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Some Unusual Structures in Thermotropic Mesophase Polymers

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SUMMARY: Random copolymers of polyester type have been shown to exhibit simultaneous crystallization into two different crystalline forms which are transformed into different hexagonal mesophase structures on heating. Some of these polymers have been found to form LC aperiodic smectic structures. Liquid Crystal elastomers, H-bonded networks and grafted LC materials are discussed. Mechanical field creates the director reorientation in monodomain elastomers and H-bond networks which is discussed in terms of "soft elasticity". Grafting of particular LC polymer on fluorine containing polymer support results in the formation of composite sandwich-type material. Mechanical deformation leads to the macroscopic alignment of the LC grafted layer. There is a pronounced memory effect, which is manifested in the macroscopic alignment of the grafted layer under cooling from an isotropic to a LC state. The phenomenon observed results from the strong influence of the polymer support on the LC director orientation. The optical and mechanical properties of sandwiched samples can be regulated in wide limits.

Introduction

The topic of our issue is related with the structure in solid state of polymers which attract the attention of researchers during the last 20 years - mesophase polymers including Liquid Crystalline ones but not only those. The more we synthesize and study them the more we learn that Mother Nature is much cleverer than it seemed before. Wide varieties of structural forms are discovered in these polymers and in particular structures, which can be considered as rather unusual comparing with what we knew not so long ago. Some examples of these structural forms are discussed in this paper.

One family of mesophase polymers under study is thermotropic copolyesters. Despite the chemical irregularity copolyesters can crystallize at practically any comonomers ratio[1,2]. 3-D order exists even in as-spun polymers and the degree of crystallinity sometimes reaches 25-30%. To explain the ability of nonregular copolyesters for crystallization two different models have been proposed by Windle[3] and Blackwell[4]. But independently of the model it means in our case that polyesters should be at least two-phase systems. In the first part of our paper we will focus on structural particularities of crystalline and non-crystalline parts in such systems.

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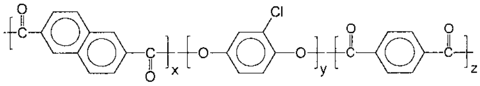
The other families of mesophase polymers exhibited an unusual behavior are LC elastomers, H-bonded polymer networks and LC polymers grafted on polymer films. One of the main priorities in this area of research is the creating of monodomain (uniformly aligned) structures that show a great deal of special properties which make them significant for both academic study and probable applications. In the second part of our paper we will focus on creation of monodomain structures resulting in unusual mechanical and optical properties of such systems.

Results and Discussion

1. Structural particularities of copolyesters and copolyamides

The representatives of mesophase polymers which contain no flexible spacers and show unusual behavior are discussed in this part of our issue. Let us here consider the crystalline part of specially synthesized copolyesters shown below.

PES-1



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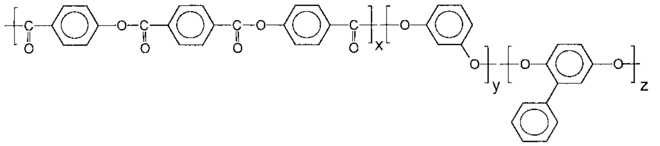
PES-2



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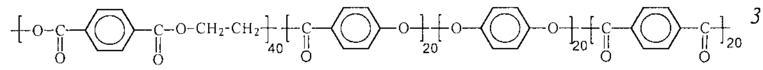

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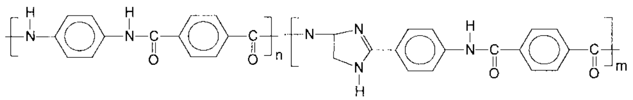
CPA



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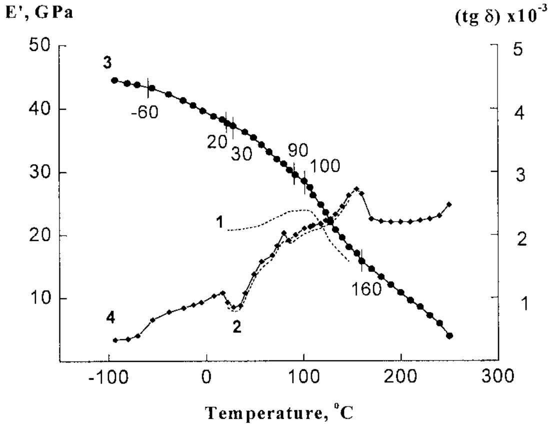


Fig. 1. Dynamic Young' modulus (1,3) and loss tangent (2,4) for as-spun (1,2) and preheated (3,4) PES-1.

