Γ_i whilst N decreases. A decrease in N with Γ_i once again leads to a decrease in K_1, but with readily adsorbed substances the separation is improved more substantially than with weakly adsorbed materials if Γ_i is increased, *e.g.* the temperature is decreased, or the film thickness is increased.

The analysis and the results which have been presented demonstrate that a correct choice of method and of experimental parameters must involve both the static and the kinetic aspects of the separation criteria, which often present conflicting requirements.

To maximise the separation criterion certain conditions have to be fixed. A fixed analysis time is perhaps the commonest practical requirement, but we have considered the more general case in which limitations are imposed on the resistance to flow as well as on the time of the analysis.

For a fixed analysis time the separation criterion increases to a limiting value with flow rate. If the resistance to flow is fixed, the criterion decreases with flow rate to some other optimum value. High flow rates are desirable in the former case, low rates in the latter. The kinetic characteristics of the column are determined, in the two cases, by inner diffusion and by longitudinal diffusion, respectively.

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THE DIELECTRIC INVESTIGATION OF MOLECULAR RELAXATION IN POLYMERS

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CONTENTS

I. Introduction 386

II. Effect of structure of polymer chains on molecular relaxation 388

1. Copolymers of methyl methacrylate and methyl acrylate with styrene 388

2. Comparison of relaxation properties of atactic and isotactic polymers 391

3. Polyesters 392

III. Effect of structure of monomer unit on the molecular relaxation of polymers 393

I. INTRODUCTION

Owing to the structural peculiarities of polymers, molecular relaxation, a process representing the establishment of a statistical equilibrium, is one of the main factors determining their mechanical, electrical, and other properties [1].

The literature now contains a great deal of experimental data on the investigation of relaxation processes in polymers by both dielectric and mechanical methods, on the basis of which several conclusions can be reached about the nature and the mechanism of relaxation. This is done by comparing the structure of macromolecules with the temperature and the frequency dependence of the dielectric and the mechanical losses, characterised by the tangent of the loss angle, tan δ, and by the dielectric permittivity ϵ' (or by the elastic modulus in the case of the mechanical properties).

High polymers are characterised by the occurrence of several processes of molecular relaxation, which are due to the thermal motion of different types of kinetic units, which may be portions of the main chain of the polymer (segments), side-radicals, or simply certain groups of atoms, that behave as independent units in the thermal motion. All such kinetic units can be described by their most probable relaxation time τ; units of a single type, which have complicated molecular interactions with their environment, can yield a spectrum of relaxation times. At the present time, however, no rigorous theory of molecular relaxation in polymers yet exists. Therefore the only method for arriving at general conclusions is to compare the structure of the polymer with the above properties.

A peculiarity of relaxation observed by the dielectric method is that the energy of the electric field applied to a polymer specimen is dissipated mainly in relaxation regions containing polar groups. Dipoles taking part in thermal motion acquire a preferential orientation in the direction of the electric field. As a result, two maxima usually appear in the frequency (or temperature) variation of tan δ for polymers. The dielectric permittivity also undergoes marked changes, increasing with rise in temperature and falling with increase in frequency.

Molecular relaxation, observed by the method of dielectric losses and polarisation, may be divided into two main types – the relaxation of polar radicals or of a polar monomer unit of the macromolecule, and relaxation of these same polar radicals together with portions of the main chain, *i.e.* the relaxation of segments[1]. This has been established for polymers of very different structures, linear and branched, containing rings in the chain, partly crystalline or completely amorphous (for example, polymers of vinyl chloride, methyl methacrylate, and its homologues, methyl acrylate and its homologues, cellulose esters, carbonates, amides, etc.).

In most papers on dipole dielectric losses the view is developed that one type of relaxation, due to the mobility of polar side-radicals or, in conformity with the terminology which we have adopted, to dipole–radical losses, can occur only within a definite temperature range corresponding to the vitreous state of the polymer, whereas a second type, so-called dipole–elastic losses, occurs only in polymers above the embrittlement point T_c. This is probably because the frequencies commonly used to measure tan δ and ϵ' correspond to relaxation times τ of dipole–radical losses at temperatures below T_c and to those of dipole–elastic losses above T_c. In the case of poly(methyl methacrylate), however, we have been able to observe dipole–radical losses at a frequency of 5 Mc/s at 190°, *i.e.* 85° above T_c.[2,3]

It can thus be accepted that dipole–radical losses are not peculiar to relaxation in the vitreous state of polymers, but, as was to be expected, can be observed in the rubber-like state if the period of the applied field is comparable with the relaxation time of these types of losses at the given temperature.

Nevertheless, with several polymers (the halogenated styrenes) it has not yet been possible to detect any appreciable dipole–radical losses at frequencies between 10 and 10^{10} c/s.[4] The molecular forces due to interaction between the benzene rings are apparently so strong that there is hardly any orientation of the CCl dipole in an electric field within this temperature and frequency range.

This hypothesis is supported by relaxation data obtained by the dielectric loss method by Müller and Huff with stretched polystyrene films, for which dielectric losses having maxima were observed below T_c.[5] The stretching of polystyrene opens up the structure of the polymer, thereby increasing the mobility of the phenyl groups.

Thus the dipole–radical losses observed in high polymers represent that type of molecular relaxation which is due to movement of polar side-groups while the main chain remains fixed during the time of observation (*i.e.* during a time comparable with the period of oscillation of the applied field). This determines the characteristic laws of dipole–radical losses. For example, the position of tan δ_{max} (or ϵ''_{max}) for different temperatures and frequencies for losses of this type is independent of the presence of impurities of low molecular weight (external plasticisers)[6], and also of the stretching of the specimen[7]. Internal plasticisation (copolymerisation) may, as will be shown below, give different effects depending on how the mobility of the polar side-group is changed.

If the period of the applied field is sufficiently long, dipole–elastic losses due to movement of portions of the main chain together with the polar attachments, *i.e.* to segmental thermal motion in the polymer, can be observed at certain temperatures. The laws characteristic of this type of loss will, of course, be determined by the relaxation behaviour of a corresponding set of kinetic units (segments), which cannot be very long. Willbourn has shown that, in the case of linear polymers, a segment can consist of 3 or 4 methylene groups[8]. No essential differences arose in the study of relaxation processes in branched and in unbranched polymers[9]. This also suggests that the kinetic units are considerably shorter than the distances between the points at which branching occurs, so that the latter have no effect on the mobility of the segments.

