

This article was downloaded by:

On: 19 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



## International Journal of Polymeric Materials

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713647664>

### Formation of Liquid-Crystalline Structure in the Process of Film Extrusion from Cellulose Diacetate

V. E. Gul<sup>a</sup>; O. A. Khanchich<sup>a</sup>; A. L. Peshehonova<sup>a</sup>; O. A. Sdobnikova<sup>a</sup>

<sup>a</sup> Dept. of Biotechnology and Polymer Processing, Moscow Institute for Applied Biotechnology, Moscow, Russia

**To cite this Article** Gul, V. E. , Khanchich, O. A. , Peshehonova, A. L. and Sdobnikova, O. A.(1994) 'Formation of Liquid-Crystalline Structure in the Process of Film Extrusion from Cellulose Diacetate', *International Journal of Polymeric Materials*, 24: 1, 167 – 176

**To link to this Article:** DOI: 10.1080/00914039408028563

**URL:** <http://dx.doi.org/10.1080/00914039408028563>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

## Formation of Liquid-Crystalline Structure in the Process of Film Extrusion from Cellulose Diacetate

V. E. GUL', O. A. KHANCHICH, A. L. PESHEHONOVA and O. A. SDOBNIKOVA

*Moscow Institute for Applied Biotechnology, Dept. of Biotechnology and Polymer Processing, Talalikhina str. 33, Moscow, Russia 109818*

Liquid-crystalline (LC) polymer properties depend considerably on the chemical structure of the rigid and flexible parts of the macromolecular chains. The relation of these factors determines a complex of physical and chemical properties and thus the operating characteristics. Realization of the LC state within a temperature range which is required by processing and operating conditions is achieved by the synthesis of LC's of a certain structure. The formation of LC structures in cellulose diacetate by selection of plasticizer level and type is considered in this article. Plasticizer selection is determined by the ratio of the polymer specific cohesion energies and the specific cohesion energies of a combined plasticizer consisting of a true plasticizer with the addition of small amounts of a precipitator.

**KEY WORDS** Liquid crystalline state, extrusion, cellulose diacetate

### INTRODUCTION

Polymer liquid crystals cannot be formed at high values of a molecular mass and higher rigidity of macromolecules. This is due to the fact that parallel alignment of such macromolecules requires great energetic expenses which will result in their destruction. If according to the ideas developed by Flory,<sup>1</sup> who used a lattice model, the energy of one effective fracture is assumed as  $\epsilon$  and lattice coordination number as  $Z$  then the Flory criterium  $f$  will be connected with  $\epsilon$  and  $T$  ratios:

$$f = f_0 = \frac{(Z - 2)\exp\left(-\frac{\epsilon}{kT}\right)}{\left[i + (Z - 2)\exp\left(-\frac{\epsilon}{kT}\right)\right]}$$

Index "O" means that  $f$  depends only on the interval energy of the macromolecule.

In conformity with real polymer systems Frenkel showed<sup>2,3</sup> that  $f_0$  may change under both the action of outside power fields and in the case of changing polymer-solvent interactions. Thus, it is possible to achieve the transition into the LC state for polymer systems with 0.63 (flexible-chain polymers) in practice not only using

outside power fields but by means of a proper solvent selection. When filling the solvent with rigid (straightened) macromolecules there is a critical drop in polymer chemical potential from the filled to the unfilled solution regions ("traps") because of their rigidity. This condition arises when the polymer volumetric portion in the mixture is achieved. Because of mutual interferences new molecules cannot penetrate into these "traps." This results in an unstable thermodynamic system. If it is so large that the interval energy can compensate the osmotic one, then a parallel packing of molecular chains is formed in a system during the transmission into an equilibrium state. The latter will correspond to the minimum Gibbs free energy. In this case the LC phase<sup>4</sup> is formed. The higher the molecular mass of a rigid-chain polymer, the more difficult it is to carry out this transition. Polymers such as cellulose, which is nearly a rigid-chain polymer (Koon segment is higher than 100 Å), practically cannot be transferred from an amorphous state into an LC state by mixing with a solvent. If spontaneous mixing is possible then it is accompanied by rigidity loss, and kinetic units will be located in the mixture "according to the law of chance." When chain rigidity is preserved then it is not possible to provide for parallel laying (packing) of such large macromolecules. The intensive intermolecular interaction of cellulose stimulated by the availability of a great number of polar oxygen containing groups excludes one relative to the other. If oxygen containing groups are screened by conversion to cellulose triacetate then the use of triacetate as a plasticizer under corresponding thermodynamic conditions, the transition into an LC state can be carried out. In this case it is essential to preserve the rigidity of the macromolecules and to ensure their mobility at the expense of alternating rigid chain section and flexible-chain/spacers. Consequently, the plasticizer content must be limited by the formation of a comparatively small number (in relation to the degree of polymerization) of spacers, the flexibility of which is determined by the screening of the polar groups. In order to obtain a material which can be processed with a small amount of plasticizer it should be less than the level at which the polymer becomes fluid under the action of gravitational force at ambient temperature.

