Translated from *Uspekhi Khimii*, 48, 563-582 (1979) U.D.C. 678.012.4:539.219.3

Electrochromism for the Investigation of Slow Movements in Macromolecules

F.P.Chernyakovskii

An account is given of the most important theoretical principles of electrochromism, and the possibility of its application is discussed. Apparatus and method of measurement are described. Results are considered for linear polymers in elastic and vitreous states over the range of relaxation times 10^{-3} - 10^{6} s. A list of 31 references is included.

CONTENTS

I. Introduction 306
II. The phenomenon of electrochromism 306
III. Investigation of amorphous polymers in vitreous-elastic transition range by quadratic electrochromism 310
IV. Study of elastic state of amorphous polymers by quadratic electrochromism 312
V. Investigation of vitreous state of amorphous polymers by linear electrochromism 313
VI. Experimental procedure 314

I. INTRODUCTION

Use of especially sensitive apparatus reveals that an external electric field deforms absorption bands associated with solutions of organic molecules. This phenomenon occurs throughout the solution and is caused by interaction between the solute molecules and the field. Such interaction is apparent in the absorption spectra as optical anisotropy of the medium—dichroism of the solutions—and as spectral shifts in the bands caused by Stark effects. The broad absorption bands of complicated organic molecules exclude the possibility of applying the techniques of observation and interpretation that have been developed in studying Stark effects on line emission spectra. Some authors therefore consider it advisable to apply the term *electrochromism* to the deformation of molecular absorption bands in solution. The most complete description of electrochromism will be found in the works of Liptay, who as early as the 1960s suggested its use as a method for determining molecular excitation parameters[1].

Our work has shown[2-4] that electrochromism has another use—to study slow molecular mobility in condensed media, in particular in polymers—for which purpose molecules are introduced into the test medium to act as probes, and their rotational movements are observed by means of electrochromism. As in all other probe methods for studying molecular dynamics, it is in turn assumed that movements of the probes are determined solely by the thermal motion of molecules of the medium.

An obstacle to investigating slow movements by the paramagnetic probe method[5] is the so called relaxation conditions, which imposes a lower frequency limit at 10^{-7} s. During recent years paramagnetic probe methods have been devised in which the frequency limit has been lowered to 10^{-4} s.[6] An advantage of electrochromism over paramagnetic probes is the absence of theoretical limits in the low-frequency region. We have investigated molecular mobility in polymers between 10^{-3} and 10^{6} s. The approximately six frequency ranges thus covered are typical of the vitreous state. A relaxation time of 10^{6} s corresponds to a period of ~2 weeks, but this does not mean that such is the lower frequency limit of the method. The hypothetical possibility remains of using electrochromism to study even infinitely long relaxation processes. On the other hand, extending the range to short times (10^{-5}–10^{-6} s) leads merely to fully surmountable technical difficulties. There was no need in our work to raise the frequency, firstly because the dielectric method and the paramagnetic probe method are successfully used in the respective ranges 10^{-1}–10^{-10} and 10^{-7}–10^{-8} s, and secondly because the low-frequency range is the most interesting and promising, for it characterises mainly the relaxation processes that govern the properties of most polymer materials.

Electrochromism, like the Stark effect, is due to orientation polarisation of the probe molecules, which makes it akin to dielectric methods for investigating molecular mobility. The advantages of electrochromism are due to its high selectivity: since the method is based on observing the absorption spectra of probes, measurement can be confined to their orientational mobility, and other types of polarisation of the medium, which make a contribution in dielectric measurements, can be excluded.

Electrochromism can in principle be studied using probes that have been grafted on or even included in the main polymer chain. Another possible and extremely promising method of measuring inherent absorption involves observing that of chromophoric groups in the macromolecule, and directly determining their mobility. For the majority of polymers such investigation are possible only in the far ultraviolet.

II. THE PHENOMENON OF ELECTROCHROMISM

The action of an electric field on an absorption spectrum was first detected experimentally in 1939 by Kuhn et al.[7] for nitrosodimethylaniline dissolved in dioxan. Kuhn suggested that considerable orientation polarisation of the dissolved dipolar molecules might be produced in a strong electric field of $\sim 10^{4}$ V cm^{-1}. Since there is a fixed angle γ between the directions of the dipole moment of the molecule in the ground state $\bar{\mu}_g$ and that of the transition moment (unit vector $\bar{m}$), under certain conditions the orientation polarisation of the moments $\bar{\mu}_g$ may

be accompanied by anisotropy in the distribution of transition moments observable by means of special apparatus, together with dichroism of the solution. The optical density measured by means of a light ray parallel to the field strength vector $\bar{F}$ then differs from that measured perpendicular to this direction. The aim of the early work[7] was to evaluate the angle γ in organic molecules from the experimental dichroism.

Considerably later Labhart[8], Czecalla[9], and mainly Liptay and his coworkers[10] established that in Kuhn's experiments the expected orientation effect was accompanied by other effects, resulting from Stark displacements of the energy levels of ground and excited electronic states of the molecules. The shift in the levels is determined by interaction of a molecule possessing dipole moments $\bar{\mu}_g$ and $\bar{\mu}_e$ and polarisability tensors α_g and α_e with the external field (here and subsequently the subscripts g and e denote ground and excited states respectively). Furthermore, Liptay subsequently examined the action of a field on the transition moment of the molecules, and showed that this effect is also included in the observed electrochromism[1].

We consider the absorption of light by one of the molecules in the ensemble under investigation, whose orientation relative to the vector $\bar{F}$ is rigidly fixed. The shift in the absorption band in the field is determined by the displacement of the ground and excited electronic levels. Fig. 1 illustrates how the mutual arrangement of the vectors $\bar{\mu}_g$, $\bar{\mu}_e$, and $\bar{F}$ influences (disregarding the contribution of polarisability) the magnitude and the direction of the spectral shift in the bands (which for clarity has been greatly exaggerated).

From the above considerations the shift of the band in the field can be calculated by means of the formula

$$\Delta\bar{\nu} = \bar{\nu}^0 - \bar{\nu}^F = -\frac{\bar{\mu}_e - \bar{\mu}_g}{hc}\bar{F} - \frac{1}{2hc}(\alpha_e - \alpha_g)\bar{F}^2$$

where $\bar{\nu}^0$ and $\bar{\nu}^F$ are wave numbers of the electron transition in the absence and in the presence of the field, h is Planck's constant, and c is the speed of light. Writing $\Delta\bar{\mu} = \bar{\mu}_e - \bar{\mu}_g$ and $\Delta\alpha = \alpha_e - \alpha_g$, we obtain

$$\Delta\bar{\nu} = \frac{\Delta\bar{\mu}\bar{F}}{hc} + \frac{\Delta\alpha\bar{F}^2}{2hc} \quad (1)$$

In the maximum practicable fields (10^5 V cm^{-1}) the shift in the bands is a fraction of an Ångström unit under optimum conditions. Direct measurement of such small shifts in wide spectral bands is an extremely complicated task, so that measurements are made not of the band shifts but of the increase in luminous flux at a fixed wave number due to the action of the field. According to Eqn. (1) in an electric field transitions will be observed at a wave number $\bar{\nu}$ that are observed at wave number $\bar{\nu}-\Delta\bar{\nu}$ in the absence of a field. A low-frequency alternating field is usually applied to the specimens, and only the modulated part of the luminous flux, due solely to electrochromism, is measured.