The position of tan δ_{max} for dipole–elastic losses as a function of frequency and temperature is greatly affected by the introduction of substances of low molecular weight, the relaxation time of the process being reduced. Cross-linking of the macromolecules has the opposite effect, impeding their movement and increasing the relaxation time of the dipole–elastic losses[10,11].

According to the few published data, the stretching of polymer specimens, which leads to orientation of the main chains, increases the relaxation time for the dipole–elastic losses[7], but this is probably not a general rule. The work of Kargin and Slonimskii[12] shows that under certain conditions stretching loosens the polymer structure, increases intermolecular distances, and weakens the interactions[12]. In such cases the relaxation times of the processes should fall.

Change in the chemical structure of the monomeric unit in the polymer chain has a still greater effect on the dipole–elastic than on the dipole–radical losses. Introduction both of polar and of non-polar groups, which may be added either directly to the main chain or to the side-group, is of importance here.

Hoff *et al.*[13] have made this type of observation on a series of polymethacrylates. Deutsch *et al.*[14] have shown that replacement of an α-methyl group is poly(methyl methacrylate) by a polar group such as Cl, which occupies about the same volume, retards the segmental motion of the macromolecules to a still greater extent. Polar effects are intensified when CH_3 is replaced by CN. Increase in the length of the side-group, also contributes to an increase in mobility of the chain segments by diminishing the molecular interaction. For successive members of a homologous series, the region in which tan δ for dipole–elastic losses passes through a maximum is systematically shifted to lower temperatures.

Recently great attention has been paid to the examination of the spectrum of relaxation times in the mechanical and dielectric study of relaxation processes. Here must be mentioned in the first instance the work of Ferry and his collaborators[15,16]. The method of reduced variables, suggested by Ferry, Williams, and Landel, enables the distribution of τ to be calculated.

Unfortunately, the range of application of this method is limited to cases in which the form of the distribution function for τ does not change with temperature – this is its chief premise. Our work has shown that, at a given temperature, at least two relaxation processes may occur in a polymer, which are caused by the presence of two independent sets of units with their own relaxation times[2,3].

The temperature coefficient of relaxation, or, as it is usually called, the apparent activation energy, can differ almost tenfold for the two processes. As a result, the distribution spectra of relaxation times for the two processes may approach one another and overlap in a certain

temperature–frequency range. In this region, of course, the relation $\epsilon'' = \varphi(t\,^\circ)$ will continuously change its form with variation of temperature, thus making it impossible to apply Ferry's method. Such a situation is observed with polymers of homologous series of alkyl methacrylates and chlorinated alkyl acrylates, poly(methyl acrylate), poly-(vinyl acetate), [17] etc.

In this case the formal theory of Cole and Davidson[18] can be used to resolve the partly superposed processes and to examine them separately.

II. EFFECT OF STRUCTURE OF POLYMER CHAINS ON MOLECULAR RELAXATION

1. Copolymers of Methyl Methacrylate and Methyl Acrylate with Styrene

The influence of chain structure on molecular relaxation is clearly shown in the dielectric properties of copolymers. By varying the percentage of one of the components in the copolymer, it is possible to change both the flexibility of the chain and the nature of the molecular interaction.

We shall describe results obtained in an investigation of dielectric losses and polarisation in copolymers of methyl methacrylate (MMA) with styrene (ST)[19] and of methyl acrylate (MA) with styrene[20].

Figs.1 and 2 illustrate respectively the relationships $\tan\delta = \varphi(t\,^\circ)$ at a frequency of 20 c/s for MMA–ST copolymers of four concentrations by weight, and the functions $\tan\delta = \varphi(f)$ for a few copolymers of MMA with different styrene contents. In this temperature and frequency range, all specimens exhibit two regions of molecular relaxation where $\tan\delta$ passes through a maximum.

In conformity with the accepted terminology, dielectric losses at temperatures below T_c (≈ 110° for PMMA) must be regarded as dipole–radical losses, while those observed above the temperature of vitrification and caused by relaxation of the polymer chain are termed dipole–elastic losses.

Fig.2 shows that the plots of $\tan\delta = \varphi(f)$ also exhibit two regions in which $\tan\delta$ passes through a maximum, the high-frequency part of the curves being associated with dipole–radical losses, and the low-frequency portion with dipole–elastic losses. These results, like those of several other investigations, show that dipole–radical processes are by no means peculiar to the vitreous state of polymers, but under suitable experimental conditions can be observed also in polymers which are in the rubberlike state.

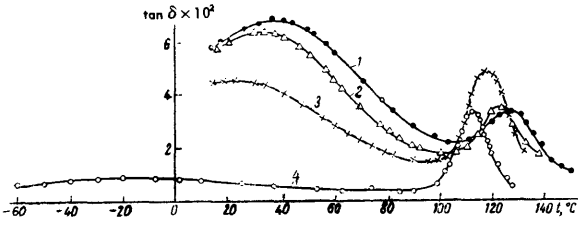


Fig. 1. Plots of $\tan\delta = \varphi(t^\circ)$ at a frequency of 20 c/s for MMA–ST copolymers containing different proportions of MMA: 1) 100%; 2) 93.3%; 3) 80.5%; 4) 24.4%.

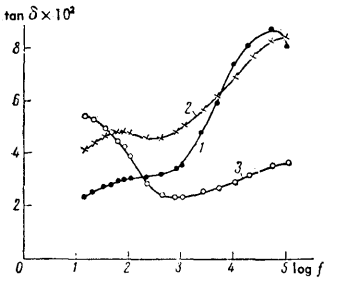


Fig. 2. Plots of $\tan\delta = \varphi(f)$ for MMA–ST copolymers:
1) 90.2% MMA, 125°; 2) 80.5% MMA, 122.5°;
3) 55.5% MMA, 109°.

Figs.1 and 2 show also that the regions of $\tan\delta_{max}$ are displaced to lower temperatures (Fig.1) or to higher frequencies (Fig.2) as the proportion of the polar MMA in the copolymer is decreased. The latter observation confirms that the relaxation times τ of both processes decrease when the concentration of the polar component is reduced.

Figs.3 and 4 give plots of $\log f_m = \varphi(T^{-1})$ for a series of copolymers of styrene containing different amounts of methyl methacrylate, f_m being the reciprocal $(2\pi\tau)^{-1}$ and T the absolute temperature. Fig.3 represents dipole–radical relaxation, and Fig.4 dipole–elastic relaxation.

