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### The Peculiarities of the Anionic Polymerization of Oligoesteracrylates

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## The Peculiarities of the Anionic Polymerization of Oligoesteracrylates

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### SUMMARY

The equilibrium distribution of the electrons in the catalyst-oligoesteracrylates system was investigated. It was found that equilibrium distribution of electron in this system is determined by the ratio of catalyst concentration and electron attracting groups and, furthermore, by the possibility of electron exchange between the phthalate and methyl methacrylate groups of oligoesteracrylates.

It was concluded that the anionic polymerization process of oligoesteracrylates has some peculiarities which distinguishes it from the anionic polymerization of vinyl monomers. That can probably be considered as a result of the "oligomer" molecules comprising two electron attracting groups that have different electron affinities which are separated by the system of  $\sigma$ -bonds.

### INTRODUCTION

The anionic polymerizations of certain unsaturated, monomeric oligoesters exhibit some peculiarities that distinguish them from the typical anionic polymerization of ordinary vinyl monomers.

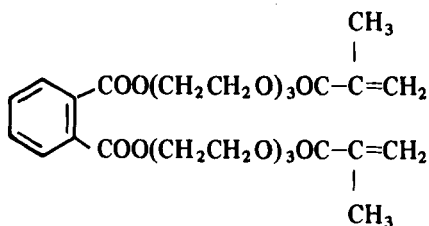
One of the distinguishing features in initiation of the anionic

polymerization of oligoesteracrylates (OEA) is the existence of the so-called "limit" concentration of the catalyst below which the polymerization cannot take place even though the coloring of the solution in the presence of catalyst is generally observed [1]. Most probably that is due to the fact that the "oligomer" molecules possess two electron attracting groups having different electron affinities separated by a system of  $\sigma$ -bonds [2]. It is known that in anionic polymerizations a catalyst-monomer-living polymer equilibrium is usually established which depends on the nature of the catalyst and monomer as well as on the ratio of their concentrations, temperature, etc. [3].

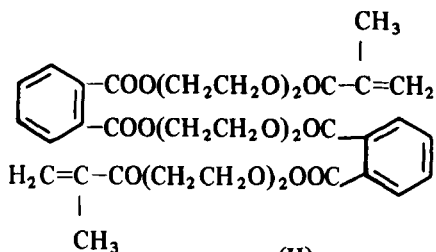
In the system catalyst-OEA there could also exist an equilibrium distribution of electrons which depends on the possibility of electron exchange between the phthalate and methyl methacrylate groups of OEA.

The purpose of the present work is the study the equilibrium distribution of the electrons in the catalyst-OEA system, namely, the peculiarities of the electron transition from sodium naphthalene to OEA and the possibility of electron exchange between the functional groups of OEA in the process of polymerization.

The techniques used in this study involved spectrophotometry in the visible region, polarography, and ESR. The specific OEA monomers used in this investigation are  $\alpha,\omega$ -methacryl(bis-triethyleneglycole)phthalate (I) and  $\alpha,\omega$ -methacryl-di-(diethyleneglycolephthalate) (II).



(I)



(II)

Since both I and II have two kinds of electrons attracting groups, dimethyl phthalate and methyl methacrylate, their mixture was chosen as model prototype systems for study.

### EXPERIMENTAL METHODS

The reactants were thoroughly purified according to the methods described in the literature [5-7]. After purification the OEA compounds had the following refractive indices: I, 1.4920; II, 1.5150 [2].

Spectrophotometric study was performed using an SF-4 apparatus. The solutions were prepared in vacuum system ( $3 \times 10^{-5}$  mm Hg residual pressure). In one section of the system the solution of sodium naphthalenate in tetrahydrofuran was prepared. In the second section the solution of oligoesteracrylate was prepared. Then, having broken the partition between the two sections, a definite amount of the catalyst solution was added to the oligoesterocrylate solution, after which the solution under investigation was transferred, under vacuum, to the optical cuvet 10 mm thick; then the electronic spectra were recorded. Similarly, the absorption spectra of the models were recorded. The same two-section vessel was used for obtaining the solutions for the study of the polymer yield dependence on the catalyst concentration.