It was found that DSC-curve for them has no strongly expressed thermal transitions[2,5-7)], but some indications on possible existence of different structures have been observed.

The more informative are relaxation spectra from dynamical mechanical analysis. Three temperature ranges for

PES-1 can be seen in Fig. 1, each of them responsible for unfreezing of local mobility of individual comonomer units. A glass point transition for a given polymer coincides with unfreezing temperature of most thermostable monomer unit. This conclusion sounds to be valid for all LC-polyesters[2,5-8] as well as for copolyamides (for example, CPA{4})[8].

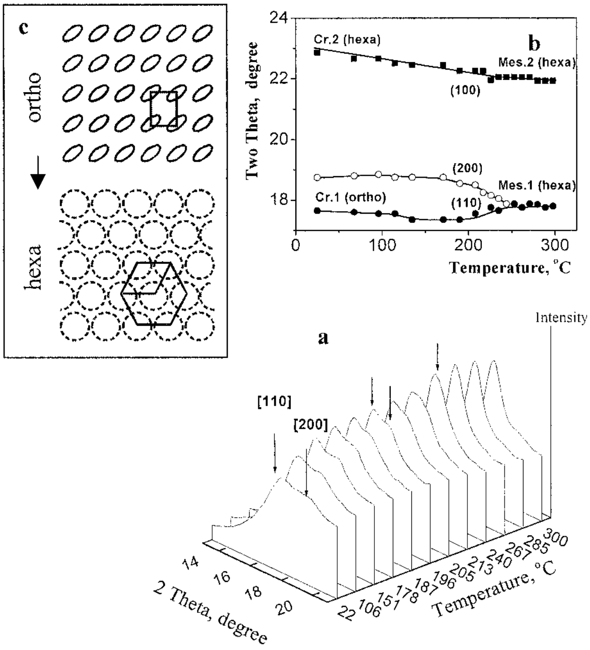


Fig. 2. Evolution of angular positions (a) for two main Bragg peaks on equator (b) for PES-1 and a model of second-order transition from an orthorhombic crystal into a pseudohexagonal mesophase (c).

It was recently established that within the crystalline phase there coexists two different structures and phase separation for two studied polyesters takes place. It was established earlier that for one copolyester two ortho-rhombic lattices could be detected[2], each of them had slightly different elementary cell parameters. When being heated two orthorhombic phases are transformed into mesophase state with

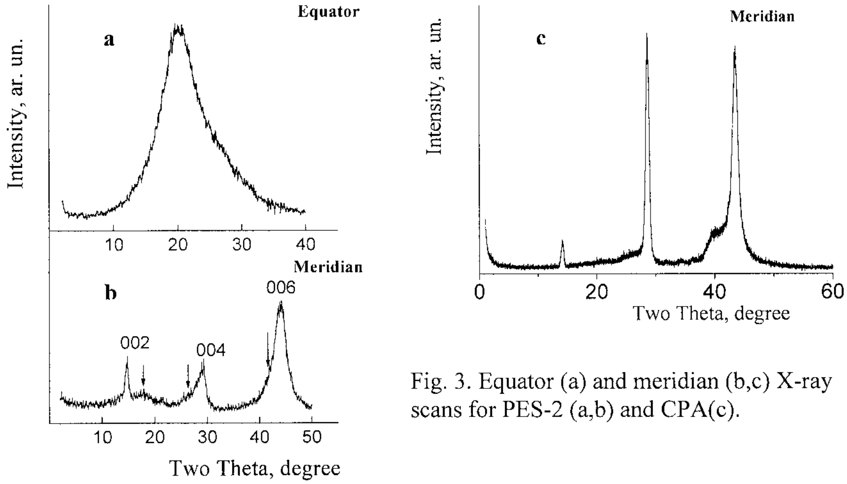


Fig. 3. Equator (a) and meridian (b,c) X-ray scans for PES-2 (a,b) and CPA(c).

corresponding, but different parameters typical for 2-D pseudohexagonal lattice. The model of such second order transition is shown in Fig. 2c. On heating this kind of thermal transition from the crystalline state to condis mesophase is observed for several copolyesters studied[5-7].

