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Order distribution function of a linear polymerized photopolymer orienting a nematic liquid crystal

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The distribution function of photogenerated cross-links in thin films of poly(vinyl cinnamate) or poly(vinyl 4-methoxycinnamate) is analyzed in terms of the irradiation time of these films with linearly polarized UV light. An exponential decay of the induced birefringence is connected to the complex effects of UV light on polymers. A scalar order parameter of cross-links is inferred from the distribution function, and is compared to the measured birefringence. The irradiation time influences also the order parameter of thin layers of nematic liquid crystals which are aligned by the polymers, assuming a finite anchoring. The UV exposure time dependence of the nematic liquid crystal scalar order parameter is also given. [S1063-651X(98)13004-0]

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I. INTRODUCTION

It is well known that the orientation of a nematic liquid crystal director is indifferent in an unstrained infinite volume. Its orientation can be induced by external fields or by anisotropic surface anchoring interactions, and, frequently, by a competition of them. Most of today's liquid crystal displays use glasses coated with thermal polymerized thin films of buffed polymer. The buffing process assumes external mechanical stress exerted on the polymer layer. This process is hard to control and, usually, is done on the whole glass plate.

Quite recently [1–3] an interesting aligning method was used, namely, polymerizing photopolymers with linearly polarized light. Apart from being ''clean,'' this method permits different orientations on the same glass substrate, something impossible with the buffing method.

Several polymers were tried, among them, polyvinyl 4-methoxy cinnamate (PVMC) [1] and polyvinyl cinnamate (PVCi) [4]. Both polymers exhibit a depletion of cinnamic acid side chain molecules along the direction of polarization, increasing in the mean time the number of photoinduced $(2+2)$ cycloaddition along a direction perpendicular to the polarization direction. Hence, preirradiated isotropically oriented molecules change into an anisotropic distribution of photopolymerized side chains, which can induce a definite orientation of liquid crystal molecules by means of their in line aromatic rings.

In this paper, we will discuss the distribution function of these side chains, and compare the UV irradiation time dependence of this function (as well as of the optical birefringence it induces) to reported results [4]. We consider that the birefringence is due both to an increase of photopolymerized side chains (along a direction perpendicular to the polarization of light) and also to a depletion of parallel side chains, which happens to be along the polarization direction of the UV light. We assume the kinetics to be of first order, and imagine a differential equation which also takes into account the fact that, in time, there are damaging effects of UV light irradiation and there is also an increasing difficulty of pairing non polymerized side chains. These facts enter the equation as an exponentially decaying factor $e^{-t/\tau}$.

II. PHOTOPOLYMER ORDER PARAMETER

Let us consider the following reference system $Oxyz$, with the Oz axis perpendicular to the polymer layer, and the Oy axis along the electric field direction of the polarized UV light, as shown in Fig. 1. We also consider the preirradiated pair of side chains making the angles θ and φ, with φ very small (i.e., we assume the polymer molecules are in the plane of the layer).

The quantum yield rate should be proportional to $(\mathbf{e}\cdot\mathbf{a})^2$, i.e., to $\cos^2\varphi\,\sin^2\theta$, where **e** and **a** are unit vectors describing the direction of the polarization, **e**, and the orientation of a pair, **a** [5]. The number of photosensitive pairs

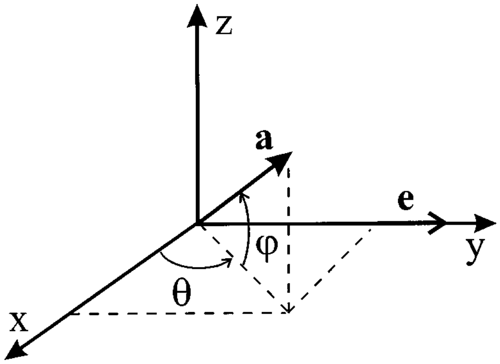

FIG. 1. The reference frame. The photopolymer film lies in the xy plane. The direction of the electric component **e** of the polarized wave is along the y axis.

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decreases in time along the Oy axis, and there is an increase of crossed-linked side chains along the Ox axis.