The absorption of light by one molecule in the absence of a field is[11]

$$\pi(\bar{\nu}) = 3|\bar{e}\bar{m}|^2 \varepsilon(\bar{\nu})/\bar{\nu},$$

where $\bar{e}$ is the unit vector in the direction of the electric vector of luminous flux, and $\epsilon(\bar{\nu})$ is a function describing the form of the absorption band. Since the displacement of ground and excited levels in the field is much smaller

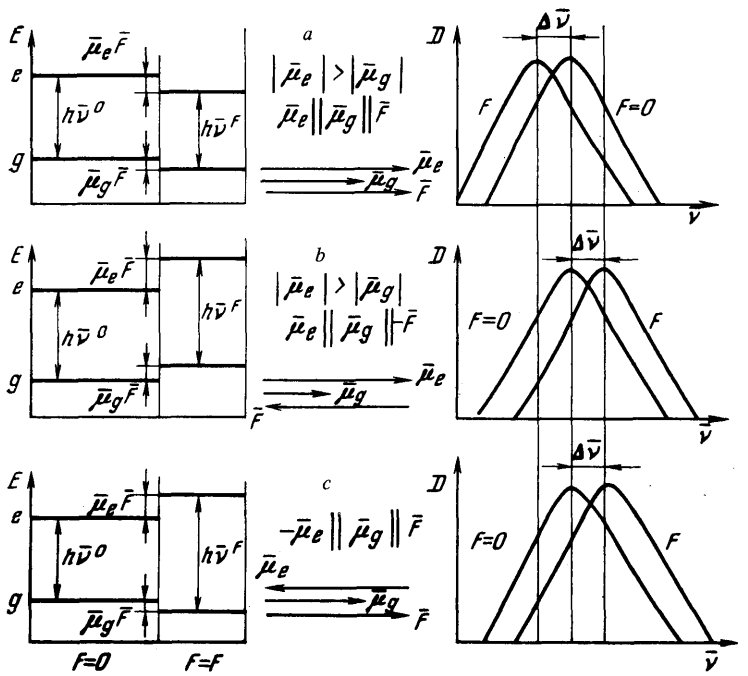


Figure 1. The effect of the mutual orientation of the vectors $\bar{\mu}_g$, $\bar{\mu}_e$, and $\bar{F}$ on the direction of displacement of the absorption band in the field: *a*) red shift; *b*), *c*) violet shift.

than the distance between them, the effect of the field can be estimated by a perturbation method:

$$\pi(\bar{\nu}^F) = \pi(\bar{\nu}^0) + \frac{d\pi(\bar{\nu}^0)}{d\bar{\nu}}\Delta\bar{\nu} + \frac{1}{2}\frac{d^2\pi(\bar{\nu}^0)}{d\bar{\nu}^2}\Delta\bar{\nu}^2 + \dots$$

Substituting for $\Delta\bar{\nu}$ from (1), we obtain

$$\pi(\bar{\nu}^F) = \pi(\bar{\nu}^0) + \frac{d\pi(\bar{\nu}^0)}{d\bar{\nu}}\left(\frac{\Delta\bar{\mu}\bar{F}}{hc} + \frac{\Delta\alpha\bar{F}^2}{2hc}\right) + \frac{1}{2}\frac{d^2\pi(\bar{\nu}^0)}{d\bar{\nu}^2}\left(\frac{\Delta\bar{\mu}\bar{F}}{hc} + \frac{\Delta\alpha\bar{F}^2}{2hc}\right)^2 + \dots \quad (2)$$

To determine the absorption of light by an ensemble of molecules it is necessary to add up the contributions by all molecules situated in the path of the light ray. Fig. 1 shows (*a* and *b*) that the spectral shifts of bands due to molecules whose dipole moments $\bar{\mu}_g$ are oriented along and against the field occur in opposite directions. As a consequence, only a slight broadening of the absorption bands, instead of a spectral shift to one side, is observed in a medium that is isotropic with respect to the directions of $\bar{\mu}_g$ and contains many molecules. This corresponds to the electrodynamic principle that effects which are linear with respect to the field cannot be observed in isotropic media. When the absorption of light by isotropic solutions is calculated, such linear effects are excluded because of the parity of the function of the cosine of the angle α between $\bar{\mu}_g$ and $\bar{F}$, and there remain only effects whose magnitude depends on $\bar{F}^2$. Effects proportional to higher powers of $\bar{F}$ can be neglected. Those proportional to $\bar{F}^2$ are termed *quadratic electrochromism*, in contrast to the linear electrochromism proportional to $\bar{F}$, whose nature will be examined in Section V.

In dilute solutions of polar molecules in a non-polar solvent an external field produces orientation polarisation, which Liptay[10] calculated from the Boltzmann distribution. In an electric field the medium becomes anisotropic, and effects that are linear with respect to the field become observable.

The final form of Liptay's equation is[11]

$$K = K_0 + A\frac{1}{\varepsilon(\bar{\nu})/\bar{\nu}}\frac{d(\varepsilon(\bar{\nu})/\bar{\nu})}{d\bar{\nu}} + B\frac{1}{\varepsilon(\bar{\nu})/\bar{\nu}}\frac{d^2(\varepsilon(\bar{\nu})/\bar{\nu})}{d\bar{\nu}^2}, \quad (3)$$

with the notation

$$K_0 = \frac{1}{10(kT)^2}\mu_g\frac{3\cos^2\gamma - 1}{2};$$

$$A = \frac{1}{5kThc}\left[\mu_g^2\frac{3\cos^2\gamma - 1}{2} - \mu_g\mu_e(\cos\gamma\cdot\cos\delta - \frac{1}{2}\sin\gamma\cdot\sin\delta)\right];$$

$$B = \frac{1}{10(hc)^2}\left[\mu_g^2\frac{3\cos^2\gamma - 1}{2} - 2\mu_g\mu_e(\cos\gamma\cdot\cos\delta - \frac{1}{2}\sin\gamma\cdot\sin\delta)\right] + \mu_e^2\frac{3\cos^2\delta - 1}{2};$$

$$K = -p_E\left[2{,}3D\left(\frac{\varepsilon_{DK}+2}{3}\right)^2\bar{F}^2\right]^{-1};$$

$\bar{\nu}$ (in cm^{-1}) the wave number, $\epsilon(\bar{\nu})$ the extinction coefficient, γ the angle between $\bar{m}$ and $\bar{\mu}_g$ with δ that between μ_e and $\bar{m}$, as before c the speed of light, ϵ_{DK} the dielectric constant of the medium, D the optical density, and p_E the measured degree of polarisation of light by the solution in the electric field. The field acting on the dissolved molecules had been calculated[10] by means of the Lorentz formula, but in later work Onsager's equation was used[12]. The theory of electrochromism and several of its applications have been discussed also in reviews[13-15].

Phenomena akin to electrochromism can be observed on application of an electric field to solutions whose components are in chemical equilibrium, provided that starting materials and final products differ in the sum of the products of the dipole moments of the ground state and the corresponding stoichiometric coefficients[16]. Electrochromism has been used to investigate charge-transfer complexes[17], conformational equilibria in which the components differ in polarity[18], and phenomena due to excitons[19].

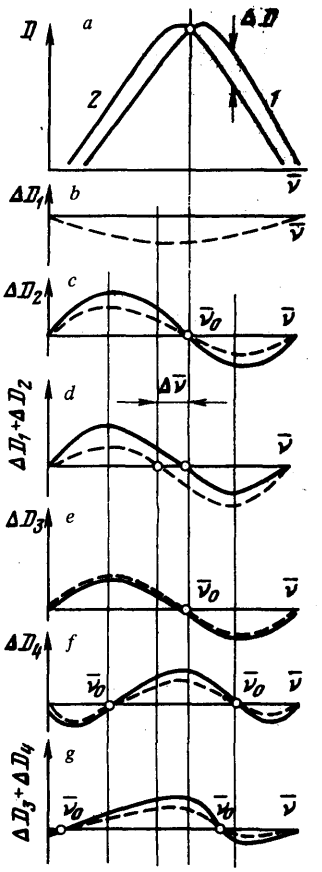


Figure 2. (*a*) Absorption spectra of solution: 1) in absence of a field; 2) under the influence of a field (the change in the spectrum has been greatly exaggerated for clarity). (*b*)–(*g*) Electrochromism spectra with $\theta = 55°$ and 90° (respectively full and broken curves), including (*b*)–(*d*) effects depending on orientation and (*e*)–(*g*) Stark effects: *b*) orientation effect ΔD_1 for molecule with $\gamma < 55°$ (when $\theta = 55°$ we have $\Delta D_1 = 0$, and the electrochromism spectrum coincides with the ordinate axis); *c*) orientation effect ΔD_2; *d*) spectral sum $\Delta D_1 + \Delta D_2$, with parameters of the electrochromism spectra $\Delta\bar{\nu}$ and $\Delta D_V/\Delta D_r$; *e*) quadratic Stark effect ΔD_3; *f*) linear Stark effect ΔD_4; *g*) spectral sum $\Delta D_3 + \Delta D_4$ (drawn with opposite sign to *f*).

