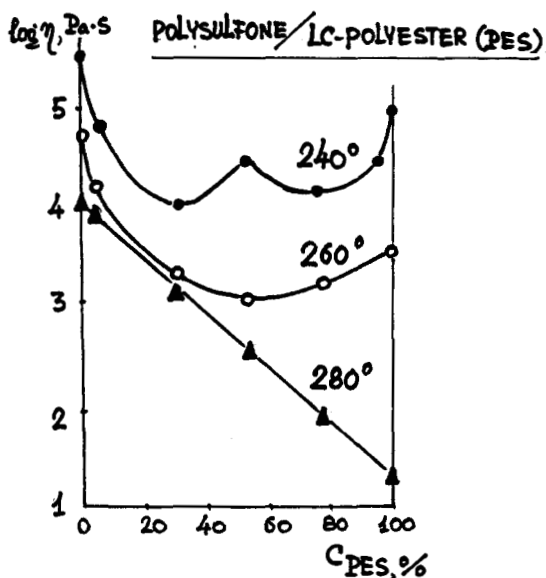


Fig. 16 Blend viscosity versus concentration at different temperatures.

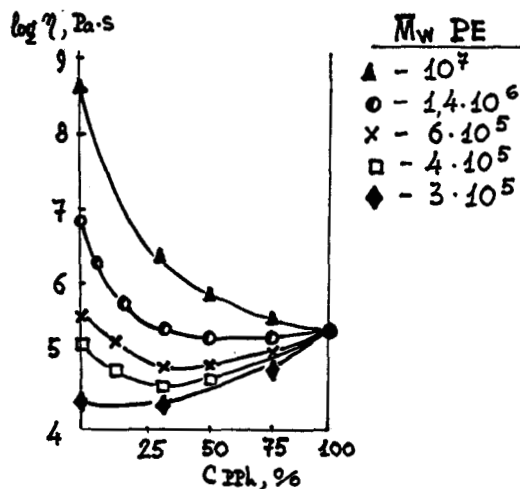


Fig. 17 Blend viscosity for system versus concentration for PE/PPh at 250°C

The viscosities ratio of initial polymers may be regulated not only by temperature but by molecular mass of components also (Fig. 17). For blends PE/PPh one can observe the sharp decrease of the blend viscosity especially at low content of mesophase PPh. The main reason for such behaviour can be migration of the low viscous PPh to the skin of the stream and formation of the original lubricant layer (ref. 31).

Although the blends extrusion depends on many factors, it is possible to use the ratio of viscosities of components η_m/η_d (η_m - matrix viscosity, η_d - disperse phase viscosity) as a criterium of blends viscosity properties (ref. 36). Corresponding dependences for 13 different pairs of polymers including mesophase polymers are given in Fig.18.

With increasing ratio η_m/η_d the blend viscosity normalized to the matrix viscosity η/η_m linearly decreases (a) while the blend viscosity η/η_d normalized to the disperse phase viscosity increases (b). The position of the triangle ABC is of particular interest. These characteristic points divided different flow morphologies which are schematically shown in Fig. 18 also. The most perfect fibrillar morphology of one component in the matrix of the other one is formed between A and B points.

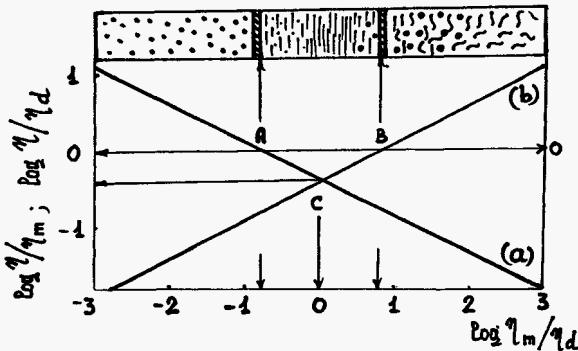


Fig. 18 Blend viscosity normalized on matrix (a) and disperse phase viscosities (b) as function of viscosity ratio of the initial components for 13 different pairs of polymers (70:30). (At the top the schematic stream morphology is shown).