Let $N(\varphi,\theta,t)$ be the number of pairs capable of undergoing photosensitive polymerization. The decrease of $N(\varphi,\theta,t)$, namely, $-dN(\varphi,\theta,t)$, should be proportional to the elementary time interval of irradiation dt, the quantum yield $\cos^2\varphi\sin^2\theta$, the number of pairs at instant t, $N(\varphi,\theta,t)$, and the exponential decay $e^{-t/\tau}$; that is,

$$-dN(\varphi,\theta,t)=\alpha(\cos^2\varphi)(\sin^2\theta)N(\varphi,\theta,t)e^{-t/\tau}dt, \tag{2.1}$$

where α stands for a suitable proportionality factor. The initial situation is $N(\varphi,\theta,t)=N_0(\varphi)$, assuming an isotropic distribution of pairs with respect to θ. We also consider that φ is practically zero, and solve a differential equation for $y(\theta,t)=N(0,\theta,t)/N_0(0)$,

$$y'(\theta,t)+\alpha y(\theta,t)e^{-t/\tau}\sin^2\theta=0, \tag{2.2}$$

with the initial condition

$$y(\theta,0)=1. \tag{2.3}$$

The solution is

$$y(\theta,t)=\exp[\alpha(\sin^2\theta)\tau(e^{-t/\tau}-1)]=e^{-A(t)\sin^2\theta}, \tag{2.4}$$

where

$$A(t)=\alpha\tau(1-e^{-t/\tau}).$$

For $t\geqslant 0$, it results that $A\geqslant 0$. One also sees that $A(0)=0$ and $A(\infty)=\alpha\tau$.

For each angle θ, the decrease starts from 1 down to $e^{-\alpha\tau\sin^2\theta}$. The largest *decrease* being for $\theta=\pi/2$, namely, $1-e^{-\alpha\tau}$, and the least *decrease* is for $\theta=0$, namely 0.

A strong decrease of pairs around $\theta=\pi/2$ results in an equivalent increase of side chains around $\theta=0$, because the cycloaddition changes the side chain long axis with $\pi/2$. In time there will be a deviation from the initial isotropic background of polymer molecules and side chains. This increasing anisotropy, which results in an increasing birefringence of the polymer layer, is due to both the increase at $\theta=0$ and the decrease at $\theta=\pi/2$.

Let us consider a distribution function (not normalized) which takes into account these two facts:

$$\begin{aligned} g(\theta,t)&=e^{-A\sin^2\theta}+(1-e^{-A\sin^2[\theta+(\pi/2)]})\\ &=1+e^{-A\sin^2\theta}-e^{-A\cos^2\theta}. \end{aligned} \tag{2.5}$$

A plot of the distribution function $g(\theta,t)$ vs the UV irradiation time t is presented in Fig. 2. For any instant t (the total irradiation time), $g(\theta,t)$ gives the distribution of angles θ between the long axes of side chains and the axis Ox (perpendicular to the polarization direction of the light). Let

$$g(\theta,t)=g(\cos\theta,t)=g(x,t).$$

Any "reasonable" function $f(x)$ on the interval $-1\leqslant x\leqslant 1$ (i.e., $0\leqslant\theta\leqslant\pi$) can be expanded in a series of Legendre polynomials

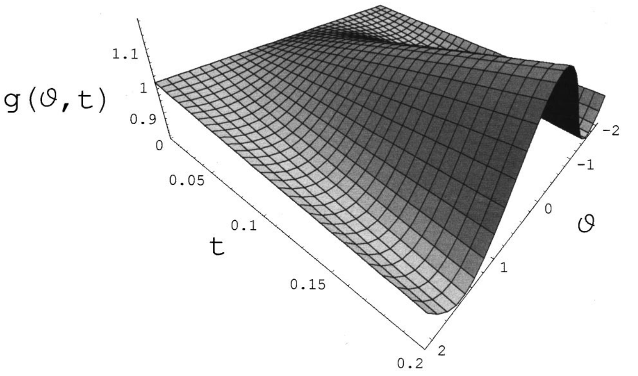

FIG. 2. A 3D plot of the distribution function $g(\theta,t)$. t is the total irradiation time, and θ is measured relative to a perpendicular to the polarization direction of UV light. The "time" t, actually, is proportional to the total irradiation dose, and it is expressed in arbitrary units in this figure and in the following ones.

$$f(x)=\sum_{n=0}^{\infty}\frac{2n+1}{2}\overline{P_n}P_n(x), \tag{2.6}$$

where

$$\overline{P_m}=\int_{-1}^{1}P_m(x)f(x)dx. \tag{2.7}$$

In our case $f(x)=f(-x)$, an even function, and we can restrict ourselves to even order polynomials

$$f(x)=\sum_{n=0}^{\infty}(4n+1)\overline{P}_{2n}P_{2n}(x), \tag{2.8}$$

where

$$\overline{P}_{2n}=\int_{0}^{1}P_{2n}(x)f(x)dx. \tag{2.9}$$

Let us normalize the function $g(\theta,t)$ in such a way that

$$\int_0^{\pi}g(\theta,t)d\theta=1. \tag{2.10}$$

It is easy to see that

$$g(\theta,t)=\frac{1}{\pi}(1+e^{-A\sin^2\theta}-e^{-A\cos^2\theta}) \tag{2.11}$$

has this property for any time t.

