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POLAROGRAPHIC INVESTIGATION OF POLYMERS* (REVIEW)

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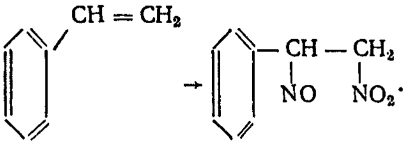
Reviews in [1, 2] have given a fairly clear picture of the potentialities of polarography in the chemistry of polymers.

This article examines some further potentialities of the polarographic method in this field, which may find extensive practical application.

The Investigation of Polymerization Kinetics

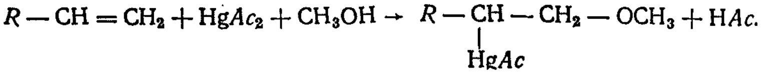
The use of polarography in this field has been based mainly on data of the direct polarographic determination of the amount of the initial substances (monomers) in the reaction media at specific intervals. Results of this type have been obtained from investigations into the polymerization rate of acrylonitrile [3, 4], methylmethancrylate [5, 6], divinyl and diallyl adipate [7], etc.

But this procedure is only applicable if the initial substances (monomers) are readily reduced (or oxidized) at a dropping mercury electrode and form distinct polarographic waves during this process. Many of the initial products of polymer synthesis are polarographically inactive or only weakly active, being reduced in the far-negative region of potentials and giving indistinct waves. In such cases the inactive compounds must be converted to polarographically active ones by appropriate chemical reactions. Tur'yan and Zhantalai's paper [8] on the polarographic analysis of caprolactam and Ryabov's investigations on determination of some monomers in the form of their bromo derivatives [9] may serve as examples. In [10] Sedivec and Flek showed that styrene, which is reduced at $E_{\frac{1}{2}} = -(2.3\text{-}2.4)$ V, may be converted by silver nitrite in glacial acetic acid to a pseudonitrosite, giving a distinct wave with $E_{\frac{1}{2}} = -0.27$ V on the polarogram:



On the basis of this reaction, T. A. Alekseeva and I have developed methods for determining styrene [11], vinyltoluene, vinylxylene, β-vinyltetralin [12] and other monomers in reaction media and polymers, which were then used for investigating the polymerization kinetics of these monomers. Figure 1 gives polarograms of 2,4-dimethylstyrene in 75% dioxan obtained by direct polarographic determination (curve 2) and the pseudonitrosite of this monomer (curve 1). The height of the pseudonitrosite wave is directly proportional to the 2,4-dimethylstyrene concentration. When this wave is used for determining the monomer content of a polymer the error (3%) is within the limits characteristic of the polarographic method.

The formation reaction of mercury acetate complexes by some vinyl-containing compounds is also of interest for the determination of monomers:



$$R-CH=CH_2+HgAc_2+CH_3OH \rightarrow R-\underset{\displaystyle HgAc}{\underset{|}{CH}}-CH_2-OCH_3+HAc.$$

Usami [13] has shown that mercury-acetate derivatives of a number of unsaturated compounds may be subjected to polarographic reduction.

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* A report given by the author, together with T. A. Alekseeva and E. K. Dvornikova, to the Second Polarography Conference at Kazan, September, 1962.

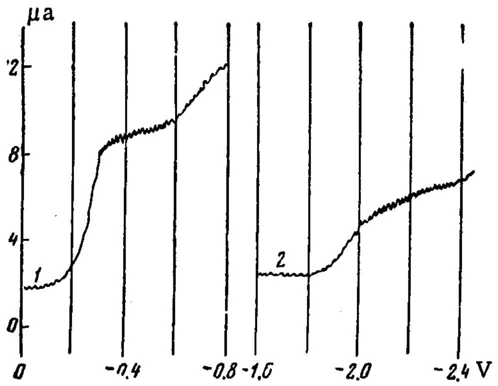

Fig. 1.

