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On the Motion of Polymer Molecules Studied by the Electrochromism Method

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ABSTRACT

It is shown that electrochromism, i.e., changes in spectral characteristics of dye solutions in an electric field, may be used to investigate the molecular mobility of polymers. The method is compared with others (NMR, ESR, and luminescence).

Changes in spectral characteristics of dye solutions in an electric field have been given the name electrochromism. Papers on theoretical and experimental investigations of electrochromism have recently been published [1-3]. The changes in absorption spectra appear to be accounted for by the medium, its viscosity, polarity, etc., as well as by the properties of dye molecules. This feature, first discovered in 1968 [4, 5], permitted the use of electrochromism in applying the probe technique to the study of polymer molecules. This paper deals in detail with certain specific features of the electrochromism method, and comparison with other methods is made. Experimental results obtained by the authors, and theoretical data reported by Liptay, Labhart, Czecalla, and by the authors [5], are used in the discussion.

A short review of the other methods for the study of polymers is given.

The method of measuring dielectric losses [6] makes use of the phase shift between the external alternating electric field and the polarization field of polar molecules in samples (electronic probe) or of those in the polymer as such (radical probe). The polymer is usually considered as a continuous medium; however, interpretation is possible at the molecular level as well. The motion of probes in samples is accounted for by the frequencies and amplitudes of the surrounding molecular chain vibrations. Consequently, the relaxation times for molecular (segments, side groups) motion and the corresponding activation energies can be found from the frequency and temperature dependencies of dielectric losses.

The NMR method is extensively developed both in its experimental and theoretical aspects [7]. Research on molecular motion makes use of this method preferable. It is highly selective with respect to nuclei in certain molecular groups exhibiting different chemical shifts. NMR studies of molecular motion are based on changes in relaxation times of nuclear magnetic momenta as a result of their interaction with the surrounding polymer molecules. The NMR technique records only molecular motion of a frequency higher than or commensurable with the width of NMR lines. This makes NMR use impossible in the low-frequency ranges.

The ESR technique is used for recording the electron spin resonance of molecules probed containing unpaired electrons [8, 9]. The relevant results reported are relatively scarce, possibly due to the novelty of the method. Its disadvantage is that it can be used only within the high-frequency range of the order 10^9 Hz.

Luminescence methods [10] involve measurements of depolarization and of the times of luminescence quenching in probes, and they permit the use of low probe concentrations. However, unambiguous treatment of the results obtained is not always possible, as in certain cases information on electron energy transformations is insufficient.

The proposed electrochromism method is based on observation of the rotational motion of probes in polymers [4, 5, 11]. A strong alternating electric field is applied to polar molecules of dyes dissolved in polymer matrices, thus creating a time-dependent anisotropy of molecular distribution over the static and transition dipole orientations. The orientation polarization and the accompanying Stark effects are determined from the field-induced changes in absorption spectra. Molecular motion of several to several hundreds cycles/second can be investigated by this method. Deorientation of preoriented samples involves, as discussed below, very prolonged relaxation processes taking days, months, and even years.

Thus electrochromism supplements other methods for investigation of molecular motion in the ranges of low and very low frequencies. Contrary to dielectric methods that can also be used in certain cases for the observation of slow relaxation [12], electrochromism displays a very high sensitivity. Addition of 10^{-5} mole/l of a dye is sufficient for recording of spectra. The high selectivity of electrochromism is based on the possibility of choosing a probe whose spectrum is not superposed by that of the polymer. A great disadvantage of the electrochromism method is the impossibility of applying it to conducting and nontransparent media.

I. DESCRIPTION OF THE ELECTROCHROMISM PHENOMENON

Application of an electric field to a liquid solution containing polar molecules induces changes in the molecular absorption spectra. This is due to several causes, mainly to orientational polarization and the Stark effects. The collective electrooptical phenomena observed in solutions in the presence of a field was named electrochromism [13, 14]. Consider the development of ideas relative to electrochromism, beginning with optical methods for the observation of orientational polarization and assuming the molecular energy levels are unpurturbed by the external electric field. Allowance will be made for the Stark effects.

The first theoretical and experimental investigation of electrochromism was conducted by Kühn, Dürkop, and Martin [15]. Solutions of polar molecules in nonpolar liquids were used. Assuming that the shape of the absorption band of a molecule can be calculated in terms of an oscillator model with a certain orientation of its axis relative to that of the dipole, it was suggested that in the presence of an electric field the optical density of an originally isotropic solution appears to be different for two directions of orientation due to the occurrence of orientational polarization. Two directions of the light beam relative to the electric field strength vector are $\bar{e} \perp \bar{F}$ and $\bar{e} \parallel \bar{F}$, where $\bar{e}$ is the unit vector in the direction of the light wave electric vector and $\bar{F}$ is the field strength. They are essential for further discussion of this effect, called the Kühn effect. The changes in light absorption in a field are such that the optical density difference for the two cases will be

$$\Delta D_{\parallel} = -2\Delta D_{\perp} \tag{1}$$

For a general case, when the angle between $\bar{e}$ and $\bar{F}$ is θ, we obtain

$$\Delta D_{\theta} = \Delta D_{\parallel} \cos^2 \theta + \Delta D_{\perp} \sin^2 \theta \tag{2}$$

Denoting by γ the angle between the oscillator axis and the orientation of dipole momentum μ_g [15], we have

$$\Delta D_{\perp} = \frac{1}{15}\left(\frac{\bar{\mu}_g \bar{F}}{kT}\right)^2 \left(1 - 3\cos^2\gamma\right) D \qquad (3)$$

or, allowing for Eqs. (1) and (2)

$$\Delta D_{\theta} = \frac{1}{15} D\left(\frac{\bar{\mu}_g \bar{F}}{kT}\right)^2 \left(1 - 3\cos^2\gamma\right)\left(1 - 3\cos^2\theta\right) \qquad (4)$$

It will be seen from Eq. (4) that at $\theta = 54° 44'$ for molecules incapable of polarization in the electric field and for molecules with $\gamma = 54° 44'$ the Rühu effect is not observed. The factor $(\bar{\mu}\bar{F}/kT)^2$ was introduced as a result of postulating a Boltzmann distribution of molecules in the field over dipole orientations.