Expanding $g(\theta,t)$ in series of Legendre polynomials and taking only the first two terms in the series, it results that

$$g(\theta,t)=\overline{P}_0(t)+\tfrac{5}{2}\overline{P}_2(t)(3x^2-1). \tag{2.12}$$

Usually $\overline{P}_2(t)\equiv S(t)$ is the scalar order parameter of the distribution, so

$$g(\theta,t)=\overline{P}_0(t)+\tfrac{5}{2}S(t)(3\cos^2\theta-1). \tag{2.13}$$

One can calculate both $\overline{P}_0(t)$ and $S(t)$:

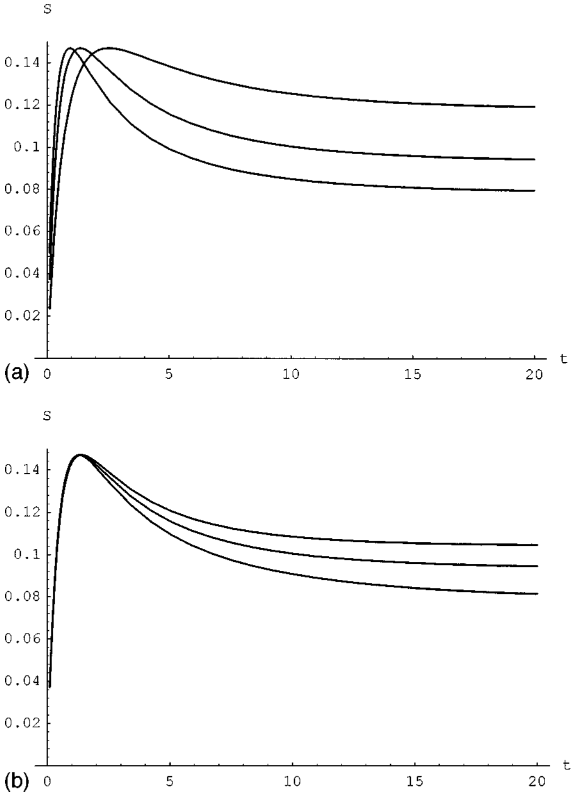

FIG. 3. (a) The scalar order parameter $S(t)$ traced at fixed τ for three different values of α. The maximum moves toward shorter t when α increases. (b) The scalar order parameter $S(t)$ traced at constant α for three different values of τ. The asymptotic value of $S(t)$ decreases when τ increases.

$$\overline{P}_0=\frac{1}{\pi}+\frac{1}{2\sqrt{\pi A(t)}}\left(\frac{i\ \mathrm{erf}[-i\sqrt{A(t)}]}{e^{A(t)}}-\mathrm{erf}[\sqrt{A(t)}]\right) \tag{2.14}$$

and

$$S[A(t)]=\frac{1}{2\pi A(t)}\left\{3(1+e^{-A(t)})+\frac{1}{2}\left(\frac{\pi}{A(t)}\right)^{1/2}\times\{[-3+2A(t)]\mathrm{erf}\left(\sqrt{A(t)}\right)-[3+2A(t)]e^{-A(t)}i\ \mathrm{erf}[-i\sqrt{A(t)}]\}\right\}, \tag{2.15}$$

where i and erf(x) stand for $\sqrt{-1}$ and $\int_0^x e^{-t^2}dt$, respectively. Although the imaginary number i enters the expression of $S(t)$, the order parameter is a real quantity.

In Figs. 3(a) and 3(b), plots of the scalar order parameter S as a function of the irradiation time t for certain values of constants α and τ are presented. The three curves of Fig. 3(a) are traced at fixed τ: the maximum of $S(t)$ moves toward shorter t when α increases. The three curves of Fig. 3(b) are traced at constant α: the asymptotic value of $S(t)$ decreases when τ increases.