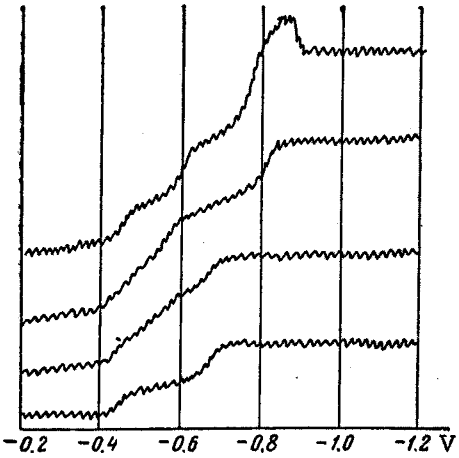

Fig. 2.

Fig. 1. Polarographic waves of pseudonitrosite of 2,4-dimethylstyrene (1) and 2,4-dimethylstyrene (2) against a background of 0.175 M $(C_2H_5)_4NI$ in 75% dioxan. Monomer concentration $1.5 \cdot 10^{-3}$ mole/liter; $E_a = 0$ and -0.443 V respectively.

Fig. 2. Polarograms of the mercury-acetate complex of α-methylstyrene ($E_a = -0.322$ V).

Together with Yu. P. Ponomarev and V. N. Dmitrieva, we have used this reaction for the polarographic determination of styrene and α-methylstyrene in pure solutions of methylmethacrylate, and in the joint presence of these monomers. Under the conditions employed, methyl methacrylate does not form mercury-acetate complexes, but styrene and α-methylstyrene do, and these complexes are reduced at a dropping mercury electrode with formation of three waves (each), as may be seen in Fig. 2. The half-wave potentials for styrene are −0.75, −0.93, and −1.11 V, the values for α-methylstyrene being −0.76, −0.92, and −1.09 V.

Although the half-wave potentials of these monomers are similar and therefore undeterminable from their waves, we found that the ratio of the heights of all the waves depends on the concentration ratios of these monomers. In particular, the ratio of the sum of all three wave heights Σh to this sum less the height of the first wave $(\Sigma h / \Sigma h - h_1)$ changes according to a definite law with a change in the styrene/α-methylstyrene ratio in the mixture (Fig. 3).

Therefore, by plotting calibration curves for different styrene α-methylstyrene ratios at a specific total concentration of these monomers the styrene and α-methylstyrene contents may be determined separately when they are present together. The error of a determination is not more than 5-8 rel. %. At the present time there are no other reports on the determination of these monomers.

Also of interest is the method of investigating polymerization kinetics (particularly in the case of low conversions) from the reduction of polarographic maxima by the polymer formed, e.g., the investigation of lactic acid polymerization by employing the capacity of its polymer to suppress the oxygen maximum [14]. This method is promising for the investigation of primary polymerization stages, which is of particular value for investigating monomer reactivity.

Determination of the Resistance of Polymers to Different Solvents

Solubility is one of the most important characteristics of polymers; it is closely related to the molecular weight, is an important factor in the investigation of polymer fractionation, their plasticization and aging.

To determine the resistance of polymers to different solvents, E. K. Dvornikova and I have used a polarographic method based on an investigation of the degree of suppression of maxima by polymer molecules passing into solution. The results of the polarographic determination were compared with those obtained by the gravimetric method. Figure 4 gives the kinetic curves of polystyrene dissolution in a mixture of benzene and methanol.

The polarographic method may be used to determine up to 10^{-3}% polymers in a solution, which is impossible with the gravimetric method.

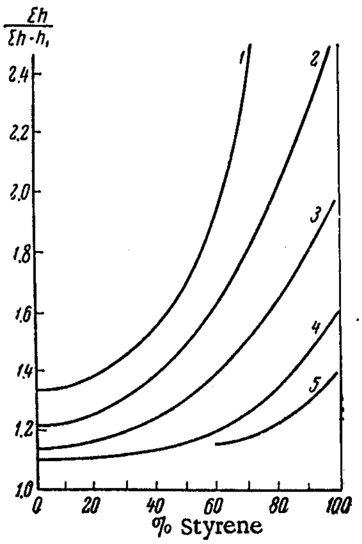

Fig. 3. Calibration curves for mixtures of styrene and α-methylstyrene: 1-5) concentrations 0.33, 0.50, 0.66, 1.00, and 1.33 mmole/liter.