A small degree of substitution by cellulose diacetate (DAC) does not allow the fulfillment of the conditions stipulated above. Attainment of the required flexibility of DAC spacers demands such an amount of plasticizer that solution is obtained before the composition melts at the processing temperature. To obtain DAC in an LC state, a highly efficient plasticizer is necessary. A comparatively small amount of such a plasticizer will considerably weaken intermolecular interactions so that the spacers formed in this case provide for the transition into the LC state. The most effective cellulose acetate plasticizer of all those known before triacetin (TA) satisfied similar requirements. Plasticizer efficiency is first of all determined by its affinity for the polymer. Free energy change during mixing with polymers of low molecular weight depends slightly on entropy changes of mixing. These changes differ a little for different plasticizers.

Polymer and low molecular weight component intermolecular interactions proved to be the main regulating factor. In Reference 5 it was shown that for a number of solvents having different values of specific cohesion energy (SCE) the highest degree of polymer swelling takes place when polymer and low-molecular weight

component specific cohesion energies are equal. When selecting an optimum plasticizer it is also reasonable to seek the use of low molecular weight components with values of SCE near to those of the polymer, if possible. In this case the tendency of the low molecular weight component to be mixed with the polymer<sup>6</sup> is realized at the maximum. In practice it is complicated to achieve equality. The idea of leveling these values at the expense of mixing in a low molecular weight component having a different value of SCE has arisen.<sup>7</sup> As an example polyisoprene + a system of benzene with different levels of methyl alcohol<sup>7</sup> was used. For the analyses of structural changes occurring at the molecular level, the change of molecular light dissipation for polyisoprene solution in benzene was investigated for coagulation by addition of methyl alcohol. It was proved that in the course of adding a precipitant to the benzene in small amounts with a relatively high value of SCE, the value of light dissipation is decreased. This corresponds to a decrease in system optic non-uniformity, to more a uniform distribution in the mixture of low-molecular weight component molecules and to the increase of solvent SCE and the increase of polymer and combined solvent SCE difference. In this system, turbidity increases until polymer coagulation from the solution begins. This principle was taken by us as a basis for selecting a combined plasticizer for carrying out the transition of DAC into the LC state.

The first information concerning a lyotropic mesomorphism of cellulose derivative solution was obtained only recently.<sup>8-10</sup> However, until now the conditions under which the LC-state is realized have been already determined for a great number of such systems. The research of an anisotropy in melts of cellulose derivatives is of great interest because a plurality of articles are made from a melt. However, all the published works on cellulose derivatives refer to their solutions.

In this work the following is examined: structure changes in the course of the transition from DAC melt to a plasticized system and also an anisotropy and supermolecular structure of diacetate films being produced.

## EXPERIMENTAL

The object of this research was DAC based on cotton cellulose with an average polymerization degree (PD) of 200–250 with various contents of bonded acetic acid ( $j$ ) and made of different raw materials (Table I). As objects of comparison 40% DAC solutions ( $j = 55-56\%$ ; PC = 300–350) and methyl cellulose solutions (MC) with  $j = 43\%$ ; PD = 200–300) were used. As a solvent trifluoroacetic acid (TFA) was used. It has the ability to form LC solutions of the indicated polymers at lower concentrations than other known solvents.<sup>9,11</sup> Film based on DAC-TA were made by an extrusion method with melt temperatures at the outlet being 453 K. The components were mixed in a high speed turbomixer at a temperature of 273 K, mixing time was 12 minutes. The mixture was homogenized in an extruder-plasticizer with a melt temperature of 453 K at the extruder outlet. The rods obtained were cooled, cut into granules from which a belt with thickness of 0.03 cm was formed by an extruder with temperature per cylinder zones of 438, 451 and 468 K. The test samples were cut from the belt in a longitudinal direction.