Attention has been directed[2-4] to the dependence of the terms K_0 and

$$\frac{A}{\varepsilon(\bar{\nu})/\bar{\nu}}\frac{d(\varepsilon(\bar{\nu})/\bar{\nu})}{d\bar{\nu}}$$

in the Liptay equation (3) on the rotational mobility of the molecules. Quasi-stationary conditions are established in experiments on dilute solutions of polar molecules in a liquid non-polar solvent at external field frequencies far lower than those determining the movements of the solvent

molecules: dipole polarisation of the dissolved molecules is able to follow changes in the external field, and such molecules were termed "free". In other solvents or at other frequencies of the electric field "hindered" molecules may exist, for which the opposite frequency relation holds. Formula (3) characterises free molecules, whose orientation in the field obeys Boltzmann statistics. For hindered molecules the terms K_0 and A, containing the factor μ_g/kT, must be equated to zero.

Inspection of Eqns. (3) indicates that the electrochromism of free molecules has clearly defined features. The dependence of the electrochromism of polar probe molecules on the character of the molecular mobility of the test solvent forms the basis for application as a method of investigating molecular mobility in polymeric media. The Liptay equations were brought into line with the aims of the investigation by isolating as a separate group those effects of electrochromism that depend on the rotational mobility of the molecules (Fig. 2). The increase in optical density ΔD in the field, taken along the absorption band envelope, is measured as a function (termed the *overall electrochromism spectrum*) of the wavelength, frequency, or wave number (Fig. 2*a*):

$$\Delta D_{\theta=90^\circ} = (\Delta D_1 + \Delta D_2 + \Delta D_3 + \Delta D_4)_{\theta=90^\circ};$$

$$\Delta D_1 = \frac{1}{15}\left(\frac{\mu_g F}{kT}\right)^2 (1-3\cos^2\gamma)\, D;$$

$$\Delta D_2 = \frac{1}{5}\left(\frac{\mu_g F}{kT}\right)\frac{\Delta\bar{\mu}F}{hc}(2-\cos^2\gamma)\cdot\bar{\nu}\frac{\partial(D/\bar{\nu})}{\partial\bar{\nu}};$$

$$\Delta D_3 = \frac{1}{2}\frac{\Delta\alpha F^2}{hc}\cdot\bar{\nu}\frac{\partial(D/\bar{\nu})}{\partial\bar{\nu}}; \qquad (4)$$

$$\Delta D_4 = \frac{1}{10}\frac{\Delta\bar{\mu}^2\bar{F}^2}{h^2c^2}(2-\cos^2\delta)\,\bar{\nu}\frac{\partial^2(D/\bar{\nu})}{\partial\bar{\nu}^2}.$$

These equations show that the overall spectrum is the sum of the contribution ΔD_1–ΔD_4, which are also electrochromism spectra, whose nature and dependence on molecular mobility and experimental conditions will be discussed below.

Equations (4) have been written for the case in which the relative directions of the electric vector of the light ray in the medium (unit vector $\bar{e}$) and the electric field $\bar{F}$ form the angle $\theta = 90^\circ$. We can vary the angle θ and select experimental conditions under which the contribution ΔD_1 can be eliminated from the overall electrochromism spectrum. The orientation effect ΔD_1 is due to orientation polarisation of the probe molecules and disregards Stark effects. It appears as Kuhn dichroism, for which[7]

$$\Delta D_{\theta=0^\circ} = -2\Delta D_{\theta=90^\circ}. \qquad (5)$$

For any angle θ we have

$$\Delta D_\theta = \Delta D_{\theta=0^\circ}\cdot\cos^2\theta + \Delta D_{\theta=90^\circ}\cdot\sin^2\theta. \qquad (6)$$

From (5) and (6) we find that

$$\Delta D_\theta = \Delta D_{\theta=90^\circ}(1-3\cos^2\theta).$$

The expression in brackets vanishes when $\theta = 54^\circ44' \simeq 55^\circ$. Under these conditions $\Delta D_1 = 0$, and no orientation effect is observed (Fig. 2*b*). The probes usually chosen are molecules in which under conditions of symmetry the vectors $\bar{\mu}_g$, $\bar{\mu}_e$, and $\bar{m}$ are mutually parallel, while $\bar{\mu}_e > \bar{\mu}_g$ in absolute magnitude; we then have $\gamma = 0$ and $\delta = 0$, and for such molecules with $\theta = 55^\circ$ Eqns. (4) simplify to

$$\Delta D_{\theta=55^\circ} = (\Delta D_2 + \Delta D_3 + \Delta D_4)_{\theta=55^\circ};$$

$$\Delta D_2 = \frac{1}{3}\frac{\bar{\mu}_g\bar{F}}{kT}\frac{\Delta\bar{\mu}F}{hc}\bar{\nu}\frac{\partial(D/\bar{\nu})}{\partial\bar{\nu}};$$

$$\Delta D_3 = \frac{1}{2}\frac{\Delta\alpha\bar{F}^2}{hc}\bar{\nu}\frac{\partial(D/\bar{\nu})}{\partial\bar{\nu}}; \qquad (7)$$

$$\Delta D_4 = \frac{1}{6}\frac{\Delta\bar{\mu}^2\bar{F}^2}{h^2c^2}\bar{\nu}\frac{\partial^2(D/\bar{\nu})}{\partial\bar{\nu}^2}.$$

Furthermore, an orientation effect is not observed under any conditions with molecules having the angle $\gamma = 55^\circ$, since the factor $1 - 3\cos^2\gamma = 0$ then vanishes (see formulae 4). Finally, an orientation effect is absent from media in which the rotational mobility of the probe molecules is hindered.

We have termed ΔD_2 (Fig. 2*c*) a *cross* electrochromism spectrum, since it results from two simultaneous effects of the field[3]. When the field is switched on, the original isotropic distribution of dipoles with respect to direction is disturbed, and anisotropy due to the factor $\bar{\mu}_g\bar{F}/kT$ appears. This permits observation of the Stark effect, linear with respect to the field and proportional to $\Delta\bar{\mu}\bar{F}$. As a consequence, the inherently linear Stark effect becomes proportional to $\bar{F}^2$. Obviously, no cross effect is observed in media with hindered mobility of the probes. When the angle θ changes from 90° to 55°, the cross effect diminishes by a factor 5/3 = 1.66, as is evident from the coefficients in Eqns. (4) and (7).

Fig. 2*d* illustrates the spectral sum of the two contributions $\Delta D_1 + \Delta D_2$, which it is advisable to consider separately from the others, since only they depend on the rotational mobility of the molecules. The clearest indication of free rotation of the probes is a shift in the electrochromism zero point $\bar{\nu}_0$ with change in the angle θ from 90° to 55°. This is accompanied by a change in the ratio $\Delta D_V/\Delta D_R$ of the increases in the electrochromism signal on violet and red sides of the absorption band.

The contribution ΔD_3 (Fig. 2*e*) is made by the quadratic Stark effect, caused by the change in polarisability accompanying excitation of the molecule. The quadratic effect can be arbitrarily imagined to consist of two parts—an induced dipole moment $\Delta\alpha\bar{F}$ and a linear Stark effect—the former always lies in the direction of the field irrespective of the rotational mobility of the molecules, and the latter depends on the interaction of the induced moment with the same external field $(\Delta\alpha\bar{F})\bar{F}$. With $\alpha_e > \alpha_g$ this leads to a red shift of the band.