An unalloyed Kühn effect can be observed only for molecules incapable of polarization with a dipole moment independent of excitation. In all other cases the Kühn effect is accompanied by a shift of the absorption band due to shifts of energy levels and to a change in the polarizability of molecules in the ground, g, and excited, e, states under action of the electric field [14].

For the ground state

$$E_g^F = E_g - \bar{\mu}_g \bar{F} - (\alpha_g \bar{F}^2/2)$$

where α is the molecular polarizability. From a similar equation for the excited state, we find that the frequency of transition between levels g and e in the field is

$$\nu^F = \frac{E_e - E_g}{h} - \frac{\bar{\mu}_e - \bar{\mu}_g}{h}\bar{F} - \frac{\alpha_e - \alpha_g}{2h}\bar{F}^2 \qquad (5)$$

where the first term corresponds to the transition frequency in the absence of the field, and the two others to the shift of the band in the electric field $\bar{F}$. The latter will be denoted hereafter as $\Delta\nu$.

Following Liptay and Czecalla [16] and a review [14], let the probability of transition from g to e be

$$\pi_0(\nu) = A\,|\bar{e}\bar{m}|^2 f(\nu) \qquad (6)$$

where $\bar{m}$ is the unit vector in the direction of the transition moment,

$f(\nu)$ denotes the function of the absorption band shape, and A is a constant.

Taking the shift of levels as small, we may write

$$\pi^F(\nu) = \pi^0(\nu) - \frac{\partial \pi^0(\nu)}{\partial \nu} \Delta\nu + \frac{1}{2} \frac{\partial^2 \pi^0(\nu)}{\partial \nu^2} \Delta\nu^2 + \ldots$$

Substituting the value $\Delta\nu$ into this equation, we obtain

$$\pi^F = \pi^0 - \frac{\partial \pi^0}{\partial \nu} \frac{1}{h} [(\bar{\mu}_e - \bar{\mu}_g)\bar{F} + \frac{\Delta\alpha}{2} \bar{F}^2] +$$

$$\frac{\partial^2 \pi^0}{\partial \nu^2} \frac{1}{h^2} [(\bar{\mu}_e - \bar{\mu}_g)\bar{F} + \frac{\Delta\alpha}{2} F^2]^2 + \ldots \tag{7}$$

Equation (7) represents the absorption of light by one molecule in the electric field. Changes of transition moments in the field [17] are not allowed for.

Further treatment consists in calculation of the optical density for cases $\bar{e} \perp \bar{F}$ and $\bar{e} \parallel \bar{F}$. This requires calculation of the molecular ensemble absorption in the field, allowing for the distribution of molecules over the directions of dipole (and transition momenta). For a general case the distribution function is

$$F(\alpha) = 1 + a_1\bar{F} \cos \alpha + \frac{1}{3} a_2\bar{F}^2(3 \cos^2 \alpha - 1) + \ldots \tag{8}$$

where α is the angle between the dipole moment $\bar{\mu}_g$ and the field $\bar{F}$. However, experiment shows that the Boltzmann distribution is valid for molecular solutions in non polar solvents, where $a_1 = \mu/kT$ and

$$a^2 = \frac{1}{2} \left(\frac{\mu}{kT}\right)^2$$

In this case

$$D^F = B \int \pi^0(\nu, \gamma, \cos \alpha) f(\alpha) d\Omega \tag{9}$$

On integration of Eq. (9), all terms linear in the field become zero due to the odd function cos α, while terms to a power higher than $\bar{F}^2$ are small and may be disregarded. Optical density $D(\nu)$, determined by spectrophotometry, is introduced for the molecular ensemble instead of the function for the absorption of one molecule f(ν). The first and second derivatives are calculated from absorption spectra, substituting, according to Liptay, $\partial D/\partial \nu_0$ for $\nu(\partial D/\nu)/\partial \nu$ where ν_0 is the absorption band parameter.

Integration allowing for Eqs. (1) and (2) yields Eq. (10) for the electrochromism of molecules exhibiting absorption bands represented by one transition moment.

$$\Delta D_\theta = \frac{1}{15} D \left(\frac{\bar{\mu}\bar{F}}{kT} \right)^2 (1 - 3 \cos^2 \gamma)(1 - 3 \cos^2\theta) +$$

$$\frac{1}{5} \frac{\bar{\mu}\bar{F}}{kT} \frac{\bar{\mu}_e - \bar{\mu}_g}{h} \bar{F} \left[1 + \sin\theta + \cos^2\gamma\, (2 - 3 \sin^2\theta) \right] \nu \frac{\partial D/\nu}{\partial \nu} +$$

$$\frac{\Delta\alpha}{2h} \bar{F}^2 f(\theta,\gamma) \nu \frac{\partial D/\nu}{\partial \nu} +$$

$$\frac{\bar{\mu}_e - \bar{\mu}_g}{h} \bar{F}^2 f_2(\theta,\gamma) \nu \frac{\partial^2 D/\nu}{\partial \nu^2} \qquad (10)$$

Equation (10) represents the sum of individual terms, each for one of the electrooptical effects encompassed by the electrochromism dye spectrum.