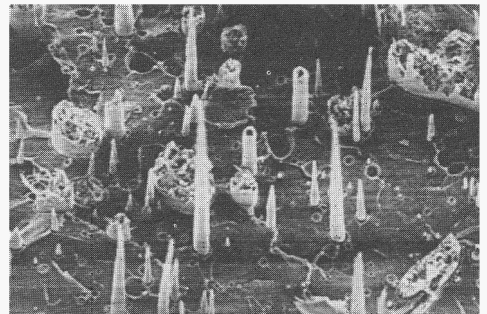


Fig. 19 Morphological picture for LC polyester /PSF composite "in situ".

Thus based on the analysis of the rheological behaviour of the blends the excellent opportunity arises to create "in situ" composite. In the later there exists the high molecular and morphological orientation of the LC reinforcing phase and the problem is to ensure the certain level of interphase interaction between components. The morphological picture of the extrudate based on such composite "in situ" containing LC polyester and amorphous PSF matrix is shown in Fig. 19.

The data existing testify that the addition of 10 - 20 % of LC polymers to thermoplast increases modulus and strength of corresponding fibers 2 - 10 times. In this case the orientational ability of LC phase is realized completely. The situation with bulky materials is more complicated.

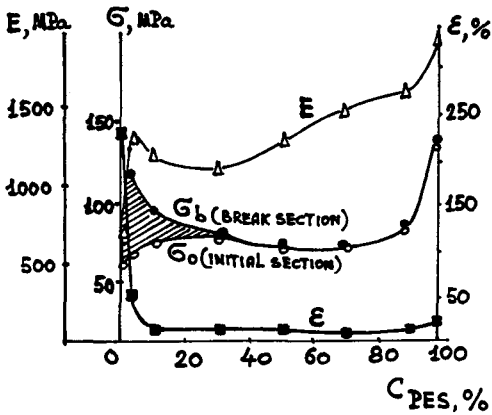


Fig. 20 Tensile modulus (E), strength (σ) and elongation break (ϵ) versus concentration for PSPH/LC PES system.

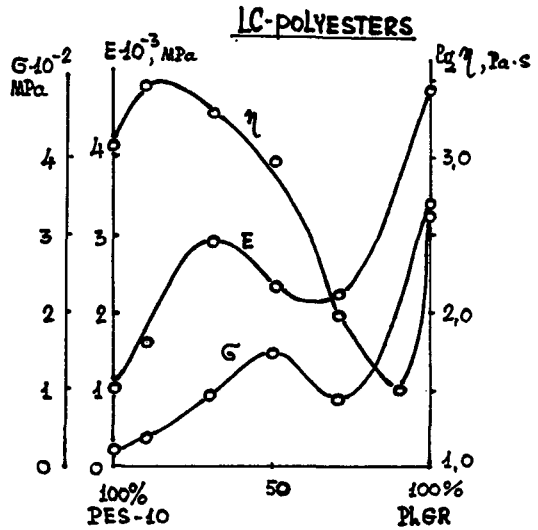


Fig. 21 Viscosity (η), tensile modulus (E) and strength (σ) versus concentration for blends of alkylene-aromatic PES-10 and wholly aromatic PhGR.

The evolution of mechanical properties of extrudates having diameter 1-3mm with the increase of the content of LC polyester Ultrax KP 4002 (BASF production) in its blend with PSF is seen from the comparison of the tenacity modulus and elongation at break for different compositions (Fig. 20) (ref. 35).

Maximal values of E and σ are observed for 3-10% compositions, and the effect attains 40 - 50%.

The mechanical characteristics are lower in the region of intermediate compositions, where the chaotic morphology with some elements of phase inversion is observed. The sharp rise of E and σ takes place at $C_{PES} > 90\%$.

The further step in the study of blends problem is the mixing of two LC polymers, for example, alkylene-aromatic and fully aromatic LC polyesters. The incorporation of the rigid fragments (phenylhydroquinone-terephthalic acid - resorcinol) in poly (decamethylene terephthaloyl - dihydroxybenzoate at low contents of the first leads to the increase of the melt viscosity, modulus and tenacity of extrudates (Fig. 21). The compatibility of components with homogeneous fibrillar morphology seems to be possible in this region (ref. 37).