The study of the interaction of the network polymer with OEA and model compounds was carried out in the following way. The network polymer of dark cherry color was obtained in bulk. Definite quantities of the polymer were introduced into 3 ampoules and, after evacuation, methyl methacrylate, dimethyl phthalate, and oligoesteracrylate were added to the first, second, and third ampoules, respectively. The ampoules were kept in vacuo for 120 hr after which the changes in color and weight of the polymer were determined.

The possibility of electron transition from dimethyl phthalate to methyl methacrylate groups of OEA was investigated in the following way: a three-section vessel was used for preparing the solutions of sodium naphthalene (Section 1), dimethyl phthalate (Section 2) and methyl methacrylate (Section 3). The catalyst was mixed with one of the components, and an electronic spectrum of the solution was recorded after which the second component was added and the spectrum of the solution was recorded again. The unreacted catalyst and monomer concentration were detected by means of polarography.

The polarograms of OEA and model compounds in dimethylformamide were taken using a LP-60 Polarograph with a dropping cathode (capillary parameters  $m^{2/3}t^{1/6} = 0.71$  and  $1.05 \text{ mg}^{2/3} \text{ sec}^{-1/2}$ ), a mercury anode on the bottom of the cell, the potential of which was taken as zero, and an indifferent electrolyte of 0.2 mole/liter tetrabutylammonium iodide.

A specially constructed V-shaped glass cell with a porous glass diaphragm was used for the experiments on electrochemical initiation. Purging with an inert gas and a connection with the vacuum system is provided for the cell. The electrodes are 8 cm<sup>2</sup> nickel plates.

The electrolysis of 0.5 mole/liter solution of OEA in dimethylformamide was investigated in the presence of 0.1 mole/liter of tetrabutylammonium iodide.

## RESULTS AND DISCUSSION

### On the Mechanism of Formation of Active Centers Responsible for the Polymerization Initiation of OEA

The absorption spectra of both I and II with Na-naphthalene in tetrahydrofuran have distinct absorption bands at 410 and 510 nm as well as maximum at about 310 nm, which is not fully observed (Fig. 1a and 1b). The solution color is light red. In order to determine which chromophore group is responsible for every absorption maximum, electronic spectra of model compounds were recorded under similar conditions. The solution of methyl methacrylate with sodium naphthalene has  $\lambda_{\text{max}}$  300 nm and a less intensive band at 450 nm.

A similar dimethyl phthalate solution has  $\lambda_{\text{max}}$  in the region of 320 and 420 nm (Fig. 1c and 1d). The electronic spectra of methyl methacrylate and dimethyl phthalate in the presence of sodium naphthalene (Fig. 1e) have absorption bands similar to those of OEA. Comparison of OEA spectra with those of the model compounds in the presence Na-naphthalene suggests that the electrons are transferred from the catalyst onto the phthalate as well as on the propagation of methyl methacrylate of OEA.

Since it is essential to know if there is any regular succession in the process of electron transition, the electrochemical properties of oligomer and model compounds, using the polarography methods, were studied for this purpose.

It is known that the transition of electron to the monomer in the electrochemical reduction is analogous to the electron transition from an anionic catalyst [8, 9].

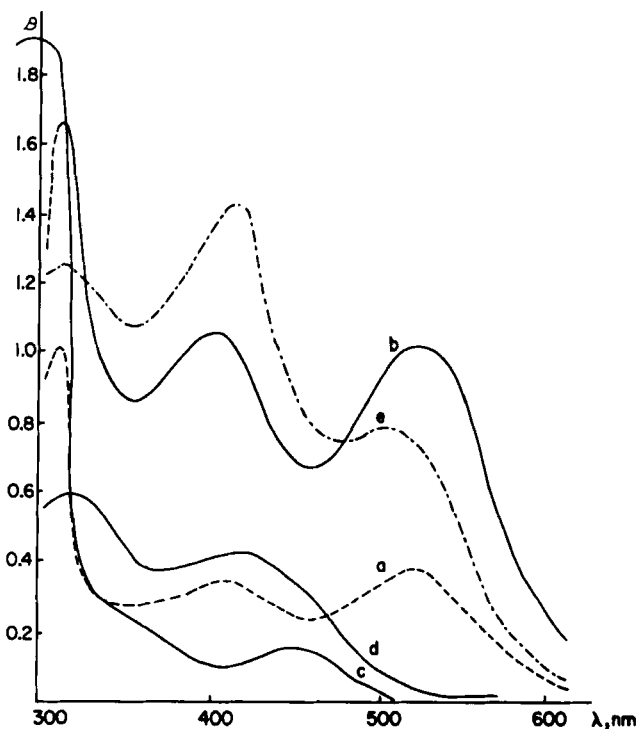
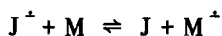