Table 1 lists activation energies for dipole–radical processes obtained from the slopes of the straight lines in Fig.3. It can be seen that the value of $U_{d.r.}$, the activation energy for dipole–radical relaxation, increases as the percentage of MMA is raised.

It is extremely difficult to obtain an analogous concentration dependence for the activation energies of the dipole–elastic processes, since in many cases the true position of $\tan\delta_{max}$ for the corresponding losses is distorted by the partial superposition of the region of dipole–radical relaxation. It is quite certain however, that for all polymers the slope of the straight line $\log f_m = \varphi(T^{-1})$ has no physical

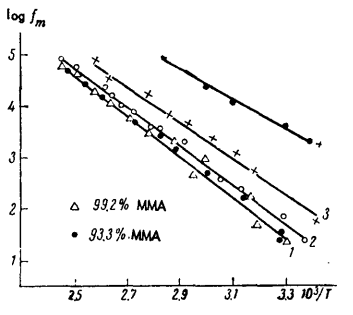


Fig. 3. Plots of $\log f_m = \varphi(T^{-1})$ for dipole–radical losses in MMA–ST copolymers containing different proportions of MMA:
1) 99.2% and 93.3%; 2) 90.2%; 3) 80.5%; 4) 55.5%.

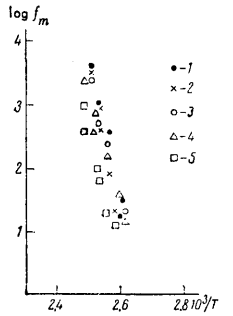


Fig. 4. Plots of log $f_m = \varphi(T^{-1})$ for the dipole–elastic process in MMA–ST copolymers containing different proportions of MMA: 1) 18%; 2) 24.4%; 3) 40.5%; 4) 55.5%; 5) 80.5%.

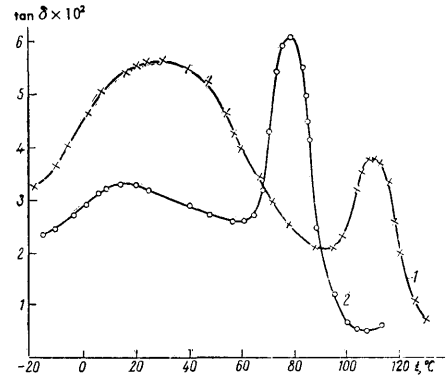


Fig. 5. Plots of tan $\delta = \varphi(t°)$ at a frequency of 20 c/s for MMA–MA copolymers having the approximate MMA contents: 1) 80%; 2) 50%.

TABLE 1. Activation energy $U_{d.r.}$ of dipole–radical processes.

% MMA	55.5	80.5	90.2	93.3	99.2
kcal mole^{-1}	13.4	16.2	17.5	17.7	18.3

meaning as regards dipole–elastic losses, since it corresponds to energies of the order of 100 kcal mole^{-1}. Shishkin[21] has shown that the slope of this plot represents not an activation energy but the temperature coefficient of the relaxation frequency. This remark applies also to dipole–radical losses, but the temperature coefficient in this case has not such a high value, and therefore, within the limits of error, the slope of the straight line log $f_m = \varphi(T^{-1})$ can be taken as the activation energy of the corresponding relaxation process.

On relating the results thus obtained to the structure of the copolymers under investigation, we conclude that, if τ is a measure of the mobility of kinetic units, this mobility increases with increasing concentration of styrene in the copolymers for both relaxation processes. With dipole–elastic losses this effect is less distinct (Fig. 4), since the temperature of vitrification of polystyrene is only 20°–30° lower than that for poly(methyl methacrylate).

A feature of the structure of poly(methyl methacrylate) is the presence of an α-CH_3 group, which causes steric hindrance to the development of relaxation processes. Introduction of styrene links diminishes the concentration of methyl groups in the chain, thereby increasing the mobility of the kinetic units corresponding to both dipole–radical and dipole–elastic relaxation.

This can be proved by results obtained for dielectric losses in MMA–MA copolymers. Fig. 5 shows that, as the concentration of methyl groups decreases, the value of tan δ_{max} for dipole–radical losses falls, and its position is displaced to lower temperatures. The magnitude of tan δ_{max} for dipole–elastic losses increases as the chain becomes increasingly mobile due to the reduction in the proportion of the α-methyl groups. Thus the introduction of styrene links into the PMMA chain and replacement of a proportion of the α-CH_3 groups in this polymer by hydrogen atoms produce qualitatively the same effect.

We suppose that intermolecular interaction is predominant in the case of dipole–radical losses. Increase in the styrene content of the polymer chain loosens the structure of the polymer by weakening steric hindrance due to the presence of methyl groups; this causes a decrease in the relaxation times and in the activation energy (Table 1).

With dipole–elastic losses the relaxing chain segment consists of monomeric styrene and methyl methacrylate links randomly distributed in the copolymer. Study of the effective dipole moments of the monomeric units has shown that intramolecular interaction predominates with dipole–elastic relaxation[22]. As the styrene content of the copolymer chain increases, therefore, this form of molecular interaction will be increasingly determined by the structure of the styrene, not the methyl methacrylate, monomeric unit.

Since the probability of finding styrene units in neighbouring links in the chain and in the space around the segment is greater at low MMA concentrations, the intramolecular interaction of the phenyl radicals is evidently weaker than that of the methyl methacrylate monomeric units.

It can be seen from Fig. 6 that tan δ_{max} for dipole–elastic losses passes through a maximum when the copolymer contains 60% of MMA. The appearance of this maximum can be explained by the action of two opposing factors. The first is the elimination of the steric effect of the α-CH_3, which blocks the movement of the chain. Introduction of styrene links into the macromolecule diminishes the quantity of such retarding units, so that the value of tan δ_{max} increases. Secondly, with decrease in the concentration of methyl methacrylate in the copolymer the number of dipoles per unit volume falls, so that the value of tan δ_{max} also decreases. At MMA contents between 100 and 60 wt.% the decrease in polarity of the polymer chain is masked by the first factor, *i.e.* by the steric effect of CH_3; with further decrease in the number of polar links, the second factor becomes dominant, and tan δ_{max} falls.