TABLE I  
Composition and properties of films based on DAC-TA

<i>N</i>	Content of bonded acetic acid, %	Content of plasticizer in a composition, mass %	Ultimate tensile stress at extension, <i>N/m</i>	Relative elongation at break, %	Glass trans. temperature, C
1	54.4	45	40	50	105
2	54.4	40	38	30	110
3	54.4	35	40	30	125
4	54.5	33	45	30	140
5	54.5	30	40	40	140
6	55.8	35	40	40	155
7	55.2	35	55	48	110
8	54.7	35	70	30	160
9	56.5	35	56	20	160

Film mechanical properties were determined with an "Instron" tensile testing machine at temperatures of 293 and 393 K and a deformation rate of 10 m/hour. Working section sizes of the samples were  $5 \times 10 \times 0.3 \cdot 10^{-3}$  mm. The purpose to find the region of DAC LC temperature-dependent conditions for the origin of the LC phase in a complex plasticizer TA + oligoester. The research was carried out by use of a photoelectric polarized microscope, polarized light transmission techniques, and small angle scattering of polarized light.<sup>12</sup>

## RESULTS AND DISCUSSION

For samples (1–5)  $H_v$  patterns of polarized small angle light scattering extended into the direction perpendicular to the polymer film (Figure 1).  $H_v$  patterns of such a type testify to the formation of optically anisotropic structures of cylindrical form oriented in the direction of growth.<sup>13–15</sup> The change in sizes and intensity of dissipation elliptical patterns similar to those which are illustrated on Figure 1a show that the parameters and the orientation of such structures change from sample to sample. As the influence of orientation is similar to the dissipation from a polymer film at its extension,<sup>16</sup> it is possible to determine the length ( $l$ ), the diameter ( $d$ )<sup>14,15</sup> and the average square angle of disorientation  $\langle C^1 \rangle^{1/2}$ <sup>17</sup> of such structures.

For this purpose, photometry of  $H_v$  scattering patterns along different elliptical axes and calculations were carried out according to the formulas given in References 14, 15, and 17. It was found out that structural element length ( $l$ ) for all the samples does not change considerably and equals tenths of a micron. At the same time the diameter ( $d$ ) for sample ( $i$ ) is 0.7–1.2 microns,  $\langle C^2 \rangle^{1/2} = 10$ –12 and for sample (2) is a smaller structural element with a thickness on the order of 0.5–0.8 microns and  $\langle C^2 \rangle^{1/2} = 8$ –9. Some parts of the films showed periodicity in the distribution of intensity in  $H_v$  patterns. Figure 1b which can be connected with the appearance of some ordering at a macrolevel, is typical for domain LC structures.<sup>18</sup>

Samples (6–9) show more intensive discrete reflexes of polarized small-angle light scattering. Figure 2 corresponds to micron size domain formation where ma-