For every moment $\Delta\bar{\mu}$ in an isotropic medium containing a large number of molecules it is always possible to find another molecule having the same moment but oriented in the opposite direction. If one orientation corresponds to a red shift of the absorption band in the field as a consequence of a first-order Stark effect, the opposite orientation corresponds to a violet shift. Only a slight broadening of the band can then be observed, proportional to $\partial^2(D/\bar{\nu})/\partial\bar{\nu}^2$. We have termed the ΔD_4 effect *linear* in conformity with its nature (Fig. 2*f*), although it is found to be proportional to $\bar{F}^2$. It does not depend on rotational mobility, so that a sensible procedure is to combine it with ΔD_3 and henceforward consider another spectral sum $\Delta D_3 + \Delta D_4$ (Fig. 2*g*). A characteristic feature of $\Delta D_3 + \Delta D_4$ spectra in media with free rotational mobility of probe molecules whose dipole moments $\bar{\mu}_g$ and $\Delta\bar{\mu}$ are a few Debyes is their low intensity in comparison with $\Delta D_1 + \Delta D_2$ (Fig. 2*d*). In this case effects depending on orientation exceed Stark effects by factors of $\sim 10^{1.5}$. In media with hindered rotation of probe molecules, on the other hand, only Stark effects can be observed with two zero points $\bar{\nu}_0$, whose positions are independent of the angle θ.

Thus, if the originally free rotation of molecules is gradually hindered, e.g. by freezing the solvent, the electrochromism spectra change from the spectral sum $\Delta D_1 + \Delta D_2 + \Delta D_3 + \Delta D_4$ to the spectrum $\Delta D_3 + \Delta D_4$ with a corresponding decrease in intensity by factors of $10^{1-1.5}$.

Inspection of Eqns. (4) and (7) shows that orientation-dependent effects diminish at different rates with rise in temperature: the orientation effect falls more rapidly. With rise in temperature to infinity both orientation and cross effects tend to zero.

For the study of slow movements in macromolecules it is very important to examine the frequency dependence of individual effects. Only molecules whose rotational relaxation time is shorter than the period of the alternating field $\bar{F}$ reveal $\Delta D_1 + \Delta D_2$ effects. Thus probe molecules are arbitrarily divided into two groups—free and hindered—by the frequency of the external field. In very high-frequency fields all molecules may be hindered, and at very low frequencies all can be regarded at least hypothetically as free. These considerations show that, by examining electrochromism spectra over a wide range of field frequencies, information can be obtained on the spectrum of relaxation times of probes in polymers. Frequency begins to influence Stark effects only in the range in which relaxation processes are appreciable in the electron shells of the molecules[20]. As a consequence, under normal conditions Stark effects make a constant contribution and provide a kind of standard, with which effects depending on orientational mobility can be compared.

Thus the concept of overall electrochromism spectra as a sum of contributions, together with specific observed features, underlies a technique for their separate determination, which is based on the following principles[2].

1. Cross and orientation effects are not observed in media with completely hindered rotational mobility. In this case the form and the intensity of the electrochromism spectra are determined by Stark effects. Parameters of the electrochromism spectra due to the latter effects, which are characteristic of media with hindered mobility, are maintained in media with free motion of the same molecules.
2. No orientation effect is observed when the polarisation of the light ray corresponds to $\theta = 55°$.
3. The cross effect and the quadratic Stark effect are zero at the peak of the absorption band, where $\partial (D/\bar{\nu})/\partial \bar{\nu} = 0$.
4. The linear Stark effect is zero at points at which $\partial^2(D/\bar{\nu})/\partial \bar{\nu}^2 = 0$.
5. For molecules having $\gamma = 0°$ the cross and linear effects increase by factors of 1.66 as the angle θ diminishes from 90° to 55°.

III. INVESTIGATION OF AMORPHOUS POLYMERS IN VITREOUS-ELASTIC TRANSITION RANGE BY QUADRATIC ELECTROCHROMISM

Electrochromism effects can be determined separately in a polymer matrix at a temperature in the region of transition from elastic to vitreous states. Fig. 3*a* illustrates the absorption spectrum (curve *1*) and the electrochromism spectra of *p*-dimethylamino-*p'*-nitrobisazobenzene in polystyrene at room temperature (below the glass point). It is evident that the electrochromism spectra for $\theta = 55°$ and 90° differ merely in intensity, with

$$\Delta D_{\theta=55°}/\Delta D_{\theta=90°} = 1.66.$$

It follows from theory that these spectra correspond to complete hindrance of probe molecules in the polystyrene. This is supported also by the presence of two electrochromism zero points, whose positions are independent of the angle θ, as well as by the similarity of the spectra to those illustrated in Fig. 2*g*. The ΔD_3 and ΔD_4 effects can be separated by means of the difference in shape between the corresponding electrochromism spectra. The ΔD_3 spectrum is proportional to the first derivative of optical density with respect to frequency, so that at the peak of the band $\Delta D_3 = 0$: the ordinate of the $\Delta D_3 + \Delta D_4$ electrochromism spectra at this wavelength gives only the ΔD_4 contribution (see Fig. 2*f*). With the second derivative $\partial^2(D/\bar{\nu})/\partial \bar{\nu}^2$ available we can normalise its value at the band maximum and then calculate the ΔD_4 contribution throughout the spectrum. The ΔD_3 contribution is found similarly from the vanishing of ΔD_4 at zero points of the second derivative, when the effects are determined solely by the ΔD_3 signals. Another possible method is based on the additivity of the optical densities: ordinates of the ΔD_4 contribution calculated throughout the spectrum can be subtracted from the $\Delta D_3 + \Delta D_4$ spectrum. The electrochromism spectra should be taken at corresponding angles θ.

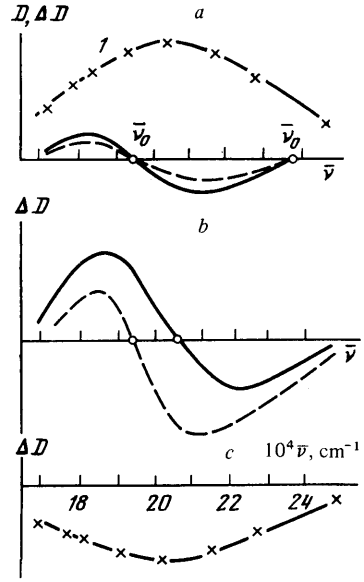


Figure 3. (*a*) Electrochromism spectra of (III) (Fig. 5) in polystyrene at room temperature: -----) $\theta = 55°$; - - -) $\theta = 90°$; 1) absorption spectrum; ×) form of contribution by orientation effect coinciding with absorption band. (*b*) Electrochromism spectra of the same specimen above the glass point. (*c*) Calculation of orientation effect.

When a specimen is heated the electrochromism spectra gradually change in the transition range (75–90°C). Fig. 3*b* shows overall electrochromism spectra for the same specimen heated to 92°C, i.e. above the glass point. Comparison with Fig. 2*d* reveals that these spectra correspond to orientational mobility of the probes. The spectra contain a single zero point, whose position depends on the angle θ: when $\theta = 55°$, the zero point is close to the peak

of the band. The slight displacement from the band maximum is attributed to a contribution by Stark effects. To determine the ΔD_1 and ΔD_2 contribution it is necessary to subtract the Stark effects obtained for the vitreous state from the overall electrochromism spectra at corresponding angles θ. After such subtraction the electrochromism spectrum at $\theta = 55°$ corresponds to the cross effect ΔD_2 with its zero point at the peak of the band. Determination of ΔD_1 requires subtraction from the electrochromism spectra at $\theta = 90°$ of $\Delta D\theta = 55°/1.66$, since the cross effect decreases by the factor 1.66 when the angle θ changes from 55° to 90° (Fig. 2*c*).

As a check we must compare the ΔD_2 contribution with the form of the first derivative of optical density with respect to frequency, and ΔD_1 with the form of the absorption band (bearing in mind that the ΔD_1 effect is negative for molecules having $\gamma < 55°$). The agreement between ΔD_1 (Fig. 3*c*) and the absorption band is shown by the points (×) on Fig. 3*a*.[21] The calculations were based on the hypothesis that the reaction field remains unchanged when specimens are heated above the glass point from room temperature. This hypothesis holds quite well for polystyrene, whose dielectric constant is only slightly dependent on temperature. With other polymers, e.g. poly(vinyl acetate), the dielectric constant increases rapidly with temperature, so that spectra obtained at different temperatures must be corrected for the reaction field when they are subtracted or added.