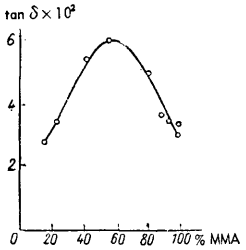


Fig. 6. Values of tan δ_{max} for dipole–elastic losses in MMA–ST copolymers as a function of the MMA content. Frequency 20 c/s.

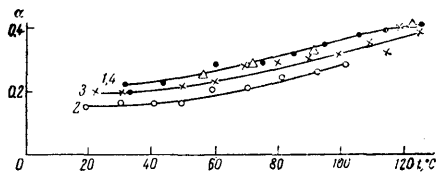


Fig. 7. Dependence of relaxation-time distribution parameter α on temperature for MMA–ST copolymers containing different proportions of MMA:
1) 24.5%; 2) 40.5%; 3) 55.5%; 4) 93.3%.

Recently the hypothesis that polymers are characterised not by a single τ, describing a given relaxation process, but by a set of relaxation times, has been generally recognised. In order to analyse the spectra of τ for molecular relaxation observed in this work, circular diagrams were plotted for the complex dielectric constant[18], and by means of them the distribution parameters α of the relaxation times were calculated.

The value of α defines the width of the spectrum, a value of unity indicating that the process is described by a single relaxation time.

Fig. 7 shows plots of $\alpha = \varphi(t\,^\circ)$, calculated from data for dipole–radical losses, for four copolymers of this type with different compositions. The curves show firstly that the distribution parameter α corresponding to the vitreous state is only about half that for the rubberlike condition. This means that the polymer is more homogeneous in structure in the latter condition. Secondly, α depends on the composition of the copolymer. The higher the concentration of one component, the greater the value of α and the more homogeneous is the structure of the polymer.

Calculations of the distribution parameters α for dipole–elastic losses give a value of the same order as that for dipole–radical losses at temperatures above T_c. It is hard to estimate the variation in the spectrum of relaxation times for dipole–elastic processes because the two relaxation regions overlap at high temperatures. Nevertheless, the basic assumption that the scatter of τ is less and the structure of the polymer is more homogeneous, is confirmed.

Fig. 8 shows plots of tan $\delta = \varphi(t\,^\circ)$ at a frequency of 1 kc/s for copolymers of MA with three different concentrations of styrene. For this copolymer, two regions of dielectric relaxation losses are also observed in which tan δ passes through a maximum. The right-hand maximum is due to dipole–elastic relaxation, while the losses observed on the left-hand portion must be ascribed to dipole–radical relaxation.

This system is characterised by a different law governing the value of tan δ in the region of the maximum: Fig. 9 shows that for dielectric losses of both types, tan δ_{max} increases linearly with the MA concentration within the limits of error of the measurements.

The temperature at which tan δ passes through a maximum does not change with the concentration of the polar

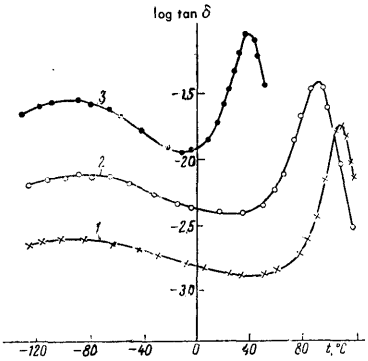


Fig. 8. Plots of log tan $\delta = \varphi(t\,^\circ)$ at a frequency of 1000 c/s for MA–ST copolymers containing different proportions of MA:
1) 14%; 2) 40%; 3) 100%.

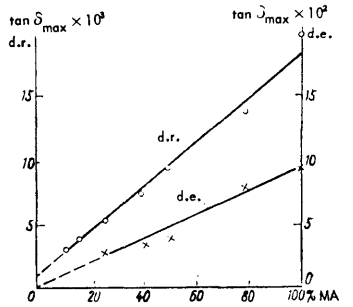


Fig. 9. Values of tan δ_{max} for dipole–radical (d.r.) and dipole–elastic (d.e.) losses in MA–ST copolymers as a function of the MA content. Frequency 1000 c/s.

component in the case of dipole–radical losses, but increases with rise in the styrene content of the chain for dipole–elastic losses.

These results are shown more fully by the plots of $\log f_m = \varphi(T^{-1})$ in Fig. 10. Points representing the dipole–radical process for different compositions of the MA–ST copolymer lie on a single straight line. Consequently the most probable relaxation time τ for this process is independent of the proportion of the polar component. In other words, introduction of styrene does not affect the mobility of the polar group in the side-chain.

Comparison of this result with data for MMA–ST copolymers makes it evident that markedly different effects are produced by the introduction of styrene into MMA and MA chains respectively. In the former case, as already stated, the styrene links open up the structure of the polymer by diminishing the influence of the α-CH_3 groups, and thereby increase the mobility of the side-radical.

Results identical with those for the MA–ST system have been obtained also for the copolymer of methyl vinyl ketone with styrene[20].

2. Comparison of Relaxation Properties of Atactic and Isotactic Polymers

Investigation of molecular relaxation by the dielectric loss method in isotactic poly(methyl methacrylate) and polystyrene has shown that the stereoregularity of the chain has a marked effect on the relaxation properties of polymers[23].

The plots of $\tan\delta = \varphi(t\,^\circ)$ for atactic and isotactic amorphous PMMA at a frequency of 20 c/s in Fig. 11 show that the stereoregularity of structure of the polymer chain affects both dipole–elastic and dipole–radical relaxation processes. The value of $\tan\delta_{max}$ for dipole–elastic losses in isotactic PMMA is three times as great as the corresponding value for the atactic polymer, while the observed dipole–radical losses have become somewhat smaller (by a factor of about 1.4). This results in a change in the distribution of dipole losses characteristic of PMMA: in the isotactic polymer, as in other vinyl polymers, the maximum value of the dipole–elastic losses is greater than that of the dipole–radical losses.

The redistribution of dipole losses in the case of the stereoregular polymer is accompanied by a reduction in the most probable relaxation time for the dipole–elastic process, as is indicated by the shift in the corresponding $\tan\delta_{max}$ region to lower temperatures. From the plots of $\tan f_m = \varphi(T^{-1})$ in Fig. 12, based on temperature and frequency measurements, it is seen that the relaxation time of the dipole–radical process is also somewhat lower in isotactic PMMA than in the atactic polymer.

The activation energy of the dipole–radical process does not change greatly on passing to a polymer having a regular chain, its value being 24 instead of 21 kcal mole^{-1}. As before, the apparent activation energy of the dipole–elastic process remains very high, 138 kcal mole^{-1}, and it can be regarded only as a temperature coefficient of the relaxation time.