As mentioned above the noncrystalline part of copolyesters and copolyamides is considered in our study. Some representatives of copolyesters and copolyamides show diffuse reflexes on equator and sharp Bragg's maxima at meridian (Fig. 3). These sharp maxima mean long-range layer type order along the macromolecular chain axis. The combination of that one together with short-range order in two other directions is typical for LC smectic type structure. Fig. 4a shows typical smectic packing for polymers with flexible spacers. Our polymers do not have flexible spacers, so other type of packing is responsible for observed reflexes. Namely, if comonomer units are of the same length[2] periodic smectic mesophase is formed as shown in Fig. 4b. If monomer units are of different length - aperiodic smectic mesophase is formed as represented in Fig. 4c. The latter has not been detected earlier for thermotropic polymers.

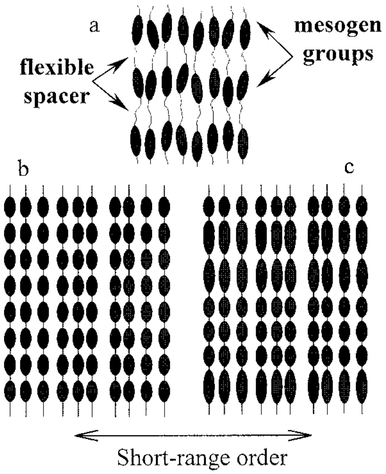


Fig. 4. Scheme representation of typical LC smectic mesophase (a), periodic (b) and aperiodic (c) smectic-like mesophases proposed.

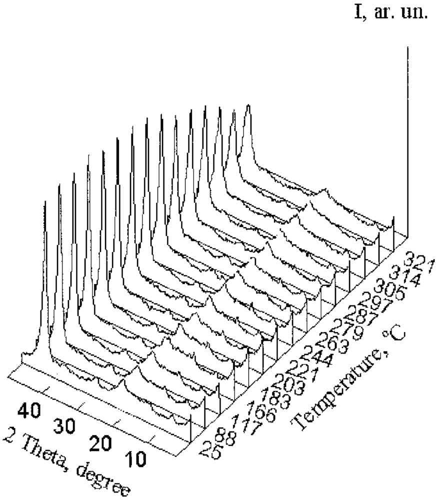


Fig. 5. Meridian X-ray scans for PES-1 at elevated temperatures

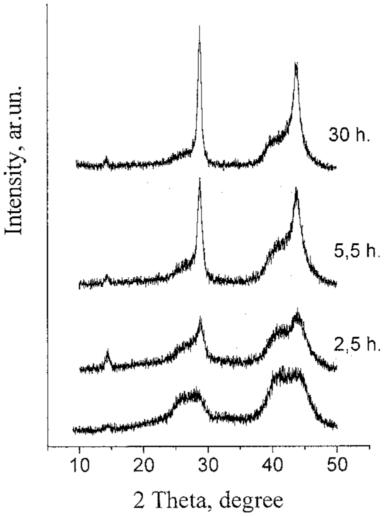


Fig. 6. Meridian X-ray scans for CPA at temperature around glass transition temperature

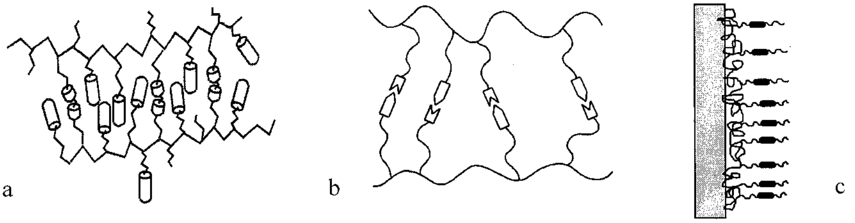
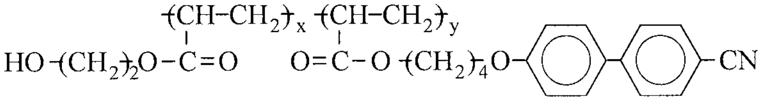


Fig. 7. Three types of side chain LC polymer structures: a - LC elastomers, b - H-bonded polymer networks and c - LC grafted polymers.