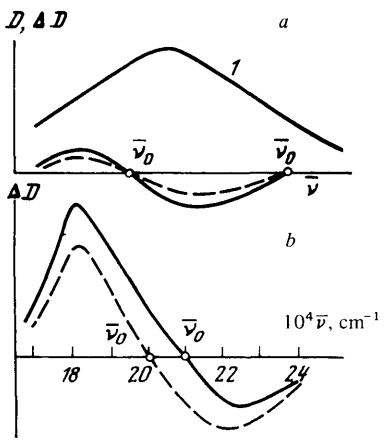


Figure 4. Effect of solvent (benzene) residues on electrochromism spectra of (II) (Fig. 5) in polystyrene specimen with different angles θ: -----) 90°; - - -) 55° at different temperatures: *a*) 20°C (specimens dried in air at room temperature for 24 h, and then in a vacuum at 60°C); 1) absorption spectrum; *b*) 95°C (dried only in air for 24 h).

A spectrophotometer is used to obtain the absorption spectrum, but the derivatives $\partial(D/\nu)/\partial\nu$ and $\partial^2(D/\nu)/\partial\nu^2$ are calculated from the spectrum, either by using a Gaussian function to approximate to the absorption band or by numerical differentiation on an electronic computer. Probe molecules are introduced into polymers by mixing separately prepared solutions of polymer and dye in a suitable solvent. The solvent is then removed initially by evaporation and then by drying the coloured polymer mass (Section VI). Benzene is a solvent for polystyrene, and therefore exerts a plasticising action on the latter; the benzene remaining in the specimen after drying affects the mobility of the probes. Specimens having different benzene contents can be obtained by varying the drying conditions.

Fig. 4*a* illustrates the electrochromism spectra of an azo-dye in polystyrene at room temperature for a specimen from which benzene has been completely removed by drying. Molecular mobility in the specimen is hindered, as indicated by the form of the electrochromism spectra and the unchanged position of the $\bar{\nu}_0$ points when the angle θ is varied. Fig. 4*b* gives electrochromism spectra for a specimen from which removal of solvent is incomplete as a consequence of milder drying conditions. The difference in mechanical properties between the two specimens is slight, with the former slightly more brittle. Yet the mobilities of probes in them differ substantially. The electrochromism spectrum (Fig. 4*b*) has clearly defined features indicating rotational mobility of the probes in polystyrene[2].

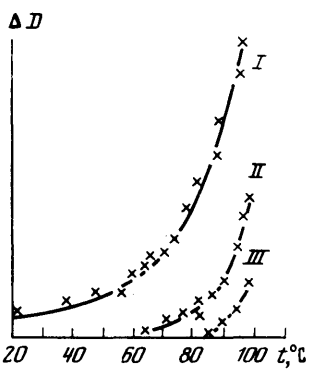
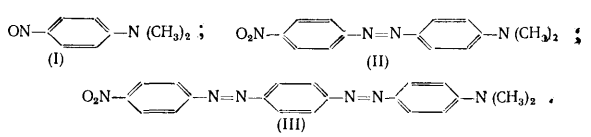


Figure 5. Temperature dependence of orientation effect in polystyrene film for the three probe molecules differing in size



The electrochromism spectra depend on the size of the probes (Fig. 5). The smallest probes—nitrosodimethylaniline (I) molecules—possess appreciable rotational mobility at a frequency of 240 Hz in polystyrene even at room temperature. *p*-Dimethylamino-*p'*-nitroazobenzene(II) molecules are able to rotate at 64°C, but the largest probes—*p'*-dimethylamino-*p*-nitrobisazobenzene(III) molecules containing three benzene rings—begin to rotate at 85°C. The results are well explained by the theory of the dynamic free volume[22].

IV. STUDY OF ELASTIC STATE OF AMORPHOUS POLYMERS BY QUADRATIC ELECTROCHROMISM

Fig. 6 illustrates absorption and electrochromism spectra of probe (II) obtained under the same conditions in certain rubbers. The form and the intensity of the electrochromism spectra obviously depend on the type of polymer. The ratio of the contributions made by two groups of effects—(i) $\Delta D_1 + \Delta D_2$, depending on the rotational mobility of the probes, and (ii) Stark effects, which are the same in all specimens—is found to determine the whole variety of spectral forms. Differences in intensity depend also on the strength of the field acting on the molecules with the same external electric field. In the investigation of molecular mobility the reaction field for media of dielectric constant ~2 can be calculated[2-4] by means of the Lorentz formula. In media of high dielectric constant (in SKN-26 and Nairit rubbers), however, this formula is inapplicable. Fröhlich calculation[12] of the field shows that the reaction field in SKN-26 of dielectric constant 11 is one-third of the Lorentz field, which diminishes the densities of field-quadratic effects by ~90%. In order to estimate rotational mobility in such cases it is advisable to compare the parameters $\Delta D_V/\Delta D_R$ and $\Delta\bar{\nu}$, which determine only the form of the spectrum (Fig. 2). It follows from these that rotational mobility of probe (II) in SKN-26 and Nairit rubbers does not greatly differ from that of the same probe in other rubbers.

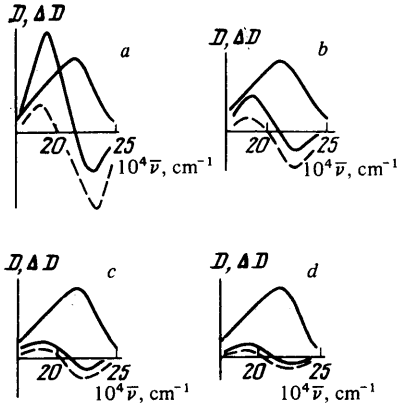


Figure 6. Absorption and electrochromism spectra of (II) at room temperature in various rubbers: *a*) SKS-30 [styrene-butadiene]; *b*) SKS-30-1; *c*) SKN-26 [butadiene-nitrile]; *d*) Nairit [chloroprene].

A very interesting question is the mechanism of the motion of probe molecules in a polymer. According to one view the polymer is a continuous, structureless medium, characterised by a single parameter—its viscosity—and thus having one rotational relaxation time of probes†. A second view assumes a broad spectrum of relaxation times[23], in which the same molecule is able to change sharply its relaxation characteristics, passing abruptly from free to hindered states and back. The two views lead to the same electrochromism spectra, so that additional information is required to make a choice between them‡. For this purpose our experiments[2] included examination of the phase shift between electrochromism signal and external field. In the former case, with viscous flow of the probes, the phase shift should differ from zero, since the proportions of free molecules $1 > \sigma > 0$ (Table 1) would appear to indicate that electrochromism measurements are made in a region of dispersion of rotational mobility of the probe. In the latter case, with a broad spectrum of rotation relaxation times of the probes, the phase shift should be zero, as was observed in all the rubbers investigated. The experiments with polystyrene (Figs. 3 and 4) and poly(methyl methacrylate) show that the rotational mobility of the probes changes significantly in the region of vitrification. It might have been expected that a phase shift would have been detected between the electrochromism signals and the external field with slow variation in temperature over the transition range. However, even in these experiments the phase shift was zero. It must thus be supposed that macromolecules in amorphous linear polymers have a broad spectrum of relaxation times. In terms of the theory of free volume[22] this implies that the probe is free at those instants in which a free volume—a cavity large enough to permit rotation of the probe—is formed around the probe as a consequence of the thermal motion of the macromolecules. In the next instant the cavity "collapses", and the probe passes into the hindered category.

Table 1.