Results of a Statistical Analysis of Data on Polystyrene Molecular Weight Determination by the Polarographic Method

$M \cdot 10^3$	n	Δh %	α	t_α	S	Σrel. %
138	6	26.6	0.95	2.571	±2.145	8.3
100	5	36.8	0.95	2.776	±1.095	3.7
81	6	52.8	0.95	2.571	±0.911	1.8
54	6	67.1	0.95	2.571	±0.938	1.5

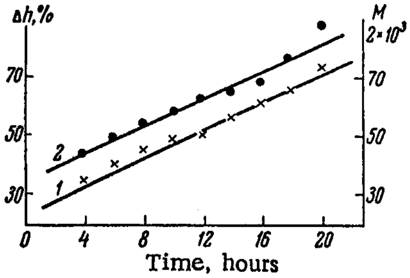

Fig. 4. Kinetics of polystyrene dissolution in a benzene-methanol mixture: 1) polarographic method, 2) gravimetric method.

Determination of the Molecular Weights of Polymers

The polarographic method may also be used for determining the molecular weight of polymers. This may be based on the property of surface-active polymer molecules adsorbed on a mercury drop to reduce the height of polarographic maxima of both first and second order. Such possibilities have already been noted in the literature. In particular, from an investigation of the relation between the degree of hydrolysis of various high-molecular substances and the height of the maximum on polarograms. Rusznak, Fukker and Kralik [15] found that the size of the molecules of the investigated molecules played the main role in maxima suppression. Badinand and Boucherle [16] investigated the relation between the capacity to suppress maxima on polarographic curves and the molecular weight of some polyethylene glycols. They found that the degree of polymerization may be determined from the capacity of polyethylene glycols to suppress maxima on the polarographic curves of lead, nickel and copper. The efficiency of maxima suppression increases with increasing molecular weight. In [17] Rusznak, Fukker and Kralik investigated the relation between the molecular weight of cellulose diacetatemonophthalate fractions and their capacity to reduce the polarographic maxima of oxygen. They found a direct relation between the molecular weight of the polymer and the degree of reduction of the height of the diffusion current maxima.

Utilization of these data for the development of methods requires primarily a high polymer solubility in such solvents which also ensure high electrical conductivity of solutions of salts in them, because otherwise the polarographic maxima would be indistinct. This greatly limits the number of polymers for which these relations may be used; E. K. Dvornikova and I have therefore developed another method. It is based on procedures used for determining molecular weights from the consumption of a solvent in which the given polymer is insoluble and which is necessary to ensure turbidity of a polymer solution of specific concentration [18]. By way of solvents we used KI solutions in a benzene-methanol mixture (1:3) in which the solubility of many polymers (including polystyrene, polyvinyltoluene, polymethylmethacrylate etc.) is limited. It is known that the latter property depends on the molecular weight. A limited number of polymer molecules dissolve in the given system, the remainder being deposited. The polymer molecules left in solution reduce the polarographic maxima. Thus, each time we add the same amount of polymer solution to the electrolyzer an increasingly smaller part of the polymer is precipitated as one passes from high molecular weight fractions to low ones. Therefore the polymer concentration in the polarographically analyzed solution increases, which also increases the degree of maxima suppression.

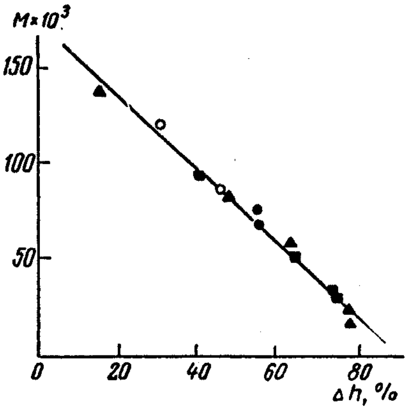

Fig. 5.