The first term gives the orientation of unperturbed molecules, i.e., the Kühn effect or the electrical dichroism of solutions. Hereafter it is called the orientational term.

The second term is obtained by multiplication of two terms for linear effects in the field. One is that for orientational polarization and for the turning of dipole molecules in the electric field; the other is for the linear Stark effect, which cannot, in principle, be observed in isotropic media [18]. It is called the mixed term.

The two last terms are not related to orientational polarization and are called molecular. They describe the quadratic Stark effect accounted for by the change of the molecular polarizability with excitation and the linear Stark effect that results in broadening of the absorption band and is proportional to the second derivative of optical density by frequency.

The parameters of excited molecules, i.e., dipole moments, polarizability, and direction of transition momenta, can be obtained from Eq. (10). Most studies on electrochromism carried out by Czecalla, Liptay, Labhart and their co-workers were aimed at such determinations.

The strength of the acting field must be carefully taken into account in determining molecular constants, which is sometimes very difficult. However, the field value to the Lorenz approximation

$$\overline{F} = \frac{\epsilon + 2}{3}\,\overline{F}_{ext}$$

is, as a rule, sufficient for investigation of rotational motion, probes with $\gamma = 0$ being chosen for convenience.

Application of electrochromism to the investigation of the rotational motion of probes in polymers is proposed. Consequently, it would be interesting to find means for distinguishing the effects that depend upon polarization. The technique proposed in Ref. 5 is based on the following.

1. The mixed and orientational effects are not observed in solid media, where motion of molecules is completely hindered, and electrochromism is given only by the molecular terms of Eq. (10).
2. The orientational effect is not observed at $\theta = 54° 44'$. In this case the mixed and Stark effects that are independent of the turning of molecules in the field (molecular terms) contribute to electrochromism.
3. The mixed effect is not observed near the band top where $(\partial D/\nu)/\partial\nu = 0$, and electrochromism is represented by the orientational and molecular terms. The electrochromism spectra were obtained for θ values of 90 and 55° [5]. Making use of the above procedure to define the terms in Eq. (10), it will be taken into account that a change of θ is accompanied with changes in the intensities of all signals in all terms. For instance, the ratio $\Delta D_{\theta=55°}/\Delta D_{\theta=90°}$ in molecular terms is 1.66 for molecules with $\gamma = 0$. The mixed term value changes under the same conditions by the same factor of 1.66, and the orientational term at $\theta = 55°$ is zero, as stated above.

The linear Stark effect can be observed in samples for certain cases of interest for polymer investigation. Indeed, it may be seen from the mixed term that the electric field function is dual: it brings about both the anisotropic distribution of molecules over dipole orientations and the Stark effect which is proportional to the first power of the field strength. Isotropic samples show no linear effect. If anisotropy is created in some other way, the linear effect will be observed. It will be proportional to the first derivative of optical density by frequency, the other terms of expansion of Eq. (10) being zero.

The intensity of an electrochromism signal appears to be proportional to the extent of anisotropy, and the absorption band will either be shifted to the red, if the dipoles are oriented along the field direction, or to the violet for an opposite orientation. With an alternating electric field these orientations will be distinguished by the ratio of the electrochromism signal phase to that of the applied field. Thus it becomes possible to observe not only the overall direction of molecular orientation as it is determined from the dichroism of extended films, but also the dipole orientations along and opposite the field in the case of unsymmetric molecules. This permits use of the linear effect for investigation of polarizational processes of different origin with independent determination of the internal field direction.

It may be seen from the above that electrochromism can be used for observation of the probe rotation. Since $\overline{\mu}_g \overline{F} \ll kT$, the orientation of probes depends upon the motion of the surrounding polymer chain fragments [19], and this is the basis of the proposed method. The freedom of probe motion can be judged from:

1. The shape and intensity of electrochromism spectra. Both depend on contribution from the terms of Eq. (10). With low viscosity solvents, such as benzene and hexane, the mixed and orientational effects are stronger than the molecular effects by an order of magnitude. In solid media, where molecules cannot turn, the electrochromism spectra are represented only by molecular effects that are independent of molecular orientation in a field. The orientational and mixed terms are proportional to the optical density D and the first derivative $\nu(\partial D/\nu)/\partial \nu$, respectively, and the molecular effect to $\nu(\partial D/\nu)/\partial \nu$ and $\nu(\partial^2 D/\nu)/\partial \nu^2$. For this reason the change in contribution from the first two effects must result in considerable and very characteristic changes in electrochromism spectra in media of moderate viscosity.
2. The phase shift between the electric signals of electrochromism and the external alternating field. This method resembles that of dielectric losses and implies that the polymers represent continuous viscous media.
3. Deorientation of molecular probes in preoriented samples. Prolonged deorientation can be followed by decreases in the intensity of electrochromism spectra, accounted for by the linear Stark effect.

Some examples illustrating the application of electrochromism to observation of rotational motion are given in Section III.