The temperature evolution of meridianal reflexes for polyester and copolyamide is shown in Fig. 5 and Fig. 6. Aperiodic structure in the case of polyester remains when all other crystalline reflexes disappear. In the case of copolyamide, during the annealing smectic structure appears among wide reflexes of thermotropic LC nematic phase (Fig.6).

2. LC elastomers, H-bonded polymer networks and LC grafted polymers

The other representatives of mesophase polymers which contain flexible spacers and which show also unusual behavior are LC elastomers, H-bonded polymer networks and LC polymers grafted on polymer films (Fig. 7). For example, elastomers based on linear nematic acrylate-based side chain polymers having the following structure



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are discussed. Linear polymers of this kind may be cross-linked either upon gamma-irradiation or with cross-linking agents.

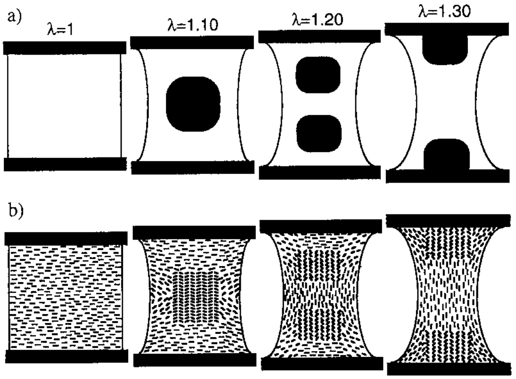

Fig. 8. Square monodomain film exposed to different strains: black spots show opaque regions formed in the optically transparent sample after deformation (a) and schematic representation of the film (initial AR=1) after deformation λ=1.3 (b): back rods indicate the local director orientation.

Creation of monodomain nematic networks generally involves two major steps[9,10]. At first, a polydomain network is exposed to the external field that causes a uniform orientation of the mesogens. The second stage is the cross-linking reaction that proceeds in the presence of an external field. Different crosslinking pathways can be used to make monodomain networks. One of them is based on the preparation of the polydomain network by chemical cross-linking which is subjected to uniaxial stretching at temperatures above Tg (glass transition temperature). The system is then cooled down to room temperature (far below Tg) which freezes-in the strain-induced orientation. In the second step the frozen monodomain films are exposed to gamma-rays that introduce covalent cross-links and fix the original orientation.

Poly-(6-acryloyl-hexyl-4-oxybenzoic acid) - POLYMER
4-[S-(-)-2-octyloxy] benzoic acid - **O*OBA**
(R)-(+)-3-Methyladipic acid - **MAA**
1,6-Diisocyanato-hexane - **DIH**

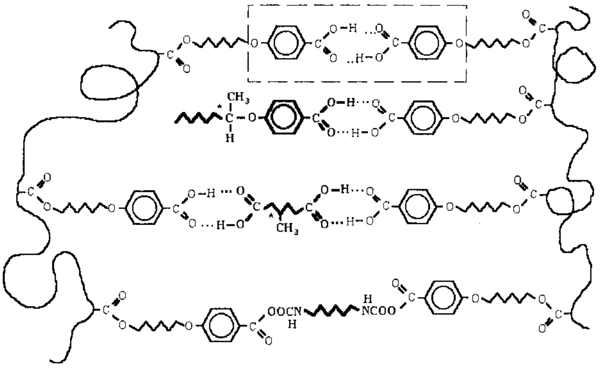

Fig. 9. Three main types of structural elements within the polymer network: H-bonded rod-like formed by carboxyl monomer units incorporated in the polymer backbone (shown schematically by the wavy line), mixed dimer containing H-bonded carboxyl unit and chiral molecule O*OBA, dimer containing 2 H-bonded carboxyl unit incorporated in the polymer chain bridged by methyladipic acid (MAA) and by the crosslinking bridge containing 1,6-hexamethylene.