Fig. 11 includes also data for a sample of PMMA whose molecules should, from the conditions of polymerisation, have an intermediate degree of regularity. Comparison of plots of $\tan\delta = \varphi(t\,^\circ)$ obtained at the same frequency readily

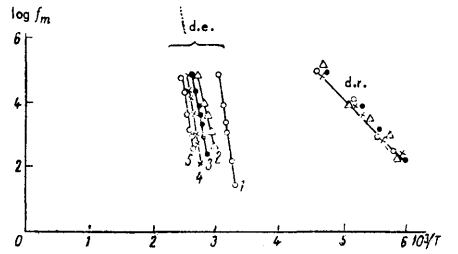


Fig. 10. Plots of $\log f_m = \varphi(T^{-1})$ for dipole–radical (d.r.) and dipole–elastic (d.e.) losses of MA–ST copolymers having different MA contents:
1) 100%; 2) 78%; 3) 49%; 4) 39%; 5) 23%.

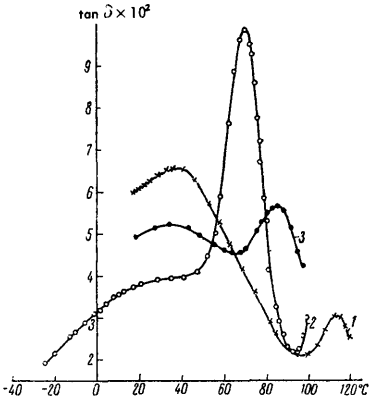


Fig. 11. Plots of $\tan\delta = \varphi(t^\circ)$ at 20 c/s for samples of PMMA having different degrees of stereoregularity:
1) atactic PMMA; 2) with a high degree of regularity (isotactic); 3) with a lower degree of regularity.

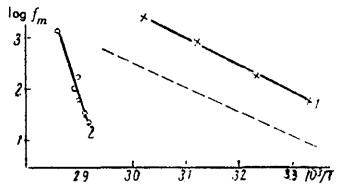


Fig. 12. Plots of $\log f_m = \varphi(T^{-1})$ for isotactic PMMA:
1) dipole–radical losses; 2) dipole–elastic losses. Broken line — analogous relationship for dipole–radical losses in atactic PMMA.

suggests that the dielectric loss method can serve qualitatively as a sensitive indicator of the regularity of a polymer chain.

Examination of the temperature dependence of tan δ for such a non-polar polymer as polystyrene also revealed a difference in the dielectric properties of isotactic and atactic specimens. By comparison with the atactic polymer, partly crystallised isotactic polystyrene has a range of temperatures in which the dipole–elastic losses are extremely diffuse. This diffuseness may, perhaps, be due to the superposition of two or more relaxation processes taking place in the crystalline and the amorphous regions of the polymer.

3. Polyesters

A study of the dipole relaxation of polyesters, especially those containing aromatic nuclei in the chain is of great interest. Some of them possess great thermal stability ($T_c > 200°$), which has attracted attention from the point of view of technical use. We shall consider here the results of an investigation of the temperature–frequency dependence of the dipole losses of polyesters based on "dian" (also called DPP) (bis-2-*p*-hydroxyphenylpropane) and some aliphatic and aromatic acids[24]. The structural formulae and the relative concentration n of aromatic nuclei in the chain, which was calculated as the ratio of the number of nuclei to the number of other atoms in the repeating unit of the chain, are set out in Table 2.

These polyesters (other than PDS) are partly crystalline; this introduces some specific features into the relationships characteristic of dielectric properties, but it does not affect the general validity of the results.

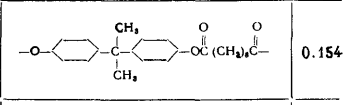
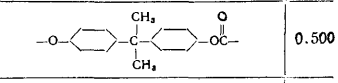
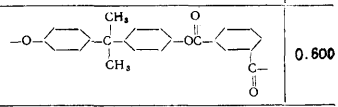
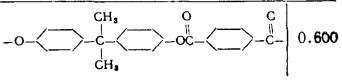
The temperature plots of tan δ for these polyesters at a frequency of 20 kc/s (Fig. 13) reveal the occurrence of two relaxation processes in these materials. One is due to segmental movement of the chains (region of dipole–elastic losses), and the other to the mobility of the dipole groups (dipole–radical type of losses).

The temperatures t_{max} corresponding to $\tan\delta_{max}$ for dipole–elastic losses rise with increase in the relative concentration n of aromatic nuclei given in Table 2, and hence the most probable relaxation time for the dipole–elastic process also increases with rise in n. However, the number of aromatic nuclei in the chain is not the only factor governing the relaxation time of this process. Account must be taken of the crystallinity of a given specimen, since crystallisation of a polymer is known to entail an increase in the relaxation time of the dipole–elastic process with a simultaneous reduction in the corresponding value of $\tan\delta_{max}$.

Comparison of the results in Fig. 13 and Table 2 shows that the concentration of aromatic nuclei in the chain does not affect the relaxation times of dipole–radical processes. The value of τ is then determined by the chemical structure of the acid from which the polyester has been synthesised.

In PDS, a polyester based on an aliphatic acid, the relaxation time of the dipole–radical process is determined by the mobility of the linear section consisting of eight methylene groups, to which is directly linked a C=O dipole. The temperature–frequency region in which tan δ passes through a maximum corresponds to that in which Willbourn observed the relaxation of linear polymer chains containing ⩾4 CH_2 groups[6].

TABLE 2. Structural formulae of the polyesters and relative concentration n of aromatic nuclei in the chain.

Conventional designation	Repeating unit	Structural formula of repeating unit	n
PDS	dian* sebacate		0.154
PDC	dian carbonate		0.500
PDI	dian isophthalate		0.600
PDT	dian terephthalate		0.600

* Bis-2-*p*-hydroxyphenylpropane.

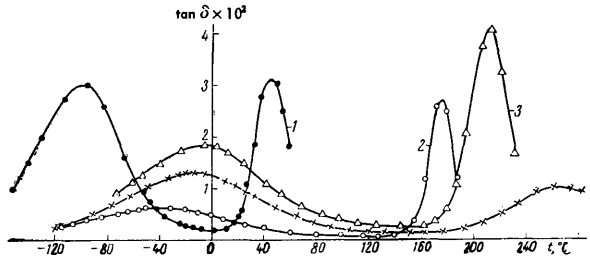


Fig. 13. Plots of tan δ = φ(t°) at a frequency of 20 kc/s for polyesters:
1) PDS; 2) PDC; 3) PDI; 4) PDT.