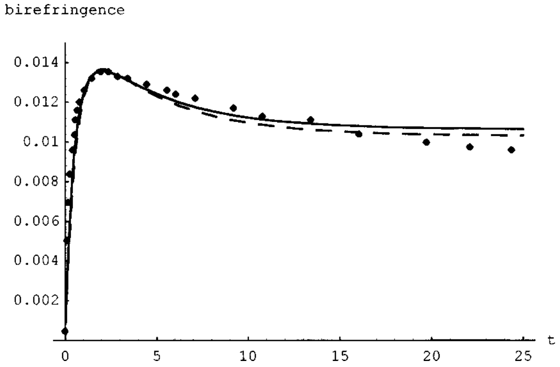

FIG. 4. Experimental data presented in Ref. [4] (dots) fitted by using Eq. (16), $\Delta n(t)$ (full line), and Eq. (15), $S(t)$ (dashed line).

III. COMPARISON WITH EXPERIMENTS

This expression of $S(t)$ allows us to fit the experimental values of birefringence given in Ref. [4]. For this aim, we used De Jeu's expression for Δn [6], where $\Delta n=n_{\parallel}-n_{\perp}$,

$$\Delta n\propto S\rho^{1/2}, \tag{3.1}$$

and where $\rho^{1/2}$ is proportional to $\overline{P}_0^{1/2}$.

We also tried to fit the birefringence with the function $S(t)$ alone. The graphs of both fits are given in Fig. 4. It can be seen that the difference is very small and, moreover, it appears only at large values of time. Of course, the proportionality constants are different. We can also see that neither $S\rho^{1/2}$ nor S alone can fit well the experimental points at large t. We presume this to be due to the fact that several independent phenomena, like UV degradation or a smaller likelihood of getting pairs after a longer irradiation time, are described by only one parameter τ. It would be better to consider an average over a certain interval for τ, using a time correlation function. Still, for both expressions, the parameters α and τ are the same, and they describe very well the extremely steep rising part of the birefringence as well as its maximum.

IV. LC ORDER PARAMETER

We are interested in PVMC and PVCi films mainly because they are used in inducing homogeneous planar alignment of liquid crystals (LC's). If we assume that the anchoring is infinite, then the order parameter of the very first layer of liquid crystal molecules in contact with the polymer film will be the same as the order parameter of the polymer film itself. Yet we must assume the anchoring to be finite. In the following we briefly discuss the order parameter of a very thin film of a nematic liquid crystal in contact with a photopolymerized film of PVMC or PVCi. This layer could be considered as the ''adsorbed'' part of the nematic on the polymer surface.

In Fig. 5, the angles which define the long axes of liquid crystal molecules and of side chains of polymer molecules are shown. We consider that only the cross-linked side chains induce the alignment of liquid crystal molecules. In the planar case in which $\varphi_1\approx\varphi_2\approx 0$, the distribution function of polymer side chains is the one already obtained, namely, $g(\theta_2,t)$.

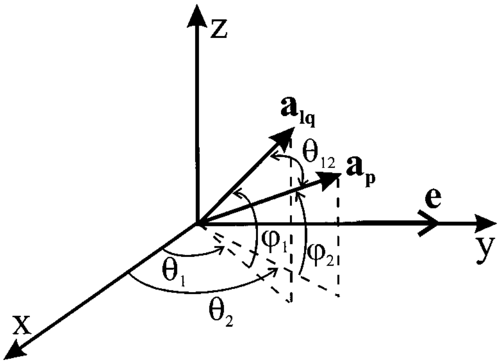

FIG. 5. The angles θ_1, θ_2, φ_1, and φ_2 relative to the plane xy of the polymer film and the direction **e** of the polarization. $\mathbf{a}_{lq}$ is the direction of a liquid crystal molecule long axis, and $\mathbf{a}_p$ is the direction of the polymer side chain. θ_{12} is the angle between a liquid crystal molecule and a polymer side chain.