The variation of optical properties is usually related to the process of the optical axes (or LC director) reorientation. The uniaxial stretching results in the circular scattering spot that emerges in the center of the sample (Fig. 8a). Further deformation gives rise to splitting of the opaque circle into two equal spots which then migrate along the stress axis in opposite directions from the center of the film to the clamps. The X-ray analysis of the orientation process carried out in several different spots shows the following. Two sharp reflections in the X-ray patterns obtained from transparent regions indicate the preservation of the monodomain alignment with the change in the optical axes orientation. During the entire deformation process these regions remain optically transparent. Diffraction patterns collected from opaque spots show 4 reflections which give an idea about the formation of different domains. The analysis of the X-ray diffraction patterns shows the non-homogeneous alignment of the LC director within the entire sample which is schematically shown in Fig. 8b. This scheme indicates different mechanisms of the LC director reorientation.

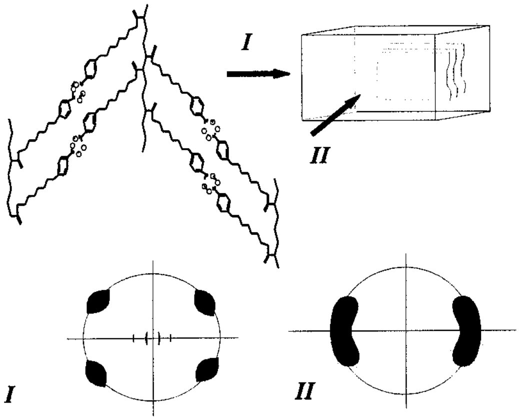

Fig. 10. X-ray diffraction patterns of the H-bonded polymer measured in two different projections: parallel (I) and perpendicular (II) film plane.

A uniform continuous rotation of the director occurs in a clockwise and counter-clockwise manner in the corner regions of the film without distortion of the monodomain structure. The formation of light scattering domains shows the different reorientation pathways - through domains formation where director rotates clockwise towards the stress axis in one half of the domains and counter-clockwise in the other. The mesogens are uniformly aligned within each stripe domain and rotate continuously when an external stress is applied.

Two different orientation mechanisms of the director reorientation observed in one and the same sample results in the non-homogeneous distribution of the director or optical axes. This can be related to the inhomogeneity of the mechanical field generated in the square sample during deformation. Therefore, regulation of the mechanical stresses within the sample may provide a unique opportunity to control the reorientation process. The easiest way to show this would be variation in geometrical shape of the sample, in particular, changes in aspect ratio (length/width) of the film since this feature significantly affects the extent of the mechanical field homogeneity. The variation of the aspect ratio provides control over the director distribution and optical properties of the bulky material. This approach for the monodomain LC elastomer preparation gives a unique opportunity to perform a multi-step fixation of any alignment of mesogens at any stage of the strain induced process. This method appears to

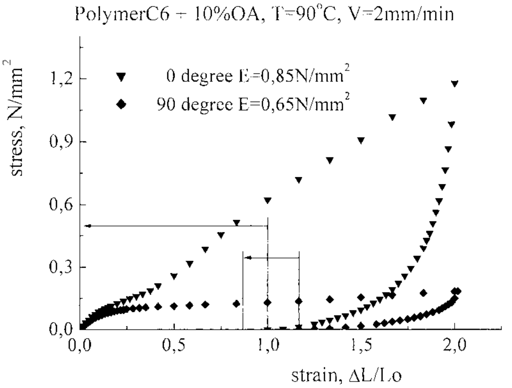

Fig. 11. Stress-strain curve of the H-bonded network for stretching along and perpendicular to the c-director.

be interesting for the preparation of LC networks with variable and easily controlled distribution of local director orientation.