II. EXPERIMENTAL. CERTAIN TECHNIQUES OF ELECTROCHROMISM RECORDING AND OF SAMPLE PREPARATION

The instrument for recording electrochromism spectra was described earlier [4, 11]. An alternating electric field of 240 Hz was applied to the samples. The field strength in samples was usually 2 to 5×10^5 V/cm. In certain cases electrochromism could be studied in the range of 20 to 1000 Hz by using a superheterodyne system with an additional low-frequency generator. The instrument consisted of a monochromator scanning the visible spectrum, a vacuum photocell connected with a narrow-band amplifier adjusted to 480 Hz with a band of 0.4 Hz and an amplification coefficient about 10^4, a phase detector, and a recording device with a paper tape. However, the spectra obtained by the point to point method appeared to be more accurate. An incandescent lamp fed from a continuously charged storage battery through an electron current stabilizer was the source of light. A light chopper was used for correction of the receiver and source spectral characteristics and of the monochromator dispersion over the spectrum. Recording of the spectrum in the absence of field and with the light chopper switched on was also necessary for recording. Programming of the instrument aperture was necessary to obtain spectra by the point to point method. This was attained by adjustment of the aperture width for every wavelength in order that the light chopper signal be the same for all points of the spectrum. An electrochromism spectrum obtained under these conditions appears to be corrected for the spectral characteristics of the instrument.

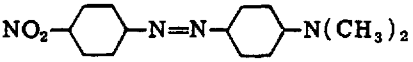
A corrected signal is given by

$$\Delta D = -\frac{m}{2.3}\frac{\Delta T}{\Delta T_{csw}}$$

where ΔD is the change of optical density in the electric field; m is the amplitude of the light beam modulation by the chopper, $m = 3 \times 10^{-3}$; and ΔT and ΔT_{csw} are changes of the electrochromism signal given by the light beam and of that from the chopper, respectively.

Measurements of the phase shifts between the electrochromism signal and the external field were made from the Lissajous figures using an oscillograph. A somewhat modified technique compared to that described in Refs. 20 and 21 was used for sample preparation. The dye and polymer solutions in identical solvents were poured together and the combined solution was dried on glass, first in air and then in vacuum at 50 to 70°C, for complete removal of the solvent. Then a 50-100 μ film of 0.4. optical density coated with mica foils was obtained from the solution by using a heated press. The film was placed between 2 × 2 glass plates, was sealed with an epoxy resin, and the glass plates were covered with transparent conductive coating. The sample was then fixed in a holder and connected with the high-voltage winding of the transformer by means of flexible electrodes. The whole device was placed into a cell filled with petroleum jelly oil acting as heat carrier and was used for investigation of the temperature dependence of electrochromism spectra. The light beam was passed through the cell and directed to a polaroid prism that could be turned around the optical axis. The cell walls were normal to the direction of the incident beam, but the sample was turned in such a way that the angle between the electric field vector normal to the sample plate and the beam direction, with allowance for refraction of all optical media, was 55° for one and 90° for another position of the polaroid.

The following dyes were used as probes:



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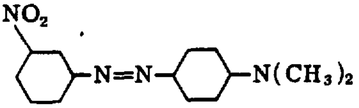

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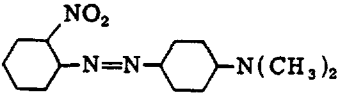

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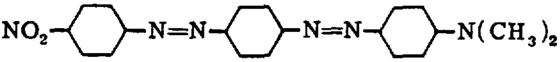

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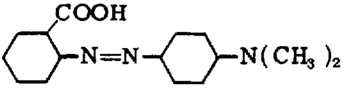

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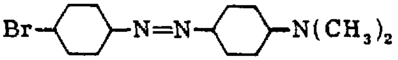

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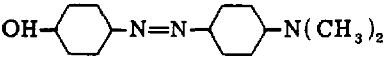

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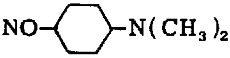


VIII

These dyes were purified by recrystallization in a chromatographic column filled with Al_2O_3. The polymers used are listed in Table 1.

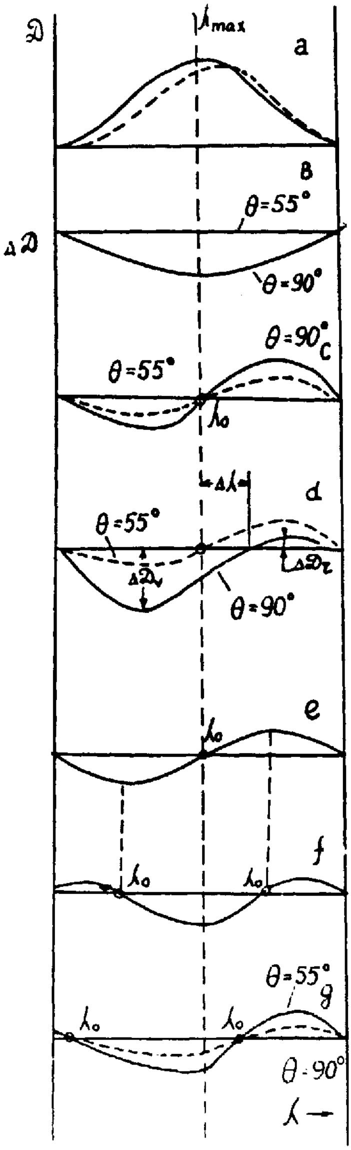
The electrochromism spectrum represents the optical density change in the electric field, recorded over the absorption band contour. Characteristic electrochromism spectra are given in Figs. 1d and g with certain definitions that will be used hereafter.

III

1. Spectral Criteria for Rotational Motion of Probes in Polymers

The electrochromism spectra in nonpolar liquid media, such as benzene and heptane, are represented primarily by the first two terms of Eq. (10). The molecular terms can be disregarded [22] because their contribution comes to only some 10%. The magnitude of the orientational effect can be estimated by coefficient $K = -\Delta D/D$ for probes with $\gamma = 0$ (Fig. 1). The orientational effect adds to the mixed one in the violet (ΔD_ν) and is subtracted from it in the red (ΔD_r). Consequently the shape and intensity of the electrochromism spectrum must change essentially as a function of the ratio of these effects.