Polymer	σ	$10^{-16}a$	$10^{-5}k_{tr}$, min^{-1}
SKS-30-1	0.22	74	3.4
Polyethylene	0.26	93.5	350
Natural rubber	0.40	137	250
SKMBP-5	0.44	153	2.9
SKB [butadiene rubber]	0.44	153	16.5
SKS-30	0.49	180	8.0

Interpretation of the electrochromism spectra as the summation of contributions by Stark effects and effects depending on orientational mobility enables the proportion of free molecules to be found. This requires comparison of $\Delta D_1 + \Delta D_2$ electrochromism spectra obtained under the same conditions in the test medium and in a liquid solvent of low molecular weight and closely similar dielectric constant, in which rotational mobility has characteristic times of 10^{-10}–10^{-12} s and all probes can be regarded as free. Instead of determining the spectra in the liquid we can use formulae (4) and (7) to calculate $\Delta D_1 + \Delta D_2$ for probes whose parameters have already been measured. Table 1 lists proportions σ of free (II) molecules at 240 Hz in various rubbers at room temperature. It includes the

† Actually, three relaxation times are possible for non-spherical molecules, corresponding to rotation about the three principal axes, but this does not affect the generality of the argument.

‡ Criteria for establishing whether the motion of molecules in liquids occurs by diffusion or in jumps were defined in Ref. 24.

corresponding orientation coefficients $a = \Delta D_1/DF^2$, which contain the contribution ΔD_1 isolated from the overall electrochromism spectrum by the method described above. The proportion of free molecules σ was obtained by comparing the intensities of the electrochromism spectra of the probe (II) in the rubbers and in benzene. It may be supposed *a priori* that the ratio a/σ of the values in Table 1 should be constant for all the rubbers: in fact, the relative variation in the ratio is ~3%, which supports the general physical significance of a and σ.

It was of interest to establish the relation between rotational and translational diffusion of probe molecules in polymeric media. A method was therefore devised for studying translational diffusion by measuring rates of crystallisation of the probes from polymeric media[25]. Table 1 gives true crystallisation rate constants k_{tr}, which characterise the translational mobility and must be compared with the orientational coefficients or the proportions of free molecules σ. The comparison reveals no correlation between parameters characterising slow rotational and translational diffusion for the probe (II) in the rubbers at room temperature.

V. INVESTIGATION OF VITREOUS STATE OF AMORPHOUS POLYMERS BY LINEAR ELECTROCHROMISM

When a specimen is subjected to the simultaneous action of two electric fields—an alternating field $\bar{F}\sin\omega t$ and a constant field $\bar{F}_0$—the resultant field $\bar{F}\sin\omega t + \bar{F}_0$ produces in quadratic electrochromism effects proportional to

$$\bar{F}^2\sin^2\omega t + 2\bar{F}\bar{F}_0\sin\omega t + \bar{F}_0^2 = -1/2\bar{F}^2\cos 2\omega t + 1/2\bar{F}^2 + 2\bar{F}\bar{F}_0\sin\omega t + \bar{F}_0^2.$$

The first term defines the quadratic electrochromism considered above; it is observed in the frequency channel 2ω, i.e. at double the frequency of the electric field. The second and fourth terms are responsible for effects independent of the frequency of the field, which can be detected in the channel $\omega = 0$. The third term represents effects that are linear with respect to the alternating field, which are recorded in the frequency channel ω, i.e. at the frequency of the field. Thus the combined action of two fields produces electrochromism effects that are recorded in different frequency channels and have several specific features. By superposing the fields $\bar{F}\sin\omega t + \bar{F}_0$ we can investigate all the electrochromism effects discussed already—Eqns. (4) and (7)—but examination of the ΔD_2 effect is of especial interest for determining molecular mobility. This effect has a dual nature (Fig. 2*c*): one component factor $\Delta\bar{\mu}\bar{F}$ is due to the linear Stark effect, and the other $\bar{\mu}_g\bar{F}/kT$ to the degree of anisotropy in the directions of dipole moments resulting from the action of the same electric field $\bar{F}$. Anisotropy can in principle be produced by the additional independent constant field $\bar{F}_0$. The formula for the effect that is linear with respect to the field can then be written for $\theta = 55°$ in the form

$$\Delta D_2^l = \frac{1}{3}\frac{\bar{\mu}_g\bar{F}_0}{kT}\frac{\Delta\bar{\mu}\bar{F}}{hc}\bar{\nu}\frac{\partial(D/\bar{\nu})}{\partial\bar{\nu}}. \qquad (8)$$

Elongated probe molecules having $\bar{\mu}_g$ and $\Delta\bar{\mu}$ of a few Debyes and the angles $\gamma = 0$ and $\delta = 0$ are usually chosen for the investigation of molecular mobility. With $\theta = 55°$ the orientation effect ΔD_1^l is not observed, while ΔD_3^l and ΔD_4^l are small in comparison with ΔD_2^l. The ΔD_2^l effect therefore predominates, and the contributions by other effects can be neglected. It has been suggested[2,3,26] that linear electrochromism can be used to investigate very slow relaxation processes in vitreous polymers. For this purpose a procedure was devised in which a polymer specimen into which probes had been introduced was heated above the glass point and placed in an alternating field $\bar{F}$. Only quadratic electrochromism at frequency 2ω can then be observed: no linear effect is observed at the frequency of the field $\bar{F}$. If at the same time a constant field $\bar{F}_0 = 10^3$–10^4 V cm^{-1} is applied to the specimen, anisotropy appears in the directional distribution of dipoles $\bar{\mu}_g$, observation of the linear effect for molecules oriented by the constant field becomes possible, and a linear electrochromism signal is produced.

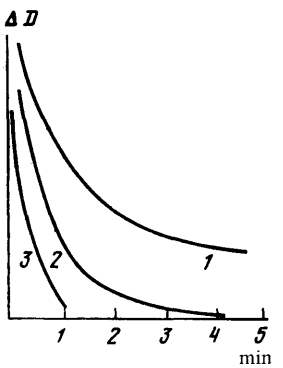


Figure 7. Kinetic curves for the decay of the linear electrochromism signal of (II) in polystyrene at (°C): 1) 78; 2) 85; 3) 99.

The specimen can then be cooled below the glass point (to the experimental temperature) without removal of the constant field $\bar{F}_0$; this freezes the rotational mobility, after which the constant field is removed. At the instant at which the field $\bar{F}_0$ is switched off the anisotropy begins to disappear at a rate depending on the molecular mobility in the medium at the experimental temperature; at the same time the linear electrochromism signal becomes weaker. In liquid solvents of low molecular weight this signal disappears almost instantaneously when the constant field is switched off. In polymeric plastics with sufficiently dense packing at temperatures below the glass point it remains for a long time[2]. The variation in the linear electrochromism signal with time gives a kinetic curve characterising the dynamics of molecular movements in the medium (Fig. 7).[26] One of the most interesting experimental results is the discrete spectrum of relaxation times of molecular motions in vitreous polystyrene, poly(methyl methacrylate), and poly(vinyl acetate) with substantially different characteristic times. The corresponding processes can easily be separated by a simple method based on isolating the straight segment in the terminal regions of the kinetic curves plotted in the semi-logarithmic coordinates $\ln\Delta D$ against time on the assumption that all the relaxation processes forming the spectrum begin simultaneously at the instant the field $\bar{F}_0$ is switched off. The first component $\Delta D'$ isolated in this way, with the longest relaxation time τ', is subtracted from the overall spectrum, and the procedure is repeated for the difference $\ln(\Delta D - \Delta D')$; and so on, until the whole kinetic curve has been exhausted[27].