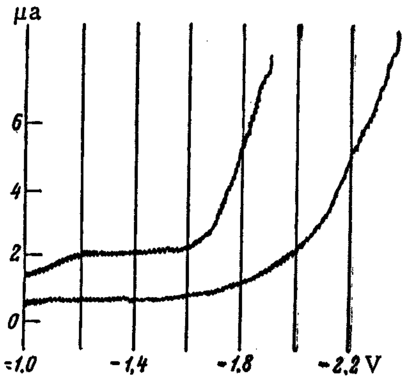

Fig. 6

Fig. 5. Relation between the degree of reduction of the oxygen maximum and the molecular weight of polystyrene. Series of experiments: ▲) first; ■) second; ○) third; ●) unfractionated polystyrene.

Fig. 6. Polarogram of freshly distilled styrene ($E_a = -0.30$ V).

The measurement method was as follows: 5 ml of 0.1 N KI in a benzene-methanol mixture is poured into the electrolyzer and the polarogram (with a distinct oxygen wave maximum) is recorded. To this solution is added 0.5 ml of a $4.10^{-2}\%$, they are thoroughly mixed, and the polarogram is recorded again. Similar measurements are made for polymer fractions with different molecular weights, the height of the maximum is determined and the capacity of each fraction to depress the maxima is assessed; the reduction is expressed as a percentage of the initial height of the maximum.

Figure 5 gives the results of several series of such experiments carried out with different polystryene batches; it may be seen that the points denoted by black circles and relating to polystyrene unfractionated beforehand also lie satisfactorily on the straight line. The table gives data of a statistical analysis of the results, from which it follows that the relative error of a polymer molecular weight determination is not more than 8.5%. Similar data were obtained for polyvinyltoluene and polymethylmethacrylate.

Provided the system of solvents and depolarizers is correctly selected, this method of determining the molecular weights of polymers may therefore be used for many other polymers. However, it should be noted that not all the factors determining these relations are sufficiently clear. In this connection a considerable amount of research is required and we are now carrying out investigations with maxima of both the first and second order.

Investigation of the aging of monomers and polymers

We solved this problem jointly with N. P. Shimanskaya by way of example of an investigation of styrene and its polymer. The amount of peroxide compounds formed in polystyrene and causing further processes (including polymerization) served as one of the criteria of the change in styrene.

The peroxide compounds, accumulated in styrene in an amount depending on the storage conditions, affect the aging periods of styrene and its activity and reduce the optical transparency of the polystyrene produced from it. Determination of the peroxide compounds and their destruction products makes it possible to investigate the kinetics of their formation and disintegration; this is very important when checking the resistance of polymers to spontaneous polymerization in relation to the storage conditions. Figure 6 shows the polarogram of styrene freshly distilled in vacuum, and Fig. 7 gives the results of its polarographic analysis after storage in different conditions. For the polarographic analysis after storage in different conditions. For the polarographic analysis, 2 ml of 0.02 N $(C_2H_5)_4NI$ in 92% methanol and 0.5 ml each of different styrene samples were placed in the electrolyzer.

The polarographic method may also be used for investigating the aging of polymers. By way of example we give data from an investigation of the changes taking place in polystyrene due to the effect of various radiations (particularly ultraviolet ones) [19]. Investigation of irradiated samples showed that addition of a benzene solution of polystyrene, pre-subjected to ultraviolet radiation, to a $(C_2H_5)_4NI$ solution leads to formation of a wave with $E_{\frac{1}{2}} = -1.5$ V on the polarogram. The polarogram of a solution of unirradiated polystyrene (after the polymer has been kept for 3-4 months in air) also contains a hitherto unobserved wave with $E_{\frac{1}{2}} = -1.5$ V (Fig. 8a). To determine the nature of this