The distribution function $f(\theta_1)$ of liquid crystal molecules can be obtained by minimizing the total free energy of the system

$$\mathcal{F}=\varepsilon-T\mathbb{S}. \tag{4.1}$$

Here two competing phenomena take place: first, an attraction between polymer side chains and liquid crystal molecules, which gives the energy ε, and second, the contribution of the orientational degrees of freedom of liquid crystal molecules to the entropy of the system. In other words the ''anchoring force'' between a side chain and a liquid crystal molecule is perturbed or attenuated by the thermal motion. The orientational entropy is

$$\mathbb{S}=-k\int d\Omega_1 f(\theta_1) lg[4\pi f(\theta_1)], \tag{4.2}$$

where k stands for the Boltzmann's constant, and 4π is used just for convenience (it merely adds a constant term to the entropy). $d\Omega_1$ is a solid angle element around θ_1 and φ_1. Both ε and $\mathbb{S}$ are referred to a unit volume of the interfacial layer. The interaction energy is

$$\varepsilon=\int d\Omega_2 g(\theta_2,t)\int d^3r\ d\Omega_1 \xi(r,\Omega_1/\Omega_2)V(r,\theta_{12}). \tag{4.3}$$

We assume that the interaction potential between polymer and liquid crystal molecules depends only on the mutual separation r, and orientation θ_{12}. $\xi(r,\Omega_1/\Omega_2)$ is a pair correlation function which, for a given Ω_2 may be considered as the simple product $\xi(r,\Omega_1/\Omega_2)\rightarrow g'(r)f(\theta_1)$, $f(\theta_1)$ being the distribution function of liquid crystal molecules.

Introducing

$$U(\theta_{12})=\int d^3r\ V(r,\theta_{12})g'(r), \tag{4.4}$$

it results that

$$\varepsilon=\int d\Omega_2 g(\theta_2,t)\int d\Omega_1 f(\theta_1)U(\theta_{12}). \tag{4.5}$$

One has to determine the distribution function $f(\theta_1)$ which minimizes the free energy $\mathcal{F}$ with the given constraint

$$\int f(\theta_1)d\Omega_1=1.$$

Using one Lagrange multiplier, a standard procedure gives [7]

$$f(\theta_1)=\frac{e^{(-M\theta_1/kT)}}{\int e^{(-M\theta_1/kT)}d\Omega_1}, \tag{4.6}$$

where

$$M(\theta_1)=\int g(\theta_2)U(\theta_{12})d\Omega_2. \tag{4.7}$$

The distribution function is just the Boltzmann distribution where, in lieu of the energy, we have the average interaction of one liquid crystal molecule around Ω_1 with the distribution of polymers. Let us analyze in more details this average interaction. $U(\theta_{12})$ must be even in θ_{12} and minimum for $\theta_{12}=0$. We can develop $U(\theta_{12})$ in a series of Legendre polynomials

$$U(\theta_{12})=\sum_n U_{2n}P_{2n}(\theta_{12}). \tag{4.8}$$

Disregarding constant terms in the potential and also terms higher than the second order, we can write

$$U(\theta_{12})=-uP_2(\theta_{12}), \tag{4.9}$$

u being a constant, $u>0$.

Then

$$\begin{aligned}\int g(\theta_2)uP_2(\theta_{12})d\Omega_2 \\ =u\int_0^{\pi}\left[\int_0^{2\pi}P_2(\theta_{12})d\varphi_2\right]g(\theta_2)\sin\ \theta_2 d\theta_2,\end{aligned} \tag{4.10}$$

but

$$\begin{aligned}\int_0^{2\pi}P_2(\theta_{12})d\varphi_2={}&2\pi P_2(\theta_1)P_2(\theta_2)\\ &+\tfrac{1}{3}\int_0^{2\pi}P_{21}(\theta_1)P_{21}(\theta_2)\cos(\varphi_1-\varphi_2)d\varphi_2\\ &+\tfrac{1}{12}\int_0^{2\pi}P_{22}(\theta_1)P_{22}(\theta_2)\\ &\times\cos 2(\varphi_1-\varphi_2)d\varphi_2.\end{aligned} \tag{4.11}$$

The last two terms, involving associated Legendre polynomials, cancel out when integrating from 0 to 2π. It follows that

$$M(\theta_1) = -2\pi u \int_0^{\pi} P_2(\theta_1) P_2(\theta_2) g(\theta_2) \sin\,\theta_2 d\theta_2$$
$$= -2\pi u S_{\mathrm{pol}} P_2(\theta_1), \tag{4.12}$$

where S_{pol} stands for the order parameter of the polymer distribution already discussed.