To estimate the lower frequency limit to the determination of relaxation times by means of linear electrochromism we assume the possibility that a specimen can exist with an infinitely long relaxation time, in which the anisotropy of the directional distribution of dipole moments of probes always remains the same. Theory shows that this case corresponds to a linear electrochromism signal that remains unchanged with time. It is evident from this example that the method has no lower frequency limit. A polystyrene specimen containing the probe (III) exhibited a linear electrochromism signal at room temperature for a month, after which observation was discontinued[2]. Calculation showed that the decay process corresponded to a mean relaxation time of about 2 weeks or 10^6 s. The most rapid processes that can be observed with our apparatus (see below) have relaxation times of a few seconds (this limit is determined by the time constant of the recording instrument). Table 2 gives relaxation times τ for three exponential processes isolated from the kinetic curves, together with their contributions δ, at various temperatures. These data can be used to calculate energies corresponding to the two slowest processes, by means of the equation

$$\tau = \tau_0 \exp(-\Delta E/kT),$$

which gives for ΔE_1 and ΔE_2 the respective values 1.87 and 0.78 eV. These quantities are difficult to interpret, since information on the mechanisms of relaxation processes in vitreous media is extremely limited. From Table 2 it can be concluded that the structure of the spectrum of relaxation times changes with rise in temperature, in such a way that the contribution by rapid relaxation processes increases, while that by slow processes diminishes. Analogous changes in spectra of relaxation times are observed in the plasticisation of specimens[2].

Table 2. Relaxation times τ (s) and contributions δ of rotational motions of *p*-dimethylamino-*p'*-nitrostilbene in polystyrene at various temperatures, isolated from the relaxation-time spectrum.

t, °C	τ_1	δ_1	τ_2	δ_2	τ_3	δ_3
71	4800	0.18	445	0.23	160	0.08
78	1620	0.145	160	0.23	30	0.15
84.5	525	0.11	45	0.20	—	—
88.5	240	0.12	24	0.18	—	—
90	188	0.095	20	0.11	—	—
92.5	40	0.10	—	—	—	—
94	15	0.09	—	—	—	—

VI. EXPERIMENTAL PROCEDURE

The electrochromism of molecules having large dipole moments in ground and excited states can be detected with a mass-produced spectrophotometer designed for chemical analysis using electric fields of limiting permissible strength $\sim 10^6$ V cm^{-1}.[28] This method is completely unsuitable for recording electrochromism spectra in the most common cases, in which the signals do not exceed 10^{-4}–10^{-5} unit of optical density. Several types of equipment have been described for special purposes, mainly for investigating excited states of molecules[29]. An idea of the simplest apparatus for recording electrochromism spectra in the investigation of molecular mobility in polymers can be found in a previous paper[30]; an improved form will be described below, together with the procedure.

1. Preparation of Specimens

Probes are introduced into linear polymers—plastics and rubbers—by dissolving the latter in a suitable solvent, e.g. benzene, and mixing the resulting solution with a solution of the probe dye in the same solvent[28]. The relative volumes of the solutions are so chosen that specimens having a dye content of 10^{-3}–10^{-4} mole per 1000 g polymer are obtained after the solvent has vaporised. Firstly the solvent evaporates from a Petri dish at room temperature, and then the coloured film is dried in a vacuum drying vessel at 50–60°C for 24 h. Under these conditions benzene is completely removed from the polymer, as can be checked from the electrochromism spectra (Fig. 4). Films having plane-parallel surfaces are formed by placing the coloured mass between small sheets of pure transparent mica free from cracks, air bubbles, or foreign inclusions. The sheets are separated by gaskets 100 μm thick located along the edges of the sheets, and are compressed in a press heated to 100–110°C. On softening, the polymer fills the space between the mica sheets and bonds to them firmly. The mica prevents the films from buckling and determines the breakdown voltage of the specimen. The coloured film together with the mica sheets is glued by means of an epoxy-resin between transparent ground-glass electrodes 20 × 20 mm in size. A conducting coating is obtained by depositing tin dichloride vapour on the glass surfaces heated to 400–420°C.[31]

2. Apparatus for Recording Electrochromism Spectra

The probe molecules chosen for studying molecular mobility in polymers are dyes, whose absorption spectra are located in the visible spectrum. Therefore an overrun lamp *1* (Fig. 8) was used as source, the luminous flux from which was stabilised by using a device *2* to stabilise the current. The polychromatic light from the lamp is directed to the inlet slit of a monochromator *3*, the ray first passing through a light modulator *4*, which is necessary to record the action spectra of the apparatus (the modulator is disconnected for the determination of electrochromism spectra). The monochromatic light passes through an inclined quartz plate to balance the inherent polarisation of the monochromator (not shown in Fig. 8), and then falls on the Polaroid film *5*. The polarised monochromatic light is directed on the specimen *6* placed in a thermostat *7* filled with mineral oil as heat-transfer agent. The temperature of the specimen can be varied from 20 to 150°C and maintained constant to 0.5 deg by means of a thermostatic unit *8* connected to an electric heater immersed in the thermostat and provided with a resistance thermometer. The light ray emerging from the specimen, modulated to an extent of 10^{-4}–10^{-5}, falls on a photocell *9* placed in a detachable photometric head *10*. The electric signal is fed to the input of the low-frequency amplifier *11*, which has an amplification band of 420 Hz with band-width 0.8 Hz and amplification factor 12000. The amplified signal reaches the phase-sensitive detector *12* and the oscillograph *13*; the latter is designed

to record the most intense electrochromism signals, but is used mainly to observe the noise in the apparatus. From the phase-sensitive detector the signal enters an *RC* circuit (not shown in the diagram), which determines the time constant of the system, and then the input of a direct-current amplifier *14* followed by the pen-recorder *15*. The motion of the chart of *17* is synchronised with the spectrum-scanning device *16*.

An alternating voltage of frequency 210 Hz is fed from an oscillator *18* through a step-up transformer *19* to the specimen. By controlling the output of the oscillator the voltage on the specimen can be varied over the range 0–2 kV. Linear electrochromism effects are observed at the field frequency ω, but quadratic effects at the doubled frequency 2ω. In order to be able to use in both cases the same amplifier tuned to the frequency 420 Hz, the field frequency was set at 210 Hz for the investigation of quadratic effects. As a consequence, measurement of such effects required that the frequency of the reference signal should also be doubled, which was achieved by means of the unit *20*. In the investigation of linear effects the frequency doubler *20* was disconnected. The signal of the reference voltage is fed through the phase shifter *21* to the phase-sensitive detector *12*. In the investigation of linear electrochromism a constant voltage from a high-voltage source *22* is superimposed on the alternating field on the specimen.

The field-modulated luminous flux is

$$I_F = I_0 T T' T_F,$$

where I_0 is the luminous flux incident on the specimen, T the transmission of light by the specimen, T' the light losses due to the cuvette, and T_F the transmission of light by the specimen that is due to the action of the field $\bar{F}$. Expanding T_F as a series and retaining only the first two terms in view of the smallness of $\Delta D'$, we obtain

$$T_F = e^{-\Delta D'} = 1 - \frac{\Delta D'}{1!} + \frac{\Delta D'^2}{2!} - \ldots;$$

on passing to a decadic base, we find that

$$I_F = I_0 T T' - 2{,}3 I_0 T T' \Delta D.$$

The first term is a constant component of the luminous flux, which is not recorded by the instrument. The second term includes the alternating unknown quantity ΔD, whose variation with wavelength gives the electrochromism spectrum.

The luminous flux I_0 depends on the action spectrum of the apparatus, which must be corrected for. However, it is more expedient to correct not the incident but the transmitted luminous flux, thereby allowing for the transmission both of the specimen and of the cuvette. Two methods are employed for this purpose[26].

1. In order to correct the form of the electrochromism spectra the luminous flux of the instrument with the specimen fitted in it is modulated by means of a light chopper with the electric field switched off. The signals from the chopper are recorded on the pen-recorder chart as a function of wavelength. This involves switching the unit *12* from a phase-sensitive to an amplitude detector. A particular wavelength is then selected within the electrochromism spectrum, the chopped signal at which is taken to be unity, and signals obtained at other wavelengths are normalised to this value. The true form of the electrochromism spectrum is obtained by dividing its ordinates by the normalised values of the chopped signals at corresponding wavelengths. Such plots can be used in most cases in investigating molecular mobility on specimens for which the relative intensities of the electrochromism spectra are quite high. Absolute increases in optical density can be found by comparing the electrochromism spectrum of the test substance with that of a standard substance recorded under the same conditions. *p*-Dimethylamino-*p'*-nitrostilbene, for whose molecules the parameters of ground and excited states are well known, has been used as standard in our work.