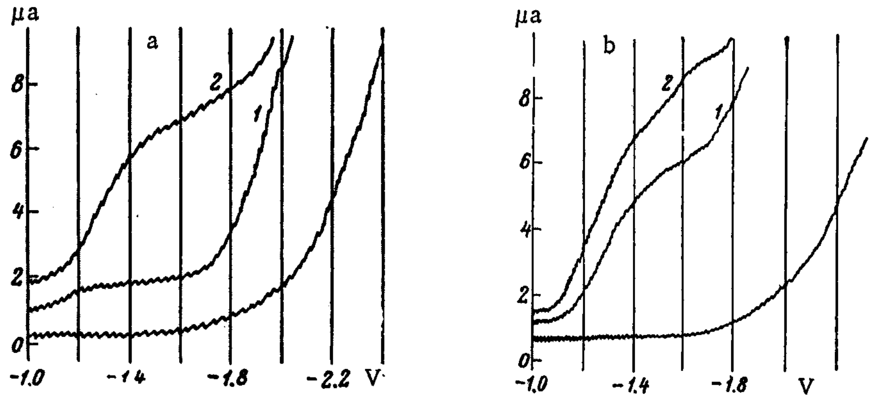

Fig. 7. Polarogram of styrene after aging: a) in 100 days: 1) in a sealed ampoule; 2) in a flask with a ground glass stopper; b) in 30 days: 1) in the dark; 2) in the light.

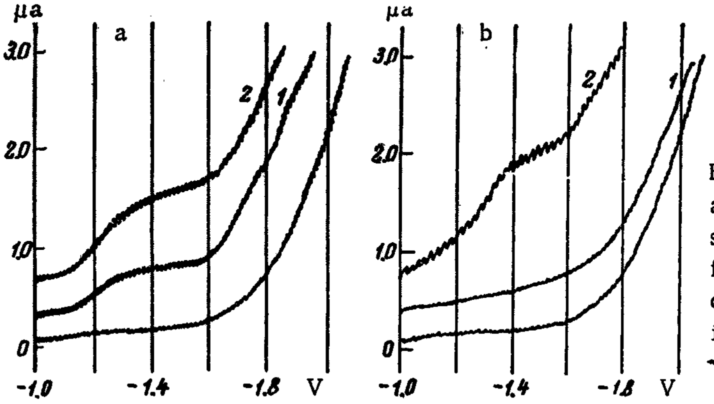

Fig. 8. Polarograms of a polystyrene solution against a background of $(C_2H_5)_4NI$ ($E_a = -0.30$ V): a) polystyrene; 1) kept for 4 months in air; 2) irradiated for 40 hours; b) polystyrene: 1) irradiated in an cxygen-free atmosphere for 200 hours; 2) irradiated in air for 200 hours.

wave, polystyrene samples in sealed quartz ampoules were irradiated in nitrogen and in vacuum. It was found that when polystyrene is irradiated in an oxygen-free atmosphere the wave is not observed on the polarograms (Fig. 8b).

The literature gives data on the formation of peroxide compounds by reaction of styrene with oxygen, and the determination of their polarographic characteristics. Barnes and Elofson [20] give the value of the half-wave potential for styrene peroxide in a $(CH_3)_4NBr$ solution containing 58% benzene, 37% ethanol and 5% water, as $E_{\frac{1}{2}} = -(1.4\text{-}1.5)$ V. This is confirmed by the results of a parallel iodometric determination of the peroxides. The height of the polarographic wave increases with increasing irradiation time. The peroxide content determined by the iodometric method increases accordingly, therefore the peroxide content of polystyrene may be determined by employing the polarographic calibration curve. In contrast to conventional chemical methods which give the total peroxide content, the polarographic method makes it possible to identify the nature of these peroxides from the $E_{\frac{1}{2}}$ value.

SUMMARY

Some new trends in the use of the polarographic method for the invesitgation of polymers are examined, in particular as follows:

1) from an investigation of polymerization kinetics it is shown that extensive use may be made of the indirect determination of monomers in reaction mixtures;

2) the potentialities of the polarographic method for investigating aging under different conditions are shown by way of example of styrene and its polymer;

3) it is shown that polarographic maxima can be used for investigating the resistance of polymers to solvents, and for determining their molecular weights.

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