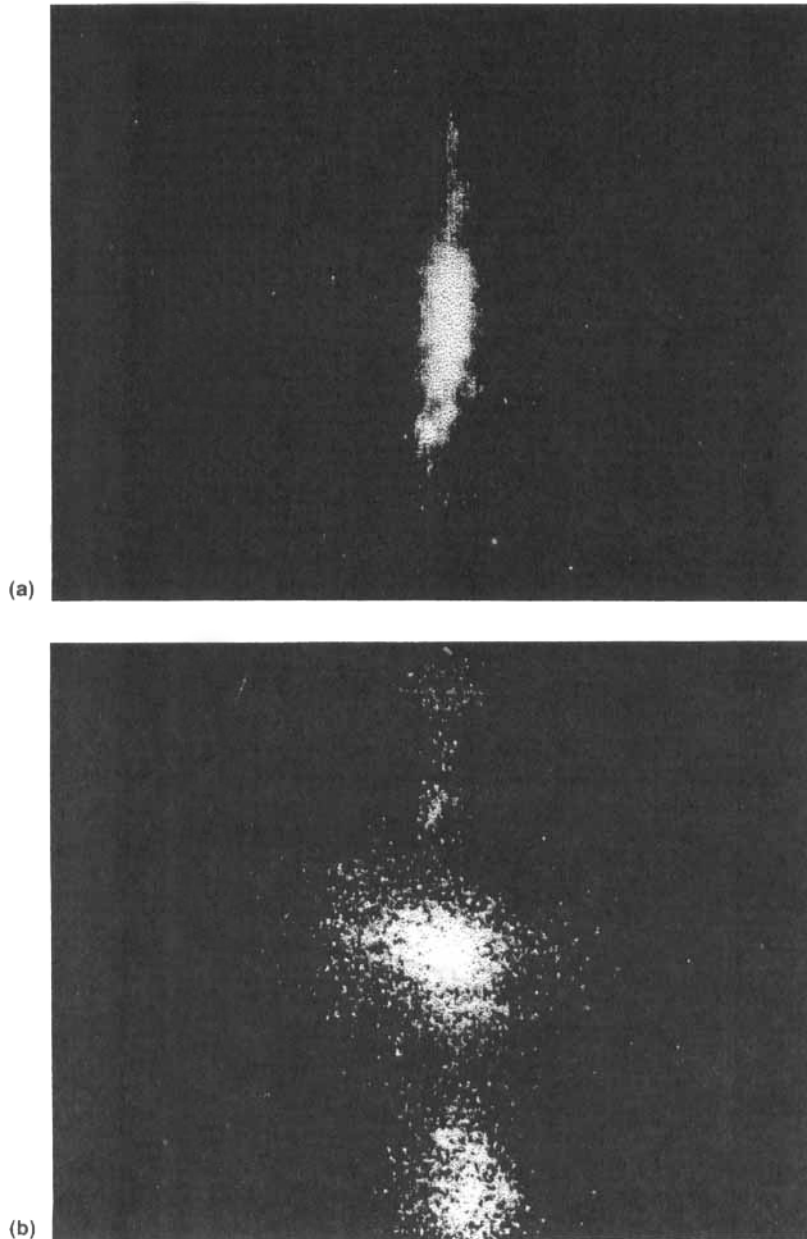


FIGURE 1 Light scattering patterns for DAC films with a substitution degree of 55.4% and plasticizer content (a) 45 mass% TA (b) 40& mass % TA.

chromolecules are oriented parallel to each other but at a certain angle to the optical axes of neighbouring domain molecules.

For determining the value of an optical anisotropy of the samples at different temperatures, the light transmission integral intensity was measured. It was discovered that the value of optic anisotropy increases (Figure 3) with an increase in

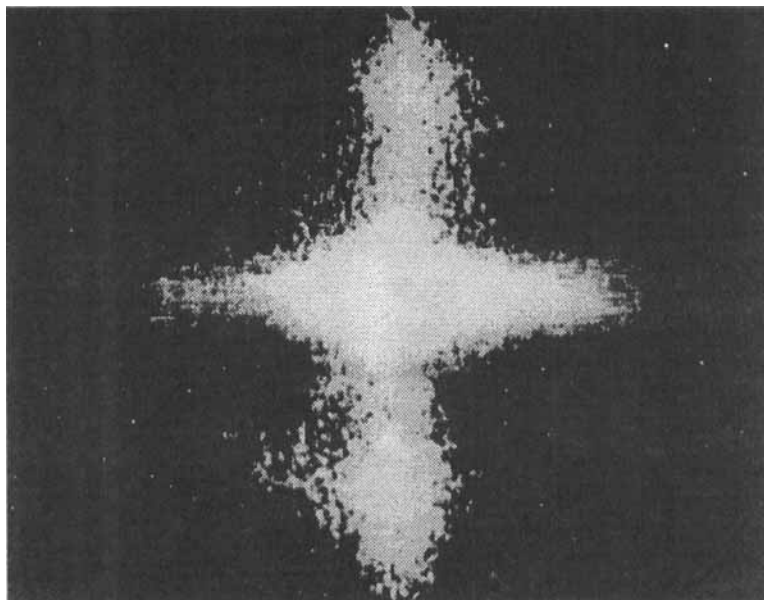


FIGURE 2 Light scattering patterns for DAC films with a substitution degree of 55.2% and plasticizer content 35 mass % TA.