It follows from Eq. (10) that the temperature dependence of the orientational and mixed effects is different. Both decrease with increasing temperature, but the decrease is faster for the former. Thus $K, \Delta D_\nu/\Delta D_r$, and $\Delta\lambda$ will at first decrease with rising temperature. With further temperature rise the electrochromism signal becomes weaker and commensurable with the molecular effects. At the limit, at $T \to \infty$, it is due to molecular effects only (Fig. 1g). Similar changes may be expected for solvents in the order of increasing viscosity. The criteria for Dye I motion in various rubbers are shown in Table 1. The $K, D_\nu/D_r$, and $\Delta\lambda$ values change in parallel except for SKN-26 and Nairit. However, the sequence of electrochromism spectra changes could better be followed by using one medium of varying viscosity. Polystyrene (PS) and polymethyl methacrylate (PMM), solid in the glassy state and rubberlike in the elastic state, represent such media. The electrochromism spectra of Dye IV in PS are shown in Fig. 2a. A polaroid turn induces a change in the spectrum intensity only, the ratio of peaks and the position of the two points λ_0 remaining the same. This is evidence that the spectrum is due to molecular effects only (Fig. 1g), the orientational and mixed effects being absent. Heating of the sample



𝔇
λmax
a
B
θ=55°
Δ𝔇
θ=90°
θ=90°
c
θ=55°
λ₀
Δλ
d
θ=55°
Δ𝔇₁
Δ𝔇₂
θ=90°
e
λ₀
f
λ₀
λ₀
θ=55°
g
λ₀
λ₀
θ=90°
λ →

up to about 70°C results in no appreciable changes in the spectrum. At higher temperatures the signal intensity markedly increases, and the shapes of spectra suffer changes (Fig. 2b). At 95°C the spectrum is of a shape shown in Fig. 1d and exhibits considerable deformations with turns of the polaroid, resembling those observed for electrochromism spectra from solutions. Thus rotation of probes occurs for PS in a highly elastic rubberlike state at temperatures higher than that for glass transition.

The mixed and orientational effects and their temperature dependence may be distinguished using the procedures described in Section I. It will be seen from Fig. 3 that decay of the signal that would be expected for solutions is not observed, even at maximum temperatures. The plot shows a strict proportional dependence between the orientational and mixed effects over the whole temperature range (Fig. 4). This dependence is observed also for Dye I dissolved in various rubbers. Thus the proportional dependence between the orientational and mixed effects shows that the shapes of electrochromism spectra are independent of the ratio of their contributions. It may be conceived that the shapes of spectra and the ratio $\Delta D_{\nu}/\Delta D_{r}$ are determined by the relationship between two groups of terms: orientational + mixed and the molecular terms. This suggestion was verified by calculation of all terms of Eq. (10) for several temperatures.

Figure 5 shows the consecutive electrochromism spectra changes for Dye V in a solidifying epoxy resin. The curves obtained for $\theta = 55°$ show the changes of the mixed term and the constant contribution from molecular terms. Contribution from the orientation and molecular terms was recorded for $\theta = 90°$. The electrochromism spectra retained their shape and intensity for the first 45 min. The formation of a cross-linked

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FIG. 1. Contributions from the orientation, mixed, and molecular effects to electrochromism spectra. (For convenience the spectral changes are exaggerated.) (a) Absorption spectrum of a dye in solution. Change of the spectrum in the presence of an electric field is shown by the dotted line. (b) Contribution from the orientational effect for molecules with $\gamma = 55$. (c) Contribution from the mixed effect proportional to $\partial D/\partial \nu$. (d) The sum of (b) and (c) spectra. The values of $\Delta\lambda$, $\Delta D_{\nu}/\Delta D_{r}$, and the coefficient K in Fig. 1b are taken as parameters characteristic of the spectrum shapes and the freedom of probe rotation. (e) Contribution to the molecular effect from the quadratic Stark effect proportional to $\partial D/\partial \nu$. (f) Contribution to the molecular effect from the linear Stark effect proportional to $\partial^2 D/\partial \nu^2$. (g) Contribution from two molecular effects (e) and (f) to the electrochromism spectrum.

TABLE 1. Parameters of Electrochromism Spectra of Dye I

	λ_0				$\Delta D_\nu/\Delta D_r$		K	
Polymer	$\theta = 55°$	$\theta = 90°$	λ_{max}	$\Delta\lambda$	$\theta = 55°$	$\theta = 90°$	(10^{-6})	ϵ^a
Natural rubber NK	462	498	462	36	3.6	0.6	350	2.9
Rubber SKN-26	490	535	490	45	4.4	0.6	40	11
Polyethylene	462	493	462	31	2.0	0.6	240	2.2
Rubber SKS-30	465	509	470	44	5.2	0.6	460	2.8
Rubber SKS-30-1	473	506	470	33	3.6	0.7	190	2.7
Rubber SKMVP-5	469	509	470	40	4.4	0.6	390	3.0
Chloroprene rubber Nairit	498	517	494	19	3.0	1.1	37	5.1
Rubber SKB	465	503	462	38	4.3	0.6	390	2.8

[a] ϵ = the dielectric constant.