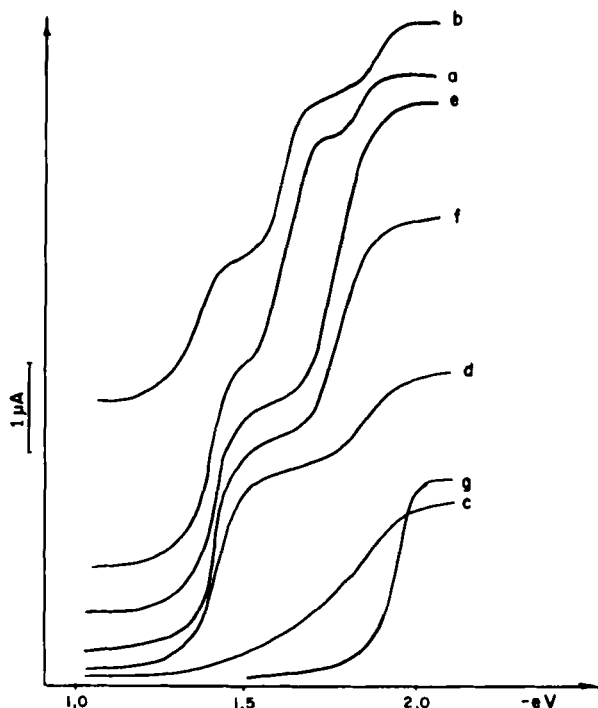
Fig. 1. Electron spectra of oligoesteracrylates and model compounds in the presence of sodium naphthalene dissolved in tetrahydrofuran. a: I. b: II. c: Methyl methacrylate. d: Dimethyl phthalate. e: Mixtures of methyl methacrylate and dimethyl phthalate in 2:1 molar ratio.

The catalyst activity in anionic polymerization is determined by the difference of electron affinity of the catalyst,  $J$ , and monomer,  $M$ , [10], i.e., the reaction equilibrium, is determined by the difference of electron affinity of the monomer and initiator, thus:



This difference is characterized by the polarographic potentials of half-waves of the initiator and monomer obtained under strictly similar conditions [11].

When the "monomer" is an OEA molecule containing two reducible types of groups, the electron transition process from the catalyst is much



**Fig. 2.** Polarographic waves in the presence of the supporting electrolyte 0.2 m  $N(C_4H_9)_4I$  in dimethylformamide. a: I. b: II. c: Methyl methacrylate. d: Dimethyl phthalate. e: Mixtures of methyl methacrylate and dimethyl phthalate in 1:1 molar ratio. f: Mixtures of methyl methacrylate and dimethyl phthalate in 1:2 molar ratio. g: Naphthalene.

more complicated. The polarographic waves of OEA (Fig. 2a and 2b) were obtained to determine different stages of the process.

Having estimated the  $\Delta E_{1/2}$  value of naphthalene and of the reducible groups of OEA, we tried to establish some of the stages of the process. The polarograms comprise three diffusion waves; in order to identify which of the polarograms are characteristic of dimethyl phthalate, methyl methacrylate, and their mixtures in molar ratios of 1:2 (Model I) and 1:1 (Model II), they were taken under similar conditions (Fig. 2c-f).