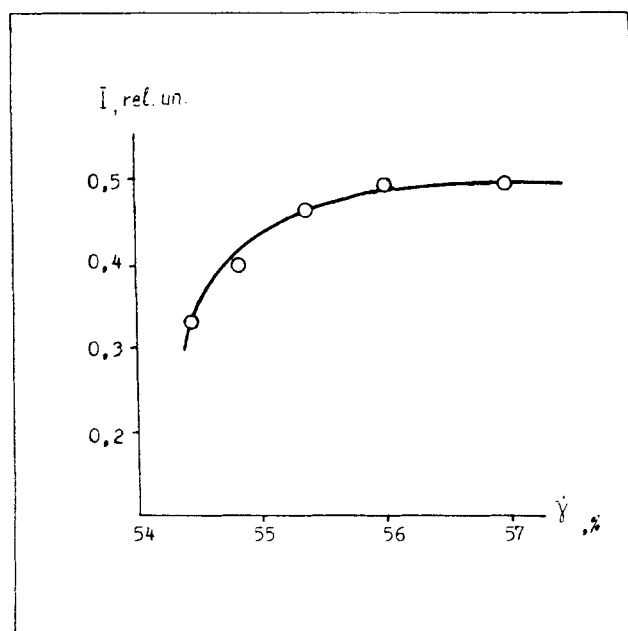


FIGURE 3 Integral intensity dependence of polarized light transmission (nicols are crossed) for samples having different contents of bonded acetic acid.

bonded acetic acid content. The increase in sample strength properties (Table I) is an additional confirmation of a direct relationship between  $j$  and the formation of an ordered structure. As is seen from Table I, the observed ordering in the system DAC-TA is connected with an increase of  $j$  from 54.4 to 56.5% and is accompanied by an increase strength of 1.5–1.7 times. The increase in the film strength in a longitudinal direction for the increase in  $j$  equal to the anisotropic dissipation patterns of the light and with the increase of polarized light transmission intensity may correspond to an LC phase system.

At the same time it is necessary to point-out that the values of the effects in films of DAC-TA described above are small as compared with similar optic phenomenon observed in LC solutions of MC in TFA. It is testified to by a study of structure formation processes during formation of DAC and MC films from a melt. On Figure 4 you can see curves for polarized light transmission intensity and  $H_v$  scattering patterns arising at different moments of film formation during the course of TFA evaporation from a MC solution (Figure 4, curve 1) and DAC (Figure 4, curve 2) and also during cooling of DAC-TA melt (Figure 4b). From Figure 4 it is seen that for methylcellulose a LC structure is fixed in the film. This is proved by the appearance of unchangeable patterns as the solvent is removed and a practically constant value for the light transmission integral intensity (Figure 4, curve 1). More complex structural transmissions are observed during TFA evaporation from a DAC solution. In this case the effect of the transition to an isotropic state during coagulation is quite unexpected. The observed effect is shown as a decrease