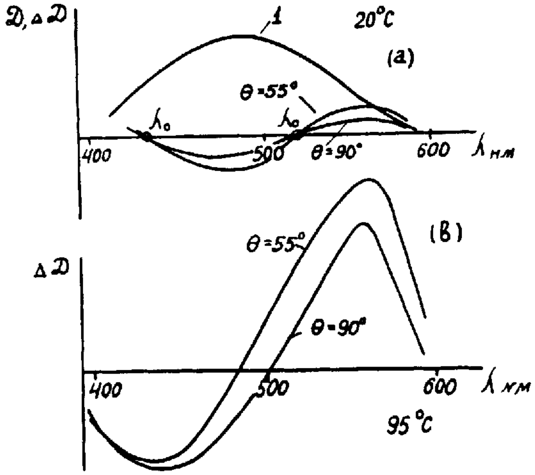

FIG. 2. Electrochromism spectra of Dye IV in polystyrene at temperatures lower (a) and higher (b) than the glass transition point. Curve 1 represents the optical density of the sample on an arbitrary scale.

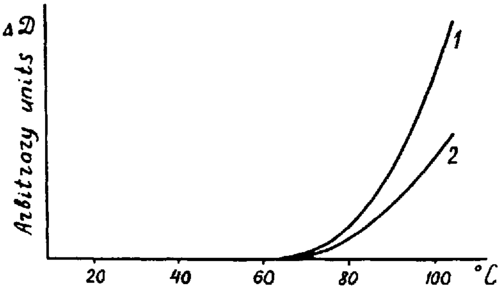

FIG. 3. Temperature dependence of electrochromism spectra for Dye I in polystyrene, measured from the mixed (1) and the orientational (2) terms.

structure hindered the rotation of molecules, the signals from orientational and mixed terms started decaying, so that for a completely solidified sample the spectrum will be given by molecular terms only.

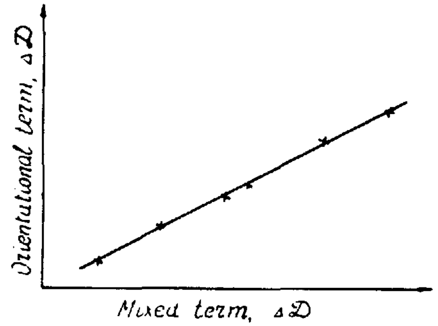

FIG. 4. Orientational versus mixed terms plotted from Fig. 3 in relative units.

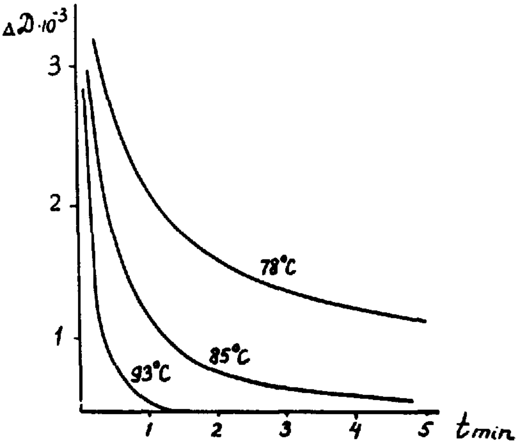

FIG. 5. Electrochromism spectra recorded in the course of epoxy resin solidification for Dye V. Curves: (1) unchanged over the range of 0 to 45 min; (2) in 80 min; (3) in 110 min; and (4) in 350 min.

2. Phase Shifts of the Electrochromism Signals

If polymers are assumed to be viscous continuous media, changes in relaxation times τ of the probe rotation would be expected with heating of PS and PMM to a temperature higher than the glass transition point or with solidification of epoxy resins. According to the Debye theory

$$\sin \delta = \frac{\omega\tau}{(1+\omega^2\tau^2)^{\frac{1}{2}}}$$

where δ is the phase shift angle between the external field strength and the electrochromism signal, τ is the relaxation time, and ω is the angular frequency. It may be seen from the equation that the frequency must be chosen such that $3 > \omega\tau > 0$.

It follows from the considerations given in Section I that the rotational mobility of probes changes to a considerable extent when PS is heated from room temperature to that of the elastic state. This would be expected to induce phase shifts in the transition region. However, they were zero over the entire range of 20 to 110°. On the other hand, phase shifts of the electrochromism signal were observed at a certain stage of solidification (Table 2).

TABLE 2. Shift of the Electrochromism Signal Phase During Solidification of an Epoxy Resin at a 240 Hz External Electric Field

Time from onset of solidification (min)	0	30	60	75	90	105	120	360
Sin δ	0	0	0	0.4	0.5	0.5	0.5	0.5

Evidently PS shows no phase shifts due to certain features of its structure. The assumption of its continuous viscosity is untenable, and the concept of a viscous liquid is not confirmed in experiments with resin, as the limiting value appears to be $\sin \delta = 0.5$ instead of the expected unity. This may explain the simultaneous occurrence of at least two relaxation processes with different τ.

3. Deorientation of Molecules. Probes Studied by the Linear Stark Effect Method.

Very slow relaxation in polymers can be studied by the probe technique by making use of the linear Stark effect. An alternating electric field of 480 Hz, equal to that of the electrochromism signal amplifier band, was applied to dyed rubber samples together with an additional static field of 5×10^5 V/cm. The static field induced anisotropic distribution of molecules along the dipole orientation, thus ensuring conditions for observation of the intensive electrochromism signals linear in the field and proportional to the first derivative by the frequency of the optical density. When the constant field was switched off, the anisotropy gradually disappeared and the electrochromism signal decayed to zero. This effect could be observed only for relaxation times of several seconds or longer with the instrument used, since there must be certainty that all electrical transition processes connected with the switching off were terminated long before the onset of deorientation.