As can be seen from Fig. 2d, the dimethyl phthalate polarogram consists of two diffusion waves; methyl methacrylate (Fig. 2c) gives one wave in a range of potentials corresponding to the second wave of dimethyl

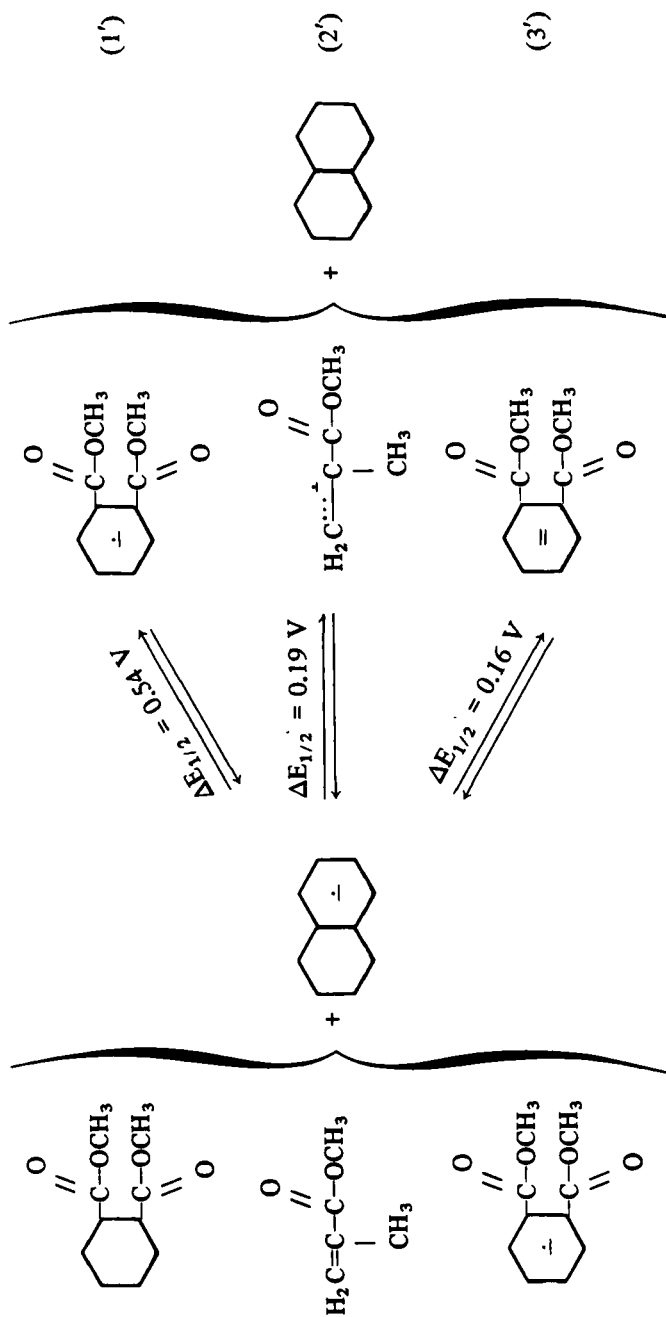
phthalate. Also, it can be concluded from the  $E_{1/2}$  values that the electron affinity of dimethyl phthalate is much greater than that of methyl methacrylate. The polarogram of the model system (Figs. 2e and 2f) consists of two waves, the first one corresponding to the first wave of dimethyl phthalate while the second is common for both dimethyl phthalate and methyl methacrylate, i.e., it corresponds to the reduction of the latter with further reduction of phthalate. The polarogram of naphthalene was taken under similar conditions (Fig. 2g) and the  $E_{1/2}$  values and the potential halfwave difference of naphthalene and of the monomers studied were calculated.