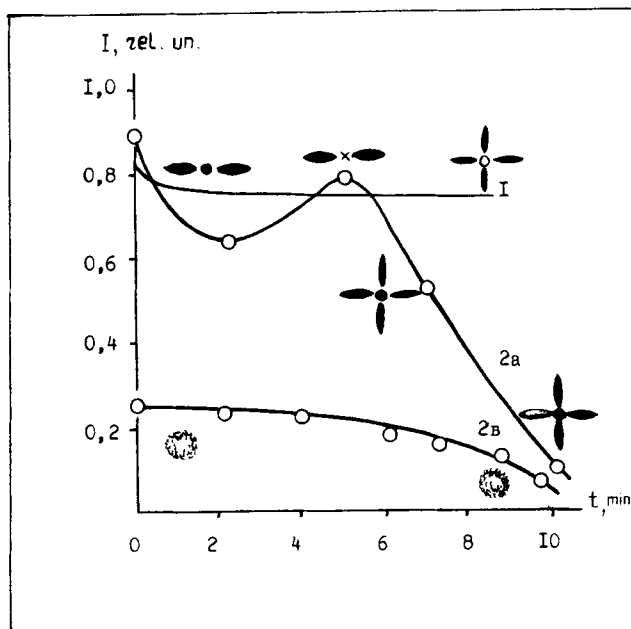


FIGURE 4 Integral intensity dependence of polarized light transmission (nicols are crossed) for samples having different contents of bonded acetic acid (a) on TFA evaporation time from MC (curve 1) and DAC (curve 2) solutions (b) on DAC-TA melt cooling  $H_v$  patterns describing the structure at different stages of film-forming formation are shown by contours.



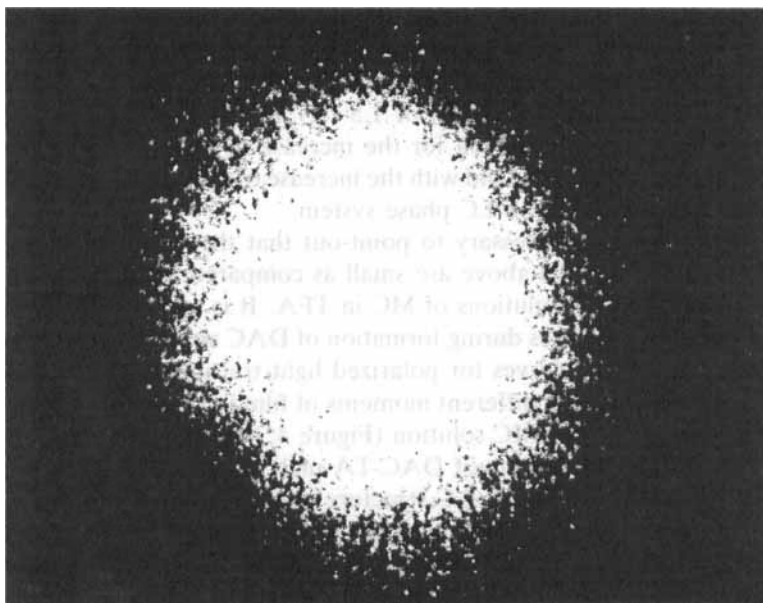


FIGURE 5 Light scattering patterns for DAC melt with TA content 35 mass % and temperature of 453 K.

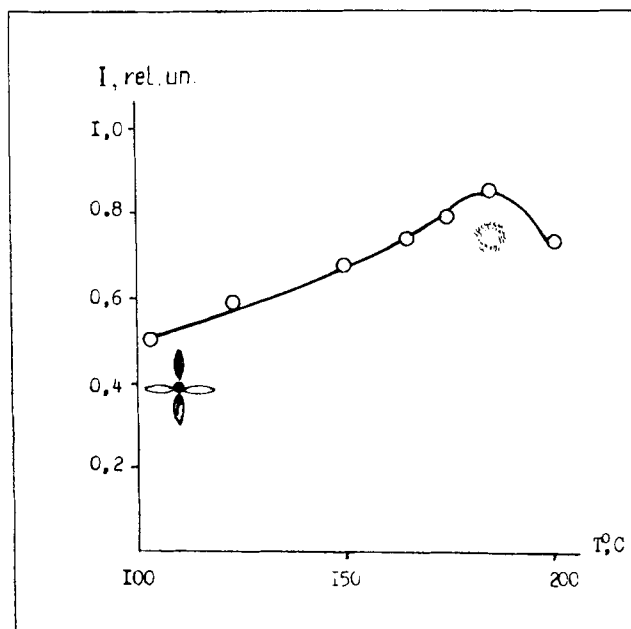


FIGURE 6 Integral intensity dependence for sample on temperatures.

in polarized light transmission intensity to a zero value (Figure 4, curve 2). A similar phenomenon of decreasing optical anisotropy is observed in the film forming process while cooling cellulose-acetate-TA melt (Figure 4b). It is possible to assume, that in the case of cellulose acetate, the order in a polymer systems is possible only in the presence of a solvent. As the solvent is removed, the dispersion degree changes sharply as per  $j$  and also per macromolecular order. From Figure 4 it is seen that optical anisotropy in DAC-TA is small as compared with test-samples, having LC structures directly in solutions, for example, DAC in TFA. It is especially noticeable in the large difference in polarized light transmission intensity (nicols are crossed) during the initial moments of structure formation from DAC solutions and melts, Figure 4a, b.