Anisotropy could be observed with PS and PMM for several months if the samples were heated to a temperature higher than that of glass transition, and rotation was then stopped by cooling the samples to room temperature in a static field. With a rise in temperature the deorientation rate of such samples increased and at 95-110°C deorientation terminated in several seconds, just as with most rubbers.

Characteristic curves for decay of the linear electrochromism signal from Dye I in PS are shown in Fig. 6 for three temperatures. It

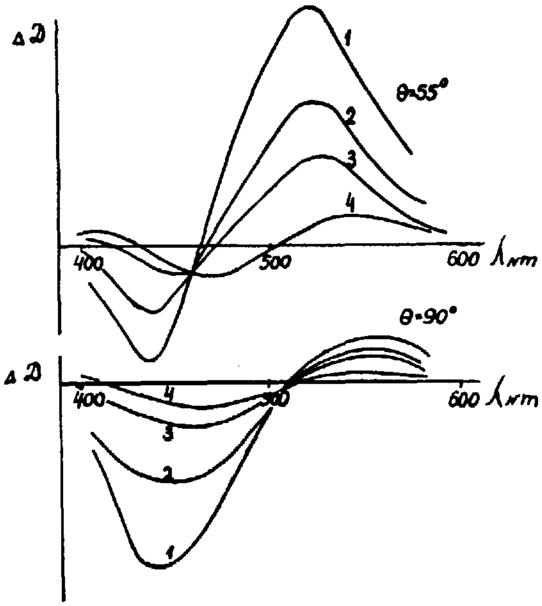

FIG. 6. Decay of the electrochromism signal for Dye I in an oriented polystyrene sample at three temperatures.

will be seen that there are relaxation processes in PS and PMM with different τ. Determination of the longest relaxation time, through use of the equation

$$\Delta D = D_{\text{init}} \exp(-t/\tau)$$

is shown in Fig. 7. The same usual procedure is valid for distinguishing the rectilinear regions of the curves of Fig. 6 and of two other exponential processes with τ_2 and τ_3. The relaxation times τ_1 and τ_2 and the fractions of molecules σ in the states corresponding to these times are shown in Table 3.

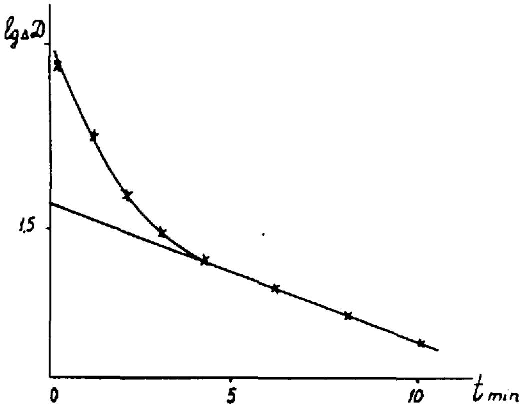

FIG. 7. Determination of the longest relaxation time by equation $\log \Delta D = \log \Delta D_{\text{init}} - 2.3t/\tau$.

The fraction of fast molecules can be seen to increase with temperature, and that of slow molecules to decrease. The activation energies for segmental molecular motion were found according to Ref. 23 and appeared to be 1.01 and 0.85 eV for the slowest motions in PS and PMM, respectively.

Changes in electric polarization of dielectrics can be followed by observing the linear Stark effect signals. Samples of crude rubbers with Dyes I, IV, and V were used. With only an alternating field of 480 Hz the amplifier adjusted to the same frequency did not record electrochromism signals, but they appeared when a static field was added. This showed the occurrence of anisotropic distribution of

TABLE 3. Relaxation Times for Dye I Rotation in PS at Several Temperatures

Relaxation times in minutes and the relevant molecular fractions	Sample temperature (°C)			
	38	48	52	60
τ_1	720	190	90	29
σ_1	0.27	0.24	0.075	0.07
τ_2	124	30	20	4
σ_2	0.31	0.33	0.5	0.82

molecules over the dipole orientation. The phase of electrochromism signals corresponded to a shift of the absorption band toward the long-wave region (dipole orientation in the field). However, in 15-20 sec the signal decayed almost to zero due to an impurity-induced increase in strength of the oppositely directed dielectric polarization field.

When the time of molecular orientation in the field at a given temperature is larger than that of the onset of dielectric polarization, then at the moment the static field is switched off the dye molecules appear to be oriented against the polarization field. An intensive electrochromism signal is observed and its phase corresponds to a band shift toward the violet. As the polarization field disappears, the electrochromism signal decays to zero. When the times of molecular orientation and onset of polarization are commensurate, the switching off of the constant field might at first lead to an increase in the signal intensity with a shift toward the violet. Then the signal will decay to zero and will increase again, with the shift of the band toward the red being due to reorientation of dye molecules in the direction of the slowly decaying polarization field, and, eventually, will again become zero.

The value of such investigations is the possibility they give of determining independently by an optical method the direction and the strength of the field in dielectrics.

DISCUSSION

It may be seen from the experimental data that changes in electrochromism spectra with change of the matrix or with its transition to another state are accounted for by different magnitude of effects which depend on the orientation of molecules in an alternating field. These effects are greatest in liquids, as the Boltzmann distribution over dipole orientation has time to set in at a given field frequency. The lower extent of orientation in viscous and solid media is usually ascribed either to the low rate of equilibrium onset or to the elastic dipole nature of polarization. However, neither provides an unambiguous explanation of the results obtained. Indeed, a decrease in effect of magnitudes with increasing relaxation times would be expected to result in greater phase shifts between electrochromism signals and the external field and in dependence of magnitude on frequency. Yet, the orientation of the probes in the experiments was usually the same and no phase shifts were observed over the frequency range of 20 to 1000 Hz.