So the transition from aromatic polyamides to aromatic polyesters gave rise to the new class of polymers that permit to create high-tenacity fibers, self-reinforcing plastics, unique composite materials utilizing LC melts.

Thermotropic LC main chain polymers serve as both reinforcing fibers and high-tenacity matrix for polymer composite materials. The difference in melting point of 10°C (for instance, due to the thermal treatment) is enough to use one and the same polymer both as reinforcing and as matrix component having unique interphase characteristics.

Self-reinforcing plastics are one of the example of the area of usage of fully aromatic LC polymers, which are characterized by high modulus and tenacity, high heat deflection temperature and thermostability and

extremely low linear coefficient of thermal expansion. High fluidity of their melts, stability of geometrical shape of products permit to produce protecting jackets for light conductors that are not fractured and deformed with the temperature, some electrotechnical and electronic details of complicated profile, etc.

In the field of polymer blends the use of LC disperse phase permits to trace a new way to solve two problems. On one hand the small amount of LC component strongly decreases viscosity and provides the processing of high molar mass, high viscosity thermoplasts. On the other hand under extrusion and injection moulding LC disperse phase particles are elongated in the form of long threads and reinforce the isotropic matrix. So far as LC polymers form highly tenacity threads this makes possible to obtain new class of composite materials from blend melts, i.e. from the liquid state.

Thus, summarizing problems discussed above it should be said that there exists a great number of different types of LC phases and mesophases in polymers in comparison with low molar mass compounds. Today there are no corresponding terms to identify all ordered systems observed, including more or less smectogenic nematics and "unusual" cholesterics. There exist no real limits for the macromolecular design of mesogenic polymers based on the great variety of mesogenic groups and nonmesogenic fragments.

CONCLUSIONS

This new area of mesophase and LC-polymers gives to the researchers a lot of new possibilities beside those described above.

LC-elastomers as models of muscle tissue and sensors, LC composite membranes for gas and liquid separation with regulated permeability and selectivity with the aid of external mechanical and electrical fields, are some examples to be studied. LC polymeric media for chemical reactions within anisotropic matrices began to be studied also.

Advances in the field of LC and mesophase polymers have fundamental scientific value and this gives a chance to estimate LC state and LC order as a great principle of Nature. In this sense we may look on coming decade with a good portion of optimism.

REFERENCES

1. V.P.Shibaev, Ya.S.Freidzon, In: Side chain liquid crystal polymers, Ed. by C.B.McArdle, Blackie, Glasgow, 260-286, (1989).
2. R.Meyer, L.Libert, L.Strzelecki, P.Keller, J.Phys.(Paris) Lett., 36, L69-174, (1975).
3. V.P.Shibaev, M.V.Kozlovsky, L.Beresnev, L.M.Blinov, N.A.Platé, Polymer Bull., 12, 299-306, (1984).
4. V.P.Shibaev, M.V.Kozlovsky, N.A.Platé, L.Beresnev, L.M.Blinov, Vysokomolec. Soedin., A29, 1470-1478, (1987).
5. G.Scherewsky, U.Muller, A.Schliva, P.Schreider, K.Kunpast, J.Springer, H.J.Coles, P.Charbischfeger, Freiburg Colloquium on liquid crystals, Book of abstracts, April 4-6, (1990).
6. S.Ujiie, K.Imura, Chemistry Lett., 1031-1034, (1990).
7. V.P.Shibaev, S.G.Kostromin, N.A.Platé, S.A.Ivanov, Yu.V.Vetrov, I.A.Yakovlev, Polymer Commun., 24, 364-367, (1983).

