

# Molecular Orientation in the Surface Layer of Polytetrafluorinethylene

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**ABSTRACT:** Attenuated total reflectance spectroscopy was used to study the orientation and deformation of molecular chains in polymers. Reflection and transmission spectra of the polytetrafluorinethylene (PTFE) films were obtained. Parameters of the macromolecule's degree of order were determined for the whole volume and for the surface layer of uniaxially orientated PTFE, and on this basis, we determined the character of dependence  $l^{\text{SL}}(L)$ , where  $l^{\text{SL}}$  is the effective thickness of the surface layer and  $L$  is the film stretching degree. © 2002 John Wiley & Sons, Inc. *J Appl Polym Sci* 83: 1596–1599, 2002

**Key words:** infrared spectroscopy; attenuated total reflection (ATR); molecular orientation; surfaces; polytetrafluorinethylene (PTFE)

## INTRODUCTION

Most characteristic properties of the deformation of polymer materials have not been investigated enough.<sup>1–3</sup> As a matter of fact, there are no quantitative data that give us the ability to judge the influence of the deformation on the structure of the surface layer of polymer films.<sup>4</sup> For this reason, in our work, we attempted to determine the parameters of the macromolecule's degree of order ( $S$ ) of the whole volume and of the surface layer of uniaxially orientated polytetrafluorinethylene (PTFE) films and, on this basis, to determine the character of dependence  $l^{\text{SL}}(L)$ , where  $l^{\text{SL}}$  is the effective thickness of the surface layer and  $L$  is the film stretching degree.

## EXPERIMENTAL

The experimental part of the work was the measurement of the spectra of reflection  $[R(\nu)]$  and

transmission  $[T(\nu)]$  of PTFE films. The objects of our investigation were commercial PTFE films [Ftorplast-4, Galogen, Russia; density ( $\rho$ ) = 2.22 g/cm<sup>3</sup>; degree of crystallinity  $\sim$  70%]. The orientation of films was at room temperature (20°C), and the method of uniaxial stretching was used. For this investigation, we used films that were stretched 1.4, 1.7, 1.9, and 2.1 times as much as initial (nonoriented) films. Stretched films were allowed to relax over the course of 24 h, and then, their lengths, widths, and thicknesses were measured. After relaxation, percent elongation ( $L$ ) was  $\sim$ 80% (Table I). The dimensions of all samples obeyed the criterion of uniaxial stretching:

$$x_0 = x \sqrt{L}$$

where  $x_0$  and  $x$  are the initial and final widths (thicknesses) of the film, respectively, and  $L$  is the film stretching degree (percent elongation) after relaxation. After stretching and relaxation, the films were not treated (thermally, chemically, mechanically, etc.)

The method of liquid spectroscopy attenuated total reflectance (ATR)<sup>5,6</sup> was used when the spec-

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**Table I** Dichroism and Parameters of the Degree of Order of the Macromolecules in the Whole Volume and in the Surface Layer of Uniaxially Oriented PTFE Films of  $l_0 = 50 \mu\text{m}$ 

$L$	In Volume		In Surface Layer			
	$A_{\parallel,\perp}^{1450}$	$S^{\text{vol}}$	$A_{\parallel,\perp}^{1160}$	$A_{\parallel,\perp}^{1215}$	$\bar{A}_{\parallel,\perp}$	$S^{\text{SL}}$
1.0	1.03	0.01	0.81	0.83	0.82	0.13
1.1	1.24	0.07	0.71	0.71	0.71	0.21
1.4	1.75	0.20	0.57	0.57	0.57	0.34
1.5	2.04	0.26	0.48	0.48	0.48	0.42
1.7	2.56	0.34	0.36	0.34	0.35	0.55

tra of  $R(\nu)$  were measured. For the optical path, ATR, liquid glass  $\text{As}_{1.0}\text{S}_{1.5}\text{Br}_{2.0}$  with a refractive exponent ( $n_D^{20}$ ) of 2.10, which is transparent over a large spectral range, was used. The samples were placed in such an order that the axis of stretching ( $z$ ) was parallel or perpendicular to the electric vector ( $\mathbf{E}$ ) of the falling light wave.  $R_{\perp}(\nu)$  spectra or  $R_{\parallel}(\nu)$  spectra were registered in accordance with the film position. These spectra were taken as the basis when the spectra of Bouguer absorption factors  $\hat{a}_{\perp}(\nu)$  and  $\hat{a}_{\parallel}(\nu)$  were calculated, according to equations by Franel, and dispersive relations by Cramers-Cronig were used.<sup>5</sup> According to our calculations, the error was 5% or lower.<sup>5</sup> The spectrum  $a(\nu)$  of PTFE, which was measured during this experiment in an interval of 1000–1300  $\text{cm}^{-1}$ , is shown in Figure 1.