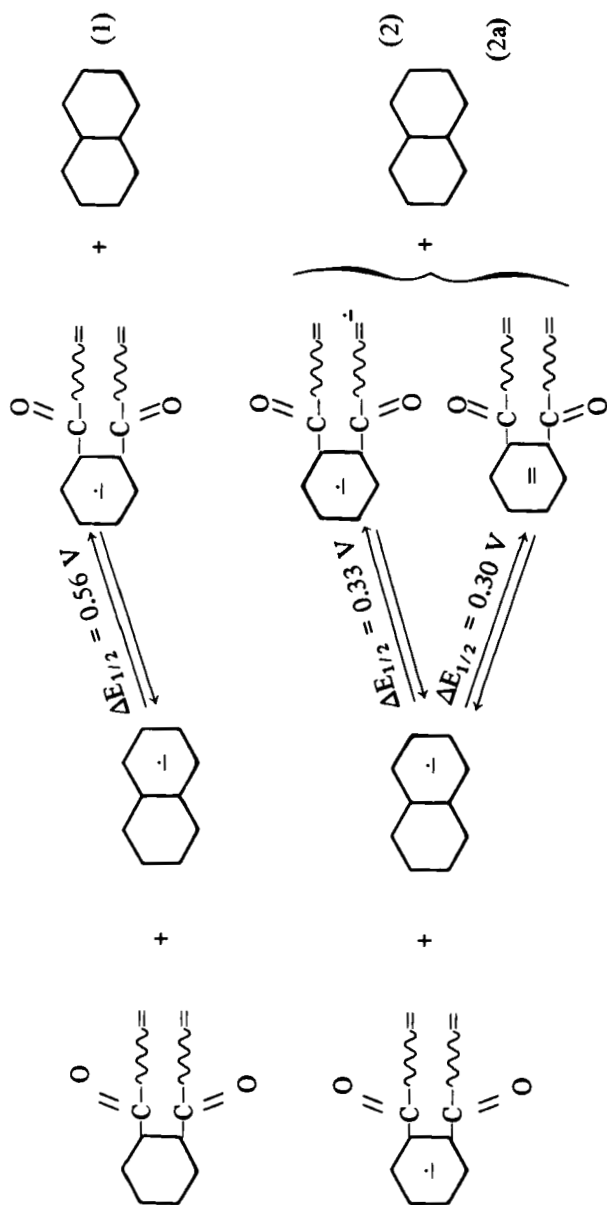
On the basis of  $\Delta E_{1/2} = E_{1/2 \text{ naphth}} - E_{1/2 \text{ m}}$ , the reaction succession in model system is as shown in Eqs. (1'), (2'), and (3'). Reactions (2') and (3') proceed practically parallel. By comparing the polarograms of the model system and OEA, one may conclude that the first wave observed for the oligomers corresponds to the phthalate group reduction and the second wave to the terminal double bond and further phthalate reduction. For the reaction of I with the catalyst, the process may be represented by the following scheme, [Eqs. (1), (2), and (2a)], where  $\sim\sim\sim$  is the double bond of the acrylate group observed in the polarogram (Fig. 2). There is evidence for a similar succession of electron transition for II.

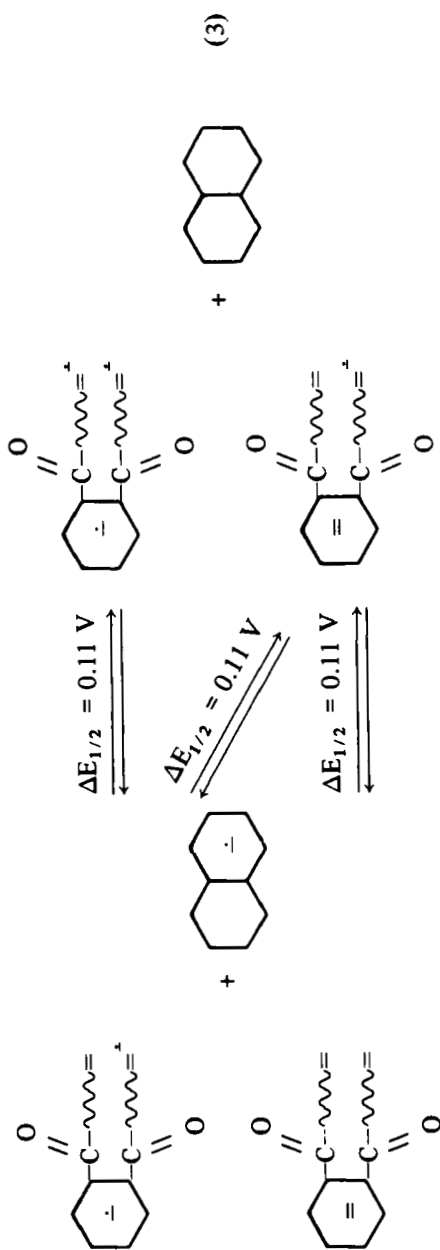
The polarograms of oligoesteracrylates, in contrast to the model system, have a third wave, its limiting current being much lower than that of the first two. Apparently this wave corresponds to the reduction of some oligomer molecules which have already received two electrons. The shift of halfwave potential to the negative area is specified by the necessity of using the additional energy in order to overcome Coulomb repulsion of the dianion from the cathode surface. The interaction of the reaction products of (2) and (2a) with the catalyst may be described as shown in Eq. (3). With regard to the values of  $\Delta E_{1/2}$ , one may conclude that the probability of a type (3) reaction is small and can be important only at a sufficiently high catalyst concentration. Thus, in the system oligoesteracrylate-sodium naphthalene, at a small concentration of the latter, only the first reaction is possible, resulting in formation of nonactive anion-radicals of OEA. Only if the concentration is above the "limit" value can the equilibrium in the system be shifted towards the Reactions (2) and (3) which initiate polymerization.