8. V.P.Shibaev, S.G.Kostromin, V.V.Motygin, I.V.Yakovlev, to be published.
9. C.B.McArdle, In: Side Chain liquid crystal polymers, Ed.C.B.McArdle, Blackie, Glasgow, 357-394, (1989).
10. H.Coles, Faraday Discuss.Chem.Soc., 79, 201-207, (1985).
11. M.Eich, J.Wendorff, B.Reck, H.Ringsdorf, Macromol.Chem., Rapid Commun., 8, 59-63, (1987).
12. M.Eich, B.Reck, H.Ringsdorf, J.Wendorff, Proc.SPIE 682, 93-94, 1986.
13. V.P.Shibaev, S.V.Belyaev, Vysokomolek.Soedin., A32, 2266-2310, (1990).
14. V.P.Shibaev, S.G.Kostromin, I.V.Yakovlev, 33rd IUPAC International Symp. on Macromolecules, Monreal, Book of Abstracts, 1.6.4., (1990)
15. R.V.Talroze, E.Valderrama, V.P.Shibaev, N.A.Platé, Dokl. Academy of Sci. of USSR, 292, 161-165, (1987).
16. Ya.S.Freidzon, R.V.Talroze, N.I.Boiko, S.G.Kostromin, V.P.Shibaev, N.A.Platé, Liquid Crystals, 3, 127-132, (1988).
17. R.V.Talroze, N.A.Plate, In: Liquid crystal polymers, Ed.by N.A.Platé, Khimia, Moscow, 296-330, (1988), (in Russian).
18. Ye.V.Kireev, L.B.Stroganov, R.V.Talroze, S.G.Kostromin, V.P.Shibaev, N.A.Platé, Vysokomolek.Soedin., B31, 261-264, (1989).
19. R.V.Talroze, E.V.Kireev, M.A.Rogunova, L.B.Stroganov, 33rd IUPAC International Symp. on Macromolecules, Montreal, Book of Abstracts, 2.8.2., (1990).
20. A.V.Volokhina, G.I.Kudryavtsev, In: Liquid crystal polymers, Ed.by N.A.Platé, Khimia, Moscow, 372-407, (1988), (in Russian).
21. V.S.Volkov, V.G.Kulichikhin, J.Rheology, 34, 281-288, (1990).
22. T.Asada, S.Onogi, Polymer Eng.Rev., 3, 323-353, (1983).
23. V.G.Kulichikhin, Mol.Cryst.Liq.Cryst., 169, 51-81, (1989).
24. J.Economy, Japan-US Polymer Symp., 3A1h9, 47, (1985).
25. L.C.Sawyer, M.Jaffe, J.Mater.Sci., 21, 1897-1903, (1986).
26. E.Baer, Scientific American, 254, 179-184, (1986).
27. V.G.Kulichikhin, E.K.Borisenkova, E.M.Antipov, D.R.Tur, N.A.Platé, Vysokomolek.Soedin., B27, 484-488, (1987).
28. R.Capasso, A.Roviello, A.Sirigu, P.Janelli, J.Polymer Sci., B25, 2431-2439, (1987).
29. B.Wunderlich, J.Grebowicz, Adv.Polymer Sci., 60/61, 1-58, (1984)
30. E.Polushkin, E.Antipov, V.Kulichikhin, N.Platé, Dokl. Academy of Sci. USSR, 315, 1413-1417, (1990).
31. N.A.Platé, E.M.Antipov, V.G/Kulichikhin, Macromol.Chem., Macromol.Symp., 33, 65-77, (1990).
32. V.Kulichikhin, N.Platé, Procced. of the 3rd European Rheology Conf., Elsevier Appl.Sci.Publ., Edinbrough, 292, (1990)
33. V.Kulichikhin, E.Polushkin, I.Parsamyan, N.Platé, Vysokomolek.Soedin., A32, 1164-1171, (1990).
34. Y.Ide, T.-S.Chung, J.Macromol.Sci., Phys., B23, 497-502, (1984-85).
35. V.Kulichikhin, O.Vasilyeva, I.Litvinov, E.Antipov, I.Parsamyan, N.Platé, J.Appl.Polym.Sci., 42, 363-368, (1991).
36. E.Borisenkova, V.Kulichikhin, N.Platé, Dokl. Academy of Sci.USSR, 314, 193-198, (1990).
37. M.Zabugina, I.Parsamyan, I.Litvinov, A.Bilibin, V.Kulichikhin, Vysokomolek. Soedin., B32, 765-767, (1990).