In PDC, PDI, and PDT, as also in poly(ethylene terephthalate),[25] the region of dipole–radical losses is observed over about the same range of frequencies and temperatures. A common feature of these polyesters is that their synthesis is based on aromatic acids, the carbonyl groups being directly linked to the aromatic nucleus. The roughly identical relaxation times and the similar values for the activation energies (11–13 kcal mole^{-1}) compel us to assume that dipole–radical losses are due to the mobility of small sections of the chains, containing COO ester groups.

This conclusion differs from that reached by Reddish in discussing experimental results on the dielectric properties of poly(ethylene terephthalate)[25]. He links the dipole–radical losses with the movement of terminal hydroxyl groups. A control experiment in which such losses are measured for polyesters of different molecular weight also disproves this statement.

In the study of the nature of dipole–radical losses in polyesters with aromatic rings in the chain, the results of an investigation of mixed polyesters are of great interest[26]. These materials are cocondensates synthesised from "dian" (or ethylene glycol) and two different acids – terephthalic and sebacic, or terephthalic and adipic – the relative proportions of the acids being varied.

Fig. 14 shows plots of tan $\delta = \varphi(t\,^\circ)$ at a frequency of 400 c/s for several cocondensates, the compositions of which are given in Table 3.

The existence of (only) one region of dipole–elastic losses for each of the mixed polyesters is a proof of the random distribution along the chain of components based on the different acids, for example dian sebacate and dian terephthalate.

Fig. 14 shows that mixed polyesters are characterised by the presence of two partly overlapping regions of dipole–radical losses. Comparison of plots of tan $\delta = \varphi(t\,^\circ)$ for polyesters based on a single acid with those for mixed polyesters, *i.e.* those prepared from two acids, suggests that the occurrence of two processes of dipole–radical relaxation is due to the presence of two types of polar radicals in the chain, one formed from a COO group together with an aliphatic acid radical, and the other from this group combined with an aromatic acid radical. Owing to the difference in mobility of these groups, *i.e.* to the difference in corresponding relaxation times, it is possible to observe both processes of dipole–radical relaxation.

Actually, the rough separation of the tan δ_{max} regions for these processes shows that, according to its temperature–frequency location and its magnitude as well as the concentration of acid radicals of a given type, each can be identified with the corresponding process of dipole–radical relaxation of the single-component polyester.

It can thus be regarded as proved that, in both mixed and single-component polyesters, the dipole–radical losses are due to relaxation of the polar COO group, the most probable relaxation time for this process being determined by the mobility of the portion of the chain directly linked to this group.

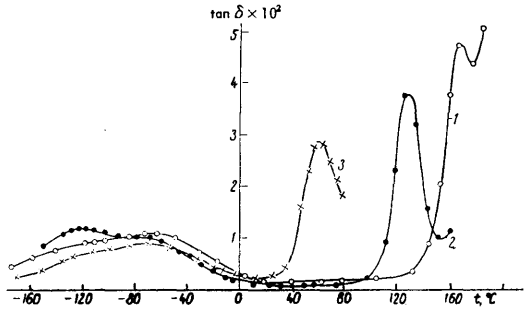


Fig. 14. Plots of tan $\delta = \varphi(t°)$ at 400 c/s for mixed polyesters:
1) TAD-60; 2) TSD-60; 3) TSE-90.

TABLE 3. Composition of mixed polyesters.

Conventional designation	Acid concentration in moles			Alcohol concentration in moles	
	terephthalic	sebacic	adipic	dian	ethylene glycol
TAD-60	0.6	—	0.4	1	—
TSD-60	0.6	0.4	—	1	—
TSE-90	0.9	0.1	—		1

III. EFFECT OF STRUCTURE OF MONOMER UNIT ON THE MOLECULAR RELAXATION OF POLYMERS

This type of investigation has been carried out with the following polymers – poly(methyl acrylate) PMA, poly-(propyl acrylate) PPA, poly-(2-chloroethyl acrylate) PCEA, poly(vinyl acetate) PVA, poly(vinyl butyrate) PVB, and poly-(vinyl β-chloropropionate) PCVP.[27]

The dipole–elastic relaxation of some of these polymers has been investigated also by Fuoss and Mead[28], and the dipole–radical relaxation by Broens and Müller[29]. It has been established that in PVA the dipole losses are due to rotation of acetate groups about the oxygen atom linking them with the main chain of the polymer. Thurn and Wolf[30] carried out similar studies on a very broad basis, and established a link between the relaxation processes observed by mechanical and by dielectric methods. With polymers in the vitreous state these workers discovered several loss regions in which tan δ passes through a maximum. These were most clearly defined in the case of mechanical losses. In particular, with PVA the temperature dependence of the mechanical losses twice passes through a maximum in the region below T_c, while corresponding jumps are observed in the dielectric permittivity ϵ'. They point out that, owing to the superposition of the relaxation processes, it is difficult to determine a relaxation time for each of them. Therefore it also becomes extremely difficult to establish a link between the observed secondary processes (dipole–radical processes in our terminology) and definite groups of atoms.

Hoff *et al.*[13] have studied molecular relaxation in an extremely large number of polymethacrylates by a dynamic mechanical loss method. By varying the structure of radicals substituted in α and β positions, they showed very clearly with what radical or group a given relaxation process was associated. From the temperature shift in the region in which tan δ_{max} occurred, it was possible to assess the changes which had occurred in the structure of the monomer unit, in the flexibility of the polymer chain, in the polarity, and in steric effects. No quantitative comparisons are given in the paper.

The investigations whose results will now be discussed were characterised by an attempt to establish not only with what group of atoms or polar radical of the monomer unit a given relaxation process was associated, but also to make some quantitative comparisons. It was of interest to compare polymers of similar chemical constitution but having side-chains differing in structure, for example PMA and PVA, etc.

The quantities tan δ_{max}, the temperature t_{max}, and the frequency f_m corresponding to tan δ_{max}, and the temperature dependence of these (two) quantities were adopted as the directly observable properties, and activation energies U and the distribution parameter α were calculated from them.