Actually, when studying the polymer yield dependence on the catalyst concentration, it was observed that at the concentration below the "limit", the solution of OEA with sodium naphthalenolate turns pink, the color being typical of anion-radical of dimethyl phthalate. Below 0.013 mole/liter









a soluble linear polymer is formed, and only at 0.02 mole/liter or higher does the network polymer of a dark cherry color precipitate.

A number of experiments on electrochemical transfer of electron of molecules substantiates this proposed scheme. At small current densities ( $0.5 \text{ mA/cm}^2$ ,  $25^\circ\text{C}$ ), the OEA solution in the cathode area turns pink. In the course of time the color becomes a more intensive cherry red yet, during 7 hr of electrolysis, no measurable change of viscosity takes place. Thus, the OEA molecules, on being reduced on the cathode (Reaction 1) may diffuse into the solution, causing no polymerization. Only at a current density of  $0.9 \text{ mA/cm}^2$ , under such reaction conditions, is a thin polymer film formed on a cathode surface.

On the other hand, at  $-52^\circ\text{C}$ , when diffusion of OEA molecules is sharply reduced (the diffusion temperature coefficient is  $1.8\%/^\circ\text{C}$ ), conditions created at the electrode surface are suitable for Reactions (2) and (3) to proceed. When the current density is  $0.3 \text{ mA/cm}^2$ , a thin polymer film appears on the electrode surface; at  $0.9 \text{ mA/cm}^2$  the polymer film thickness reaches 7-8 mm and is of a dark cherry color whereas the solution is light pink in color.

### On the Equilibrium in the System OEA-Catalyst

The existence of a limiting concentration and the dependence of polymer yield and solubility on catalyst concentration allow us to suggest that, in the course of polymerization an equilibrium in the system OEA-catalyst is established. To determine the conditions of this equilibrium, some experiments have been carried out on the model compounds to establish the possibility of electron exchange between the phthalate and methyl methacrylate groups of oligomer.

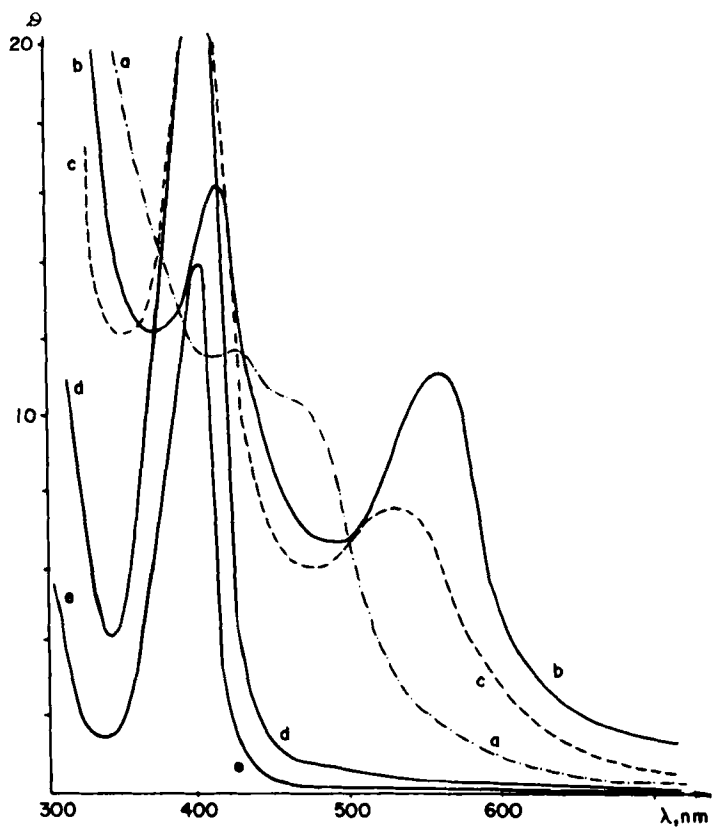
The results are presented in Table 1. As mentioned above, the electron transfer from catalyst to monomer, i.e., reaction equilibrium (1'), is dependent on the halfwave potential difference  $\Delta E_{1/2}$ , taking into account the solutions colors (Table 1) at  $\Delta E_{1/2} = \text{const}$ , it is dependent also on the ratio,  $[M]/[J]$ , of the monomer and catalyst concentrations. The solution of sodium naphthalene and dimethyl phthalate, at  $[M]/[J] = 2-6$ , has the color of strong tea. On increasing  $[M]/[J]$  up to 18-20, it becomes pink and on a further increase the solution becomes light-yellow.