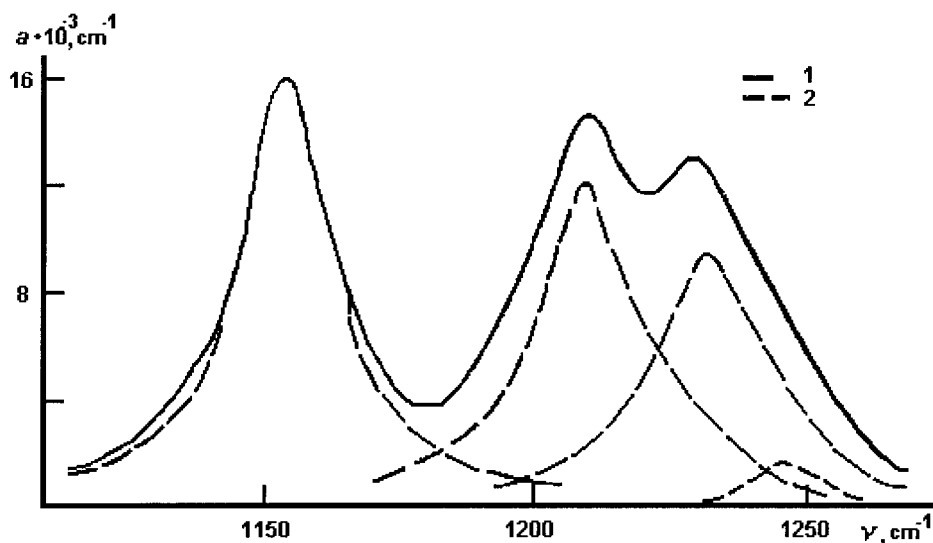
The measurement of IR spectra of the PTFE film  $T(\nu)$  was carried out in an interval of 1400–

1500  $\text{cm}^{-1}$ . The absorption factors  $\hat{a}_{\perp}(\nu)$  and  $\hat{a}_{\parallel}(\nu)$  were calculated according to the equation by Bouguer on the basis of experimental data obtained for a "packet" of the films with the same thickness. The registration of  $R(\nu)$  and  $T(\nu)$  spectra was in natural and  $s$ -polarized light. Film replicas were taken as polarizers, and they were placed into both channels of the spectrophotometer immediately before the samples.

Parameters of the degree of order  $S$  were calculated according to the known equation,<sup>7</sup> which describes the case of partial axial orientation of the rotary symmetrical type:

$$S = \frac{A - 1}{A + 2} (1 - 1.5 \sin^2 \beta)^{-1} \quad (1)$$

where  $A$  is the dichroism of IR bands and  $\beta$  is the angle between the direction of the dipole moment



**Figure 1** Spectrum  $a(\nu)$  of PTFE film ( $L = 0$ ;  $\mathbf{E} \perp z$ ): (1) experimental result and (2) result separation in Laurence approximation of contour IR band.

of the transition ( $\mu$ ) and the axis of the macromolecules ( $c$ ). The angular value  $\beta$  was chosen considering the data of the ref. 8, according to which PTFE bands with maxima in intervals of 1450 and 1160 and 1215  $\text{cm}^{-1}$  were conditioned by valency oscillations of  $\text{CF}_2$  groups relating to the  $A_2$  and  $E_1$  symmetry types respectively, for example, in the first case,  $\mu \parallel c$ , and in the second case  $\mu \perp c$ .