2. The electrochromism spectrum is drawn through points obtained at 10–15 selected wavelengths. The specimen is placed in the instrument, and the light chopper is switched on with the field switched off. For all these wavelengths monochromator slit widths are then selected to correspond to signals having the same amplitude. The slit openings thus found are then used in determining the electrochromism spectrum, which will give directly ordinates of the corrected spectrum. Absolute values of the signals are found, as in the first method, by comparison with the electrochromism spectrum of a standard substance.

3. Measurement of the Angle θ

The specimen is fixed in the thermostatted cuvette at an angle to the luminous flux (Fig. 9) such that the angle between the surface of the specimen and the direction of

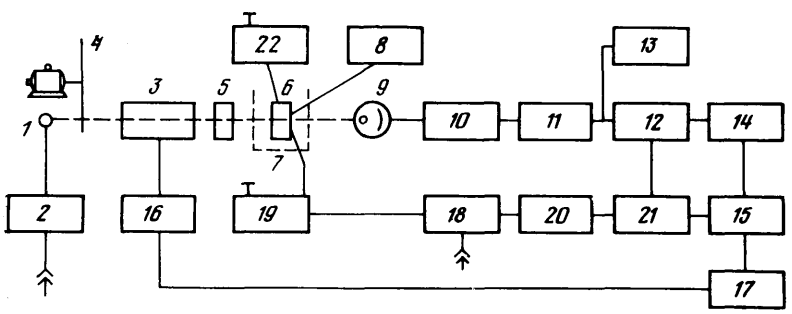


Figure 8. Block diagram of apparatus for recording electrochromism spectra (key in text).

the ray in the test medium is 54°44′ ≈ 55°. With the light polarised in a vertical plane the angle between the vectors $\bar{e}$ and $\bar{F}$ is then $\theta = 90°$, but with horizontal polarisation this becomes 55°.

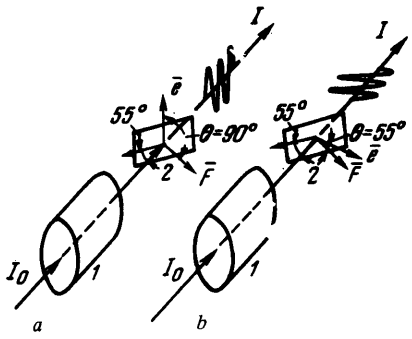


Figure 9. Diagram illustrating the variation of the angle θ as the Polaroid is rotated: 1) Polaroid; 2) specimen; $\bar{e}$) unit vector in direction of electric vector of light wave; I_0), I) luminous fluxes; *a*) vertically polarised light; *b*) horizontally polarised light.

The direction of light in the medium depends on the ratio of the refractive indices of the medium and of the oil filling the thermostat. If the refractive indices differ greatly, the angle at which the specimen is fitted must be corrected.

---o0o---

The above survey shows that the study of electrochromism will yield important information on movements in polymer molecules. The method can be developed firstly to investigate proper motions of fragments of macromolecules containing chromophores absorbing in the visible and ultraviolet, when the need for interpretation of indirect results obtained by the probe method is eliminated. A second development would be to record spectra of relaxation times of molecular movements, which can be obtained with wide variation in the frequency of the electric field and by means of the quadratic electrochromism spectrum or by analysis of kinetic curves from linear electrochromism spectra. The value of relaxation-time spectra lies in their relationship both to the motion of definite groups of atoms and to the thermodynamic properties of the medium, i.e. the properties of polymeric materials.

REFERENCES

1. W. Liptay, in "Modern Quantum Chemistry" (Translated into Russian), Mir, Moscow, 1967, Vol. 1.
2. L. A. Blyumenfel'd, F. P. Chernyakovskii, V. A. Gribanov, and N. M. Kanevskii, J. Macromolec. Sci. Chemistry, **6A**, 1201 (1972).
3. I. M. Kanevskii, V. A. Gribanov, F. P. Chernyakovskii A. V. Ryazanova, and L. A. Blyumenfel'd, Zhur. Fiz. Khim., **45**, 421 (1971) [Russ. J. Phys. Chem, No. 2 (1971)].
4. V. A. Gribanov, I. M. Kanevskii, F. P. Chernyakovskii, and L. A. Blyumenfel'd, Zhur. Fiz. Khim., **45**, 1575 (1971) [Russ. J. Phys. Chem., No. 6 (1971)].
5. A. L. Buchachenko and A. M. Vasserman, "Stabil'nye Radikaly" (Stable Radicals), Khimiya, Moscow, 1973.
6. A. N. Kuznetsov, "Metod Spinovogo Zonda" (Spin Probe Method), Nauka, Moscow, 1976.
7. W. Kuhn, H. Durkop, and H. Martin, Z. phys. Chem., B45, 121 (1939).
8. H. Labhart, Chimia (Switz.), 15, 20 (1961).
9. J. Czecalla, Chimia (Switz.), 15, 26 (1961).
10. W. Liptay and J. Czecalla, Z. Naturforsch., 15a, 1072 (1960).
11. H. Labhart, Adv. Chem. Phys., 13, 179 (1968).
12. H. Fröhlich, "Theory of Dielectrics" (Translated into Russian), Inostr. Lit., Moscow, 1960.
13. W. Liptay, in "Excited State", edited by E. C. Lim, Academic Press, New York, 1974, Vol. 1.
14. W. Liptay, Ber. Bunsengesell. phys. Chem., 80, 207 (1976).
15. H. Labhart, Ber. Bunsengesell. phys. Chem., 80, 240 (1976).
16. V. A. Gribanov and F. P. Chernyakovskii, Uch. Zap. Yaroslavsk. Tekhnol. Inst., 22, 42 (1971).
17. L. M. Blinov and N. A. Kirichenko, Fiz. Tverd. Tela, 12, 1574 (1970).
18. M. Kriszevski and B. Nadolsky, J. Polymer Sci., Part A-1, Polymer Chem., 13, 345 (1975).
19. L. M. Blinov, Doctoral Thesis, Institute of Crystallography of the USSR Academy of Sciences, Moscow, 1977.
20. S. H. Autler and C. H. Townes, Phys. Rev., 100, 703 (1955).
21. V. A. Gribanov, Candidate's Thesis, Institute of Chemical Physics of the USSR Academy of Sciences, Moscow, 1971.
22. G. Crank and G. S. Park, (Editors), "Diffusion in Polymers", Academic Press, London, 1968.
23. C. P. Smyth, in "Fizika i Khimiya Tverdogo Sostoyaniya Organicheskikh Soedinenii" (Physics and Chemistry of the Solid State of Organic Compounds) (Translated into Russian), Mir, Moscow, 1967.
24. K. A. Valiev and A. Sh. Agishev, Optika i Spektrosk., 16, 881 (1964).
25. V. A. Gribanov and F. P. Chernyakovskii, Teor. Eksper. Khim., 7, 559 (1971).
26. I. M. Kanevskii, Candidate's Thesis, Yaroslavl Institute of Technology, 1973.
27. V. E. Gul' and V. N. Kuleznev, "Stroenie i Mekhanicheskie Svoistva Polimerov" (Structure and Mechanical Properties of Polymers), Vysshaya Shkola, Moscow, 1966.
28. Y. Kumamoto, J. C. Powers, and W. R. Heller, J. Chem. Phys., 36, 2893 (1962); J. C. Powers, W. R. Heller, Y. Kumamoto, and W. E. Donath, J. Amer. Chem. Soc., 86, 1004 (1964).
29. H. Labhart, Tetrahedron, 19, 223 (1963); S. Schmidt and R. Reich, Ber. Bunsengesell. phys. Chem., 76, 559 (1972).
30. V. A. Gribanov, I. M. Kanevskii, F. P. Chernyakovskii, and L. A. Blyumenfel'd, Dep. VINITI 2724-71 (1971); Zhur. Fiz. Khim., 45, 1575 (1971) [Russ. J. Phys. Chem., No. 6 (1971)].
31. R. Gomer, Rev. Sci. Instr., 24, 993 (1961).

Yaroslavl Polytechnic Institute