One may suppose that at  $[M]/[J] = 2-6$  the reaction equilibrium (1') is shifted to the left and the solution color is caused by the ion-radicals of dimethyl phthalate and of unreacted catalyst. Indeed, the equilibrium constant of Reaction (1') calculated by us [12] for this concentration ratio is of the order of 0.15-0.30. At  $[M]/[J] = 20$  the conditions for

**Table 1.** Effect of Monomer and Catalyst Concentrations and Subsequent Addition of the Second Monomer on Solution Color

Monomer concentration (M), (mole/liter)	Catalyst concentration (mole/liter)	$\frac{[M]}{[J]}$	Solution color	Second monomer concentration $[M_1]$ , (mole/liter)	Solution color after second monomer addition
Dimethyl phthalate					
0.0050	0.0019	2.6	Yellow-green, color of strong tea	Methyl methacrylate 0.0400	Pink
0.0200	0.0048	4.1	Yellow-green	0.0800	Red, polymer precipitates
0.0100	0.0016	5.5	Yellow, with green tint	0.0800	Pink
0.0400	0.0022	18.1	Yellow-pink	0.1600	Red

0.0720	0.0036	20.0	Cherry color	0.0500	Dark red
0.0091	0.0004	22.0	Bright pink	0.0400	Red
0.0400	0.0013	30.5	Yellow, pink	0.1600	Red, polymer flocculates
0.2000	0.0046	43.0	Bright yellow	0.4000	Pink, polymer flocculates
0.2000	0.0012	165	Yellow	0.4000	Light pink
Methyl methacrylate				Dimethyl phthalate	
0.0400	0.0097	4.1	Yellow-green	0.1600	Bright yellow
0.0400	0.0048	8.0	Lemon color	0.1600	Bright yellow
0.0400	0.0011	36.0	Light lemon color	0.0400	No change
0.0400	0.0011	43.0	Light lemon color	0.0200	No change



**Fig. 3.** Electron spectra in dimethylformamide. a: Dimethyl phthalate solution obtained after the electrolysis at the first wave potential. b: Dimethyl phthalate solution obtained after the electrolysis at the second wave potential. c: Methyl methacrylate solution obtained after the electrolysis at the first wave. d: Solution of I obtained after the electrolysis at the first wave potential. e: Solution of I obtained after the electrolysis at the second wave potential

Reactions (1') and (3') to take place are present. The pink color of the solution is caused by the appearance of the double-charged dimethyl phthalate anion as a result of Reaction (3').

If  $[M]/[J] = 40$  or more, the equilibrium is shifted to the right and the conditions for Reaction (3') practically do not exist. The color of the solution in this case is caused by the ion-radicals of dimethyl phthalate.

To study this process in the absence of catalyst ion-radicals, we have tried to obtain electrochemically single- and double charged dimethyl phthalate ions. Electrolysis at the potential of the first wave of dimethyl phthalate results in the yellow solution giving an ESR signal typical of the anion-radical of dimethyl phthalate [13]. The electron spectrum of such a solution has an intensive band at 325 nm (Fig. 3a) and an intensive band at 410-420 nm which appears as shoulder at 470 nm.

The electrolysis at the dimethyl phthalate second wave potential results in a red-colored solution and the disappearance of the EST signal.