Hence the liquid crystal distribution function is

$$f(\theta_1) = \frac{e^{(2\pi u(S_{\mathrm{pol}}/kT)P_2(\theta_1))}}{\int e^{(2\pi u(S_{\mathrm{pol}}/kT)P_2(\theta_1))} d\Omega_1}$$
$$= \frac{e^{(\pi u(S_{\mathrm{pol}}/kT)(3\cos^2\,\theta_1 - 1))}}{2\pi \int e^{(\pi u(S_{\mathrm{pol}}/kT)(3\cos^2\,\theta_1 - 1))} \sin\,\theta_1 d\theta_1}$$
$$= \frac{e^{(m\,\cos^2\,\theta_1)}}{2\pi \int_0^{\pi} e^{(m\,\cos^2\,\theta_1)} \sin\,\theta_1 d\theta_1} = \frac{e^{mx^2}}{2\pi \int_{-1}^{1} e^{mx^2} dx}$$
$$= \frac{e^{mx^2}}{z(m)}, \tag{4.13}$$

where

$$m = \frac{3\pi u}{kT} S_{\mathrm{pol}} \tag{4.14}$$

and

$$z(m) = 2\pi \int_{-1}^{1} e^{mx^2} dx. \tag{4.15}$$

The scalar order parameter of the liquid crystal distribution S_{lq} is

$$S_{\mathrm{lq}} = \frac{2\pi}{z(m)} \int_{-1}^{1} e^{mx^2} P_2(x) dx = \frac{\pi}{z(m)} \int_{-1}^{1} e^{mx^2} (3x^2 - 1) dx$$
$$= -\frac{1}{2} + \frac{3\pi}{z(m)} \int_{-1}^{1} e^{mx^2} x^2 dx. \tag{4.16}$$

Of course, S_{lq} depends on the irradiation time because both $m = m(t)$ and $z(m) = z[m(t)]$. In Fig. 6, we present a plot of S_{lq} with the UV exposure time, using the same values of constants α and τ as in the fit shown in Fig. 4.

V. DISCUSSION AND CONCLUSION

An interesting question is why the nematic alignment experimentally observed on photopolymer films is generally uniform [1], and with a quite high associated anchoring energy [8] if the induced order S_{lq} is so small. A possible answer could be that it is enough to have an even small anisotropy induced by the surface in the nematic to eliminate the degeneracy of the azimuthal anchoring direction. Then, even if the nematic layer close to the surface is not well ordered, the intrinsic nematic order in the bulk will prevail, giving the appearance of a macroscopic uniform surface alignment. Nevertheless, this physical situation implies that strong order parameter variations are expected close to this kind of substrate on a nematic layer of thickness comparable with the nematic-isotropic coherence length [9]. A consequence should be that, for usual nematics, oblique anchoring should be preferred with respect to the planar one, due to the effects of local ordoelectric polarization [10].

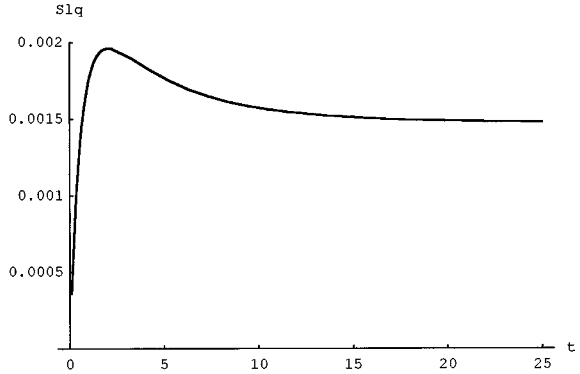

FIG. 6. The plot of the scalar order parameter of the liquid crystal distribution S_{lq} in contact with the polymer. The ''time'' t is always proportional to the total irradiation dose.

In conclusion, we have analyzed the influence of the UV irradiation on photopolymers such as PVMC and PVCi, taking into account, as an important parameter, the time used in the irradiation process. The experimentally observed very steep increase of the optical birefringence is explained well by the distribution function $g(\theta,t)$ which takes into account the ''degradation'' due to the UV damages as well as other factors. If we do not consider this effect, eventually, when the irradiation time is very long, all the polymer molecules will undergo the cross-linking reaction, and we will have again an isotropic distribution, even if this is rotated by $\pi/2$ compared to the initial one. Introducing the exponential decay $e^{-t/\tau}$, we can explain the asymptotical decrease of the birefringence to a value different from zero.

In order to use the photopolymers for aligning nematic liquid crystals, we discussed the distribution function of liquid crystal molecules in contact with the polymer film by assuming that the anchoring between the polymer film and the liquid crystal is finite. The order parameter of this liquid crystal distribution function clearly depends on the order parameter of the polymer distribution and, through this latter, on the duration of the irradiation. It is of practical importance to know the value of the irradiation time which will give the largest order parameter of the liquid crystal.

ACKNOWLEDGMENTS

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