Fig. 15 shows plots of log tan δ at a frequency of 1 kc/s against temperature for the six polymers investigated. Measurements were made also of tan δ as a function of frequency over the range 20–10^5 c/s at several constant temperatures. In the case of PMA the frequency range was extended to 10^{10} c/s. Fig. 15 shows that with each polymer tan δ passes through two maxima, the dielectric losses being of a relaxation type.

With dipole–radical losses the relationship log tan δ = $= \varphi(t\,^\circ)$ is distinguished by the great spread with respect to temperature, which may be an indication of the presence of a broad spectrum of relaxation times for this process. Values of log tan δ in the region of dipole–radical losses are practically identical for PCEA and for PCVP. These polymers are isomers, differing in the mode of linkage of the polar group with the chain. In the region of dipole–elastic losses, on the other hand, the values of tan δ differ markedly. Thus the linking of a polar group through an oxygen atom (in PCVP) considerably increases both $\tan\delta_{max}$ and the relaxation time of the dipole–elastic process (in comparison with PCEA), without having any effect on the dipole–radical losses.

Fig. 16 shows plots of $\log f_m = \varphi(T^{-1})$, *i.e.* of the relation between relaxation frequency and the reciprocal of the absolute temperature. An important feature is that all the straight line sections for dipole–radical relaxation, when extrapolated to $f_{max} = 0$, converge to one point, representing a relaxation frequency of the order of 10^{13} c/s. This indicates that this relaxation process can be regarded as a single "act", and is consistent with the well-known views of Debye[31] and of Frenkel'[32] on the passage of a dipole from one equilibrium position to another in the course of thermal motion. This is evidence also of an exponential variation of relaxation time with temperature, of the form $\tau = \tau_0 \exp(U/kT)$, where $\tau_0 = (2\pi f_0)^{-1}$ and U is the activation energy.

The results obtained for PMA deserve special attention. Above 6×10^8 c/s the frequency of both relaxation processes probably varies according to a single exponential law.

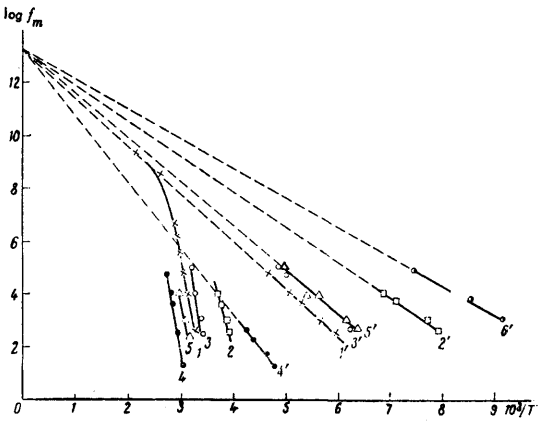


Fig. 16. Plots of $\log f_m = \varphi(T^{-1})$ for dipole–elastic (unprimed numbers) and dipole–radical (primed numbers) losses: 1, 1') PMA; 2, 2') PPA; 3, 3') PCEA; 4, 4') PVA; 5, 5') PCVP; 6') PVB.

Fig. 17 comprises cyclic loci of the complex dielectric constant (ε″ and ε′) for PMA and PVA. The temperatures at which these quantities were measured are indicated on the left of the curves. The diagrams for temperatures of -86° and -35° correspond to dipole–radical relaxation of these polymers, and those at 32° and 58° are plotted from data for dipole–elastic losses. Although measurements were made on the polymer in the rubberlike state, the loss factor ε″ is large at high frequencies, and ε′ at a frequency of 10^{10} c/s is about 30% greater than n^2, the square of the optical refractive index of the material. Such a large discrepancy may be ascribed partly to the superposition of dipole–radical relaxation at high frequencies. However, in the case of cyclic loci plotted from data for dipole–radical losses the value of ε_∞ is again greater than n^2. This could be explained by assuming the existence of a third relaxation process.

In summarising this section, let us examine the next two tables.

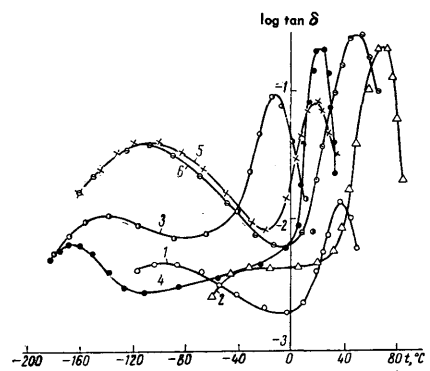


Fig. 15. Plots of log tan $\delta = \varphi(t\,^\circ)$ at 1000 c/s for polymers having isomeric side-chains:
1) PMA; 2) PVA; 3) PPA; 4) PVB; 5) PCEA; 6) PCVP.

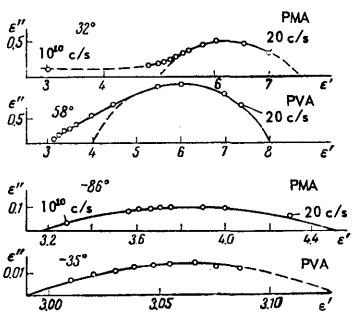


Fig. 17. Cyclic loci of complex dielectric constant for PMA and PVA.

TABLE 4. Comparison of data for dipole–radical losses in isomeric polymers.

Structural formula of polymer	$f = 1$ kc/s: t_{max}, °C	$f = 1$ kc/s: tan $\delta \times 10^2$	U, kcal mole^{-1}	α at t_{max}	Structural formula of polymer	$f = 1$ kc/s: t_{max}, °C	$f = 1$ kc/s: tan $\delta \times 10^2$	U, kcal mole^{-1}	α at t_{max}
PMA $\left\vert -CH_2-CH- \atop O=C-OCH_3 \right\vert_n$	—96	2.7	9.6	0.2	PVA $\left\vert -CH_2-CH- \atop O=C-CH_3 \right\vert_n$	—30	0.40	10.5	0.2
PPA $\left\vert -CH_2-CH- \atop O=C-O(CH_2)_2CH_3 \right\vert_n$	—142	1.3	5.7	0.2	PVB $\left\vert -CH_2-CH- \atop O=C-(CH_2)_2CH_3 \right\vert_n$	—165	0.65	4.8	0.2
PCEA $\left\vert -CH_2-CH- \atop O=C-O(CH_2)_2Cl \right\vert_n$	—110	3.9	8.6	0.2	PCVP $\left\vert -CH_2-CH- \atop O=C-(CH_2)_2Cl \right\vert_n$	—109	3.5	8.9	0.2

TABLE 5. Comparison of data for dipole–elastic losses in isomeric polymers.