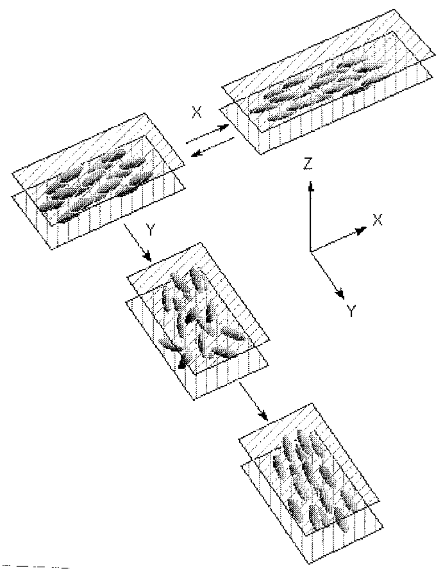

Fig. 12. Model of the monodomain SmC elastomer deformation induced by stretching in two perpendicular directions.

One may combine the polymer elasticity with LC order using the molecular recognition principle when two similar or different moieties are bonded via non-covalent interaction like H-bonds (Fig. 7). It is possible to change properties of these H-bond LC networks by just adding different low molecular weight agents (Fig. 9). The effect of such additive may be to keep the LC order via H-bonding, but disrupt the network, or reverse - to preserve the network via H-bonding but destroy the LC phase. If an additional chemical cross-link between two interacting moieties is introduced it may affect both LC and network structure.

The advantage of using this approach is the ease to modify the functional activity of H-bond polymers with the aid of different additives like chiral molecules, dyes etc., which may be attached to polymer matrix via H-bonds. One of examples is given in Fig. 3 in which different chiral additives are shown to be included in the H-bonded polymer matrix.

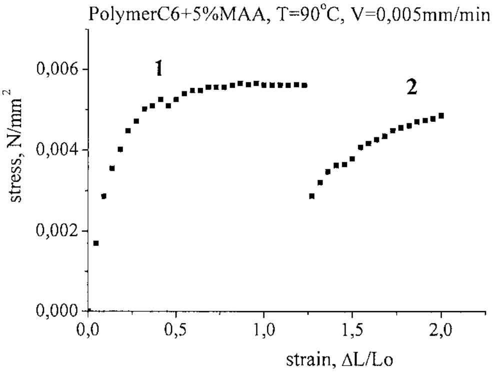

Fig. 13. Stress–strain curves related to the stretching of the polydomain elastomer containing 5 mol.% of MAA (T= 90°C). (Every point was measured by making a small step-increment of strain and allowing 20 min. of stress relaxation). Curve 2 was obtained after allowing stress to relax during 12 h.

The stretching of the polydomain H-bonded network leads to the formation of the aligned film having smectic (or layered) structure which serves as a proof for the LC order (Fig. 10) in every sample mentioned in Fig. 9. The X-ray data indicate the lack of the uniaxial symmetry of order which is identified in terms of the tilted Sm C_A phase with the regular alternating

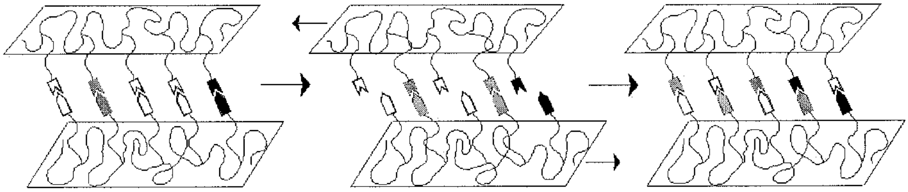

Fig. 14. Schematic representation of the deformation mechanism of H-bonded networks.

of the LC director orientation within the smectic layer. The elasticity modulus measured under stretching is fairly low, and one observes the relaxation with a strong hysteresis indicating that the system is structured (Fig. 11). However after a certain time both stress and deformation are relaxing indicating elastic properties. This is rather unusual for the elastomer built from non-covalently linked components. Moreover, as it is proved by X-ray diffraction a "perpendicular" stretching of the monodomain sample is accompanied by the director rotation and realignment whereas the stretching along the *c*-director does not involve any realignment of the LC director[11-13]. This allows us to discuss the processes observed in H-bonded LC network having Sm C_A structure in terms of "soft" and "hard" elasticity introduced and developed by Warner and Terentjev[14,15] for nematic elastomers. The schematic representation of the deformation of the monodomain induced by mechanical field parallel and perpendicular to the *c*-director is shown in Fig. 12.