## RESULT AND DISCUSSION

The meanings of dichroic relations  $A_{\parallel,\perp}$  and, calculated on their basis [according to eq. (1)], the parameters of the order of degree  $S$  are given in Table I. They characterize the orientation of dichroism of the surface macromolecules in the whole volume ( $S^{\text{vol}}$ ) and in the surface layer ( $S^{\text{SL}}$ ) of the films. Data processing according to the method of the least squares showed that the dependence of the parameters  $S$  on  $L$  had a linear character

$$S^{\text{vol}} = 0.47L - 0.45$$

$$S^{\text{SL}} = 0.59L - 0.45$$

where the correlation coefficients ( $rs$ ) were 0.998 and 0.993, respectively.

When these equations are compared, it is not difficult to make the conclusion that uniaxial stretching had essentially different influences on the orientation of macromolecules in the whole volume and in the surface layer of the PTFE films. When this is taken into account, it is natural to suppose that dichroism observed in IR spectra of the film  $T(\nu)$  was generally conditioned by the dichroism of the surface layers, and their inner layers were practically not orientated, even if  $L$  was rather higher. In other words, PTFE films with  $l_0 = 50 \mu\text{m}$  could be regarded as anisotropic systems consisting of three layers: two surface ones, which had the same degree of order, and one inner layer, that was entirely disordered. As was demonstrated,<sup>5</sup> within the framework of the model, it is easy to get the simple expression for the calculation of  $l^{\text{SL}}$  to the approximation of its homogeneous order of degree

$$l^{\text{SL}} = 0.5 \left[ l^{\text{vol}} - \frac{A_{\parallel,\perp}^{\text{SL}} D_{\perp}^{\text{vol}} - D_{\parallel}^{\text{vol}}}{a^{\text{IL}}(A_{\parallel,\perp}^{\text{SL}} - 1)} \right] \quad (2)$$

where  $A^{\text{SL}}$  is the dichroism of the surface layer, calculated according to the data of IR spectroscopy

copy ATR;  $D^{\text{vol}}$  is the optical density of the sample in the IR spectra of  $T(\nu)$ ;  $a^{\text{IL}}$  is the Bouguer absorption factor of the inner (nonoriented) layer;  $l^{\text{vol}}$  is the thickness of the sample; and the indexes  $\parallel$  and  $\perp$  designate the orientation of the vector of the light wave  $\mathbf{E}$  in regard to the axis of the sample (e.g., axis of the film stretching).

After some simple changes are made to eq. (2) and supposition, as is natural, in the case of partial axial orientation of rotary symmetrical type

$$a^{\text{IL}} = (a_{\parallel}^{\text{vol}} + 2a_{\perp}^{\text{vol}})/3$$

or

$$a_{\perp}^{\text{vol}}/a^{\text{IL}} = 3/(A_{\parallel,\perp}^{\text{vol}} + 2),$$

we have

$$l^{\text{SL}} = 0.5l^{\text{vol}} \left( \frac{A_{\parallel,\perp}^{\text{vol}} - 1}{A_{\parallel,\perp}^{\text{vol}} + 2} \right) \left( \frac{A_{\parallel,\perp}^{\text{SL}} + 2}{A_{\parallel,\perp}^{\text{SL}} - 1} \right) \quad (3)$$

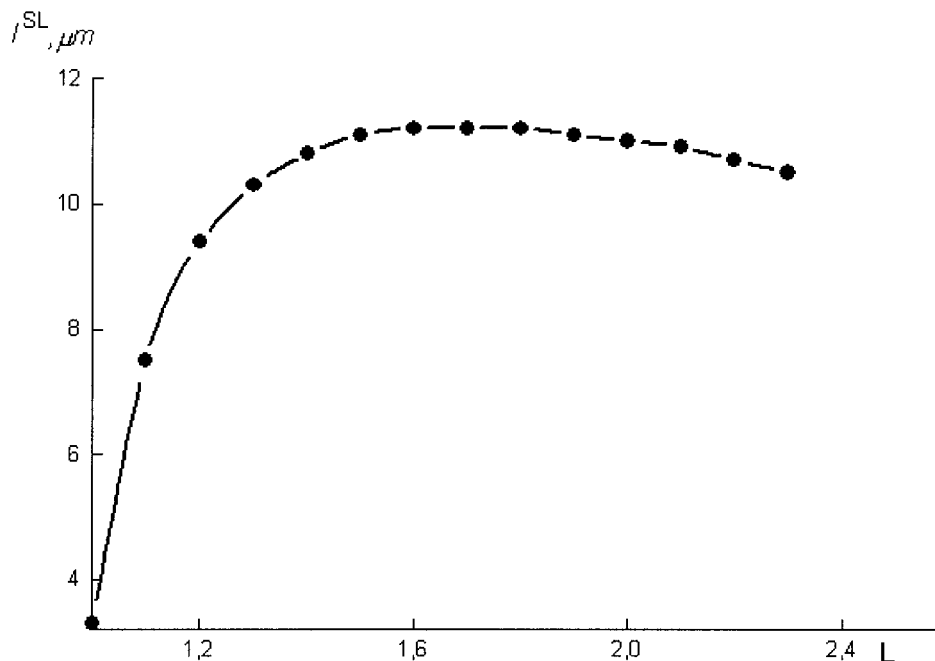
where  $a^{\text{vol}}$  and  $A^{\text{vol}}$  are the Bouguer absorption factor and dichroism of the sample in the IR spectra of  $T(\nu)$ , respectively.