Structural formula of polymer	$f = 1$ kc/s: t_{max}, °C	$f = 1$ kc/s: tan $\delta \times 10^2$	U, kcal mole^{-1}	α at t_{max}	Structural formula of polymer	$f = 1$ kc/s: t_{max}, °C	$f = 1$ kc/s: tan $\delta \times 10^2$	U, kcal mole^{-1}	α at t_{max}
PMA $\left\vert -CH_2-CH- \atop O=C-OCH_3 \right\vert_n$	38	9.9	42	0.4	PVA $\left\vert -CH_2-CH- \atop O=C-CH_3 \right\vert_n$	71	25.6	48	0.6
PPA $\left\vert -CH_2-CH- \atop O=C-O(CH_2)_2CH_3 \right\vert_n$	—14	9.3	33	0.5	PVB $\left\vert -CH_2-CH- \atop O=C-(CH_2)_2CH_3 \right\vert_n$	—	21.3	31	0.5
PCEA $\left\vert -CH_2-CH- \atop O=C-O(CH_2)_2Cl \right\vert_n$	17	9.1	39.6	0.4	PCVP $\left\vert -CH_2-CH- \atop O=C-(CH_2)_2Cl \right\vert_n$	50	27.8	46.5	0.6

Table 4 sets out the structural formulae of the monomeric units of the polymers, the temperature t_{max} of the maximum in tan δ at a frequency of 1 kc/s, and the magnitude of tan δ_{max} at this frequency, together with activation energies calculated from the results in Fig. 15.

Examination of the data for PMA and PVA in the first line of Table 4 shows that apart from U all these quantities differ sharply for these polymers. This difference is especially marked in the case of t_{max} and tan δ_{max} (the former is 60° lower, and the latter is 7 times as great, for PMA). Thus the presence in PVA of an oxygen atom directly linked with the chain lowers the mobility of the polar radical, or in other words increases the relaxation time of the monomer unit of PVA.

The second line of Table 4 gives data for the third representatives of the homologous series of poly(alkyl acrylates) and poly(vinyl esters), namely poly(propyl acrylate) and poly(vinyl butyrate). It is seen that lengthening the side-group by two methylene groups shifts the region of tan δ_{max} to markedly lower temperatures. At the same time the value of tan δ_{max} for PPA has decreased to almost half that for PMA, and the analogous change from PVA to PVB has increased tan δ_{max} by almost 50%. Thus consideration of the values of tan δ_{max} for the third members of these series indicates that they are characterised by having more similar values of the dielectric loss (the values for tan δ_{max} differ only by a factor of 2).

It is also noteworthy that the temperature t_{max} fell more with PVB than with PPA, so that the region of dipole–radical relaxation for the former is now situated at lower temperatures. It is interesting that in the homologous series of poly(alkyl methacrylates) a fundamentally different variation of t_{max} for dipole–radical losses is obtained as the series is ascended. In effect, the work of Mikhailov and Borisova[3] has established that, for the first three members of this series, lengthening the alkyl group in the side-chain has no effect on t_{max} for dipole–radical losses. The same phenomenon, *i.e.* the absence of any effect on the position of the region of dipole–radical relaxation in passing from one homologue to another, was observed by Veselovskii for a series of acetals of poly(vinyl alcohol)[11].

As regards the data for PCEA and PCVP (third row in Table 4), introduction of a chlorine atom has removed the difference between the radical relaxation characteristics of these polymers. The presence of chlorine has raised t_{max} and increased tan δ_{max} for both polymers, which is consistent with our general postulate of the dominant role of intermolecular interaction in dipole–radical relaxation.

The distribution parameter α for relaxation times calculated at t_{max} (*i.e.* at the temperature at which tan δ passes through a maximum at a frequency of 1 kc/s) is, within the limits of error, identical for all the polymers in Table 4, and has a very low value. This indicates a broad spectrum of relaxation times describing dipole–radical processes.

Table 5 is compiled from results for dipole–elastic relaxation in the same polymers. These data introduce nothing fundamentally new, but merely confirm the general principle that elongation of the side-chain by an increase in size of the alkyl group shortens the relaxation time for the dipole–elastic process. This effect can be partly compensated by the introduction of a polar group, *e.g.* a CCl dipole, into the side-chain.

The higher values of tan δ_{max} for PVA and PCVP can be explained by a decrease in dipole correlation within the chain, since the effective dipole moment calculated from values of the dielectric permeability corresponding to the dipole–elastic region of relaxation (according to the cyclic diagrams) is greater for PVA than for PMA.

The value of the distribution parameter α for relaxation times of dipole–elastic processes is considerably higher than analogous values for dipole–radical processes, and may approach unity, as in the case of PVB at 30°. This is common to all polymers, and can be interpreted as evidence that a polymer has a more homogeneous structure in the rubberlike state.

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ELECTRODE PROPERTIES OF ION-EXCHANGE MEMBRANES

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CONTENTS

I.	Introduction	396
II.	Theories of membrane potentials	397
III.	Electrode properties of ion-exchange membranes	400
	1. Mineral membranes	400
	2. Membranes based on some organic substances	400
	3. Membranes made of ion-exchange resins	401

I. INTRODUCTION

During recent years a large number of papers have appeared both in our own country and abroad on the theory and practical application of membranes made of ion-exchange materials. Such membranes can find wide use as indicator electrodes in potentiometric analysis, as well as in various processes of electrodialysis.

The study of ion-exchange membranes had already begun in the previous century. It was then discovered accidentally that, during the separation of electrolyte solutions by some plant and animal membranes, a potential difference is produced at the membrane–solution boundary. These membranes were termed "semipermeable" or "selective" membranes, since they allowed some substances to pass through and prevented others from doing so. Since then, the electrochemical properties of selective membranes have been studied by biologists and physical chemists [1-10].

Work on the glass electrode has assisted the development of the electrochemistry of semipermeable membranes and their use as electrodes. The study of the electrode and ion-exchange properties of glass membranes and the successful application of the glass electrode to the determination of pH gave an impetus to the production of reversible electrodes made of other ion-exchange materials. For this purpose use was made of various minerals, clays, collodion, cellulose, and other substances capable in various degrees of exchanging ions. Since 1949 ion-exchange resins have come to be used for the preparation