The question arises, what is the deformation mechanism for such H-bonded systems? The stress-strain curves in a close to equilibrium regime are given in Fig. 13 [13]. Every point in this curve was measured by making a small step-increment of strain and allowing 20 min. of stress relaxation. The system behaves as a cellular solid in which the stress remains constant on increasing deformation when a certain threshold level is reached. The reason is that above this "yield stress" the microstructure can re-connect, thus allowing the deformation to proceed without further increase of average stress. It then follows that if one holds the

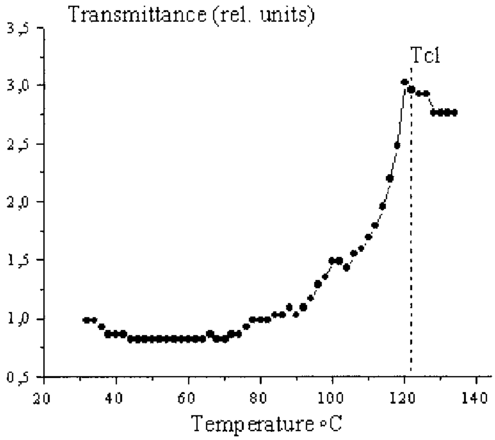

Fig. 15. Optical transparency versus temperature for LC-PTFE grafted material.

deformation constant for some time, the system will equilibrate in the new configuration and will eventually relax its stress to zero by reconnecting the H-bonds (Fig. 14). The complete "resetting of stress" must take a very long time, being a dynamic process with self-retardation. However, we see a clear signature of such an effect in Fig. 13, where the strain was kept constant at $\Delta L/L = 1.25$ for 24 hours, after which the initial strain rate has been re-started.

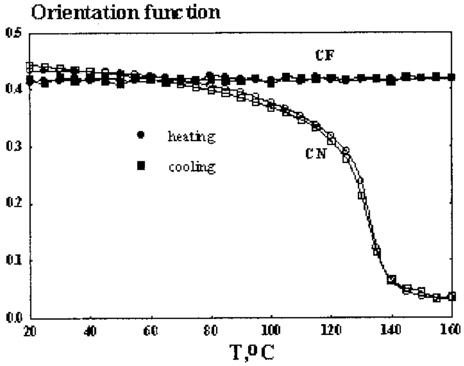

Fig. 16. The orientation function vs. temperature for IR bands: 2367 cm^{-1} (C-F); 2225 cm^{-1} (C-N); o, • - heating, □, ■ - cooling.

The above examples of ordered materials give an idea about coupling of LC order with the network structure which results in the unique mechanical and optical properties of the material in full.

A different approach to provide appropriate physical mechanical characteristics of the anisotropic side chain LC polymer material is about the preparation of the composite sandwich-like structure in which a side chain LC polymer is grafted on the polymer support during post polymerization[16,17]. Fluorocarbon polymers like PTFE and FEP are irradiated by vacuum ultraviolet (VUV) and long-term living radicals appear which serve as the active centers for the post polymerization of the monomer layer contacted with surface of matrix. The resulting polymer is characterized by the opaque texture scattering the light. The heating of the film results in the increase of the optical transmittance and above the LC polymer clearing point the transparency of the sandwiched structure is high enough and comparable with the transparency of the pure FEP film (Fig. 15). This process is completely reversible. The stretching of the composite film gives rise to the orientation of the grafted layer alongside with the basic support[18]. It is well seen from the IR data the degree of mesogenic group orientation is rather high (Fig. 16). The nematic - isotropic transition in this case is accompanied by the loose in the mesogenic groups orientation with no change in the orientation of the fluorine-containing polymer support. The latter makes possible to provide the macroscopic orientation of the LC grafted layer by just cooling the sample. This should also influence the optical properties of the material and control over the refractive index anisotropy by varying the temperature conditions.

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