Proportionality of the orientation and mixed terms (Fig. 3) is not consistent with the concept of the viscous elastic nature of polarization. In all cases the mixed and orientational effects were the same as for benzene and other liquids, and changed in parallel.

This could be explained by assuming that only a small part of the probes show relaxation times in the range of 1/20 to 1/1000 sec. The molecules with relaxation times shorter than 10^{-3} may be considered as "free," as the Boltzmann distribution has time to set in for such molecules. The molecules with a relaxation time of less than 1/20 sec have no time to react to the external field change and do not contribute to the orientation effect.

This seems to explain the absence of electrochromism dispersion over 20 to 1000 Hz and the phase shifts. Changes in electrochromism signals would be accounted for by different fractions of "free" molecules. The latter may be determined from the orientation effects, assuming that all dye molecules in benzene are "free." The contributions from free molecules of certain polymers at room temperature are shown in Table 4. With PS and PMM they differs from zero only after the samples are heated to the glass transition temperature.

Dynamic equilibrium dependence on temperature must exist between free and bonded molecules. The part of free molecules would be $t_1/t_1 + t_2)$, where t_1 and t_2 are the average lifetimes of molecules in the free and bound states. The probe is surrounded by polymer molecules suffering continuous conformational transformations. The freedom of probe rotation depends on the positions of molecular fractions in its immediate vicinity. The free and bound states of the probe correspond to certain combinations of conformational transformations.

Another mechanism of molecular motion must be assumed for very low-frequency ranges, where deorientation of molecules in preoriented samples takes considerably more time than the external electric field cycle. Several pronounced relaxation processes with different τ were distinguished in this range. The concept of viscous-elastic polymer

TABLE 4. Content of Free Molecules of Dye I in Various Polymers at Room Temperature

Polymer	Content of free molecules in %
Rubber SKS-30	49
Rubber SKB	44
Rubber SKMVP-5	44
Rubber NK	40
Polyethylene	26
Rubber SKS-30-1	22

properties seems to be more applicable here. The motion of probes might be accompanied with considerable rearrangements of the close environment and consideration of the surrounding polymer region, rather than of one probe motion, might be preferable.

The temperature dependence of the decay rate for the electrochromism signal linear in the field permits calculation of the activation energy for this process with a reliability inaccessible with other methods on account of time restrictions.

The coefficient K responsible for the orientational effect contribution to electrochromism spectra for two polymers, SNK-26 and Nairit, is different from that for other polymers. However, the ratio $\Delta D_\nu/\Delta D_r$ is within the limits of other rubber measurements. The apparent inconsistency between parameters for the probe mobility is due to the impossibility of using a field for the Lorentz approximation in polar media. The ratio is, in fact, that of orientation plus mixed terms to the molecular terms, since the former add to the electrochromism peak in the violet and are responsible for the value of ΔD_ν, whereas in the red they are subtracted from each other and the molecular terms are essential there. Taking into account the proportionality between moments μ_g and μ_e in the dye series, the ratio $\Delta D_\nu/\Delta D_r$ will be independent of the dye dipole moment μ_g and the field amplitude. However, the dipole moment and the strength of the field acting on the molecule have to be allowed for in calculating K, and this is the reason for the apparent discrepancy. These suggestions were verified by estimation of μ_{eff} which, according to Ref. 6, is $1/3\ \mu_g$ at $\epsilon = 0$. This would explain why the value of μ_{eff} is almost lower by a power of ten than those for other polymers. The rotational motion of the two rubbers can be considered to be free, as in the other polymers listed.

The characteristics of rotation had to be compared with those of translational motion for the same molecules. The concentrations of dye molecules in polymer matrices were chosen so that the dye would be completely dissolved at 100-120°C, but precipitated as crystals at room temperature. The dyed sample pressed between two mica foils at 100-120° was placed into a cell filled with water at 20°C, and absorption spectra were recorded in succession by a spectrophotometer. At 20°C the dyes formed crystals, the largest of which could be seen in a microscope. The dye migrated from the polymer to the crystallization centers and the optical density of samples decreased by a first-order kinetic process. The rate constant linearly related to the diffusion coefficient was calculated from the results obtained (Table 5).

TABLE 5. Rate Constants for Dye I Crystallization from Oversaturated Solutions in Certain Polymers

Polymer	Rate constant $k \times 10^{-5}$ ($\min^{-1}$)
Polyethylene	350
Natural rubber	250
SKD	113
SKB	16.5
SKS-10	11.0
SKS-30	8.0
SKS-30-1	3.4
SKMVP-5	2.9
SKN-26	0
Nairit	0
PS	0
PMM	0

Comparison of the crystallization rate constants with the orientation coefficients (Table 1) shows no strict parallelism between these values. It is of interest to note that translational diffusion virtually does not occur in SKN-26 and Nairit, whereas rotational diffusion is quite marked. Neither rotational nor translational motion was observed in glassy samples. Both forms of diffusion may depend on the combined motion of the surrounding molecular fractions of polymers. Different motions for various polymers may be the reason for such discrepancies. The results obtained seem to show that the concept of viscous continuous media is inapplicable to polymers, as this would imply parallelism in rotational and translational motions.

Thus the electrochromism method may be used to investigate molecular mobility in polymers. It essentially supplements the other methods available, particularly in the range of low frequencies, and permits evaluation of certain physicochemical properties of polymers, with the conclusions supplementing the present concepts. Certain results on the study of probe motion in polymers and on the structure of polymers will be reported in our next publications.

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