When heating DAC-TA films within the temperature range 443–463 K a transition from an  $H_v$  pattern oriented perpendicular to the deformation direction, (see Figure 1 and 2) to an  $H_v$  pattern having the appearance of a diffusion spot is observed (Figure 5). Within the same temperature range the intensity of polarized light transmission increases (Figure 6), which is testified to by the increase in system total anisotropy. The observed phenomenon of ordering during DAC-TA system heating, corresponds to the effect of spontaneous self-ordering within the temperature range of 433–453 K discovered before.<sup>20</sup>

## CONCLUSIONS

The research work which was carried out showed that when forming DAC films plasticized by TA the realization of an LC state is possible. The fullness of the LC phase realization depends on the DAC substitution degree, phase state of the sample and on the relationship of the specific cohesion polymer and plasticizer energies. Thus, quite a new approach to LC structure formation in polymers with increased chain rigidity is noted. This is characterized by the fact that instead of space group formation during the stage of polymer synthesis, this stage is carried out by choosing the composition of a combined plasticizer resulting in the leveling of the values of polymer and plasticizer specific cohesion energy. In this case the role of spacers is played by the plasticized sections of a semirigid polymer chain having higher strength properties through the stage of LC state. The observed phenomena require further research using other physical methods.

## References

1. P. J. Flory, *Proc. Roy. Soc. (London)*, **234**, 60–72, 73–89 (1956).
2. S. Ya. Frenkel, *Pure & Appl. Chem.*, **38**, 117–149 (1974).
3. S. Ya. Frenkel, *J. Polym. Sci.*, **44**, 49–57 (1974).
4. G. M. Bartenev and S. Ya. Frenkel, *Physics of Polymers*, Leningrad, Chemistry, 430 (1990).
5. D. Dji, *Chemistry of large molecules*, Moskow, 161 (1948).
6. V. E. Gul', *Colloid. Journal*, **13**, 99–107 (1951).
7. V. E. Gul' and G. S. Clytenik, *Colloid Journal*, **16**, 171–178 (1954).
8. R. S. Werbowij and D. G. Gray, *Molec. Cryst. Liquid Cryst.*, **34**, 97 (1976).
9. M. Panar and O. B. Willcox, Pat. 270582 (BRD), 1977.
10. R. D. Gilbert and P. A. Patton, *Progr. Polymer Sci.*, 115 (1983).

11. B. Yu. Yunusov, O. A. Khanchich, A. K. Dibrova, M. T. Primkulov and A. T. Serkov, *Vysokomol. Soed.*, **24B**, 414 (1982).
12. O. A. Khanchich, *Khem. Volokna*, **4**, 6 (1986).
13. R. S. Stein, P. Erhardt, J. J. Van Aartsen, S. Clough and M. Rhodes, *J. Polymer Sci.*, **13**, 1 (1966).
14. V. G. Baranov, T. J. Volkov and B. Ya. Frenkel, *Vysokomol. Soed.*, **7**, 1565 (1965).
15. Yu. I. Kotov and O. A. Khanchich, *Optika Spektroskopya*, **40**, 563–570 (1976).
16. R. S. Stein, M. B. Rhodes and R. S. Porter, *J. Colloid. and Inter. Sci.*, **27**, 336–354 (1968).
17. Yu. V. Brestkin and D. Raschidov, *Vysokomol. Soed.*, **15A**, 1953–1958 (1973).
18. O. A. Khanchich, A. T. Serkov, A. V. Volokhina and V. D. Kalmykova, *Vysokomol. Soed.*, **17A**, 579–581 (1975).
19. O. A. Khanchich, B. Yu. Yunusov, A. T. Serkov and M. T. Primkulov, *Vysokomol. Soed.*, **24B**, 414–418 (1982).
20. B. Yu. Yunusov, O. A. Khanchich, M. V. Shablygin and O. A. Nikitina, *Vysokomol. Soed.*, **25B**, 292–294 (1983).