An important peculiarity of eq. (3) is its invariance in regard to the constraint equation  $S(A)$ , with  $\beta = 0$  and  $\beta = 90^\circ$ . Indeed, when eq. (3) is solved and the data of eq. (1) are taken into account, in the first and the second case, we have

$$l^{\text{SL}}(L) = 0.51^{\text{vol}}(L) \cdot S^{\text{vol}}(L)/S^{\text{SL}}(L), \quad (4)$$

where  $S^{\text{vol}}$  and  $S^{\text{SL}}$  are the parameters of the degree of order of macromolecules in the sample and in its surface layer calculated according to eq. (1) on the basis of experimental data.

Equation (4) has a clear physical meaning that coincides with the definition of the "surface layer" concept, following from the anisotropic medium, which consists of three layers. In this connection, we would like to stress that within the framework of the taken model, the surface layer is regarded as a homogenous oriented surface layer of the film with the following parameters:  $S^{\text{SL}} > S^{\text{vol}} \geq 0$  and  $d \leq l^{\text{SL}} \leq 0.5l^{\text{vol}}$ , where  $d$  is the minimum thickness of the surface layer determined by the depth of the light penetration into the sample under conditions of ATR. It means the lower  $d$  is, the more accurate the calculations of quantity  $l^{\text{SL}}$  according to eq. (4) are. In the area of the intensive IR bands of PTFE with  $\nu_{\text{max}} = 1160$  and  $1215 \text{ cm}^{-1}$ , which were used to determine the level of



**Figure 2** Influence of uniaxially oriented deformation on the thickness of the surface (homogeneously oriented) layer of PTFE films with  $l = 50 \mu\text{m}$  [the calculation was made according to eq. (4)].

ordering ( $S^{SL}$ ), the depth of light penetration ( $d$ ), according to this assessment that was accepted in such cases did not exceed, apparently, 1–2  $\mu\text{m}$ .

The dependence  $l^{SL}(L)$ , found for uniaxially oriented PTFE films with  $l_0 = 50 \mu\text{m}$ , is shown in Figure 2. The calculations of the quantity  $l^{SL}$  according to eq. (4) were made with correlations for  $S^{vol}$  and  $S^{SL}$ . The value of  $l^{vol}$  was calculated in the generally accepted way.

An analysis of the graph confirmed that the process of stretching had three steps. The first of them ( $L = 1.0$ – $1.5$ ) consisted of consecutive orientation of the macromolecules, which extended to the very depth and led to the unexpected increase in  $l^{SL}$  ( $l^{SL} = 3.9$ – $12.1 \mu\text{m}$ ). The second step ( $L = 1.5$ – $2.0$ ) was characterized by considerable orientation effects localized within an ordered layer of constant thickness, which resulted in quantity  $l^{SL}$  independence of  $L$  ( $l^{SL}_{max} = 12.2 \mu\text{m}$ ). The third step ( $L = 2.0$ – $2.5$ ) consisted of the gradual destruction of the surface layer, as in this area of stretching the quantity  $l^{SL}$  was diminished to some extent ( $l^{SL}_{min} = 11.3 \mu\text{m}$ ). Thus, the received data corroborated (and on the quantitative level) that the mechanism of the deformation of crystalline polymers, consisting of three steps,

is mainly determined by changes proceeding in the surface layer of the samples.<sup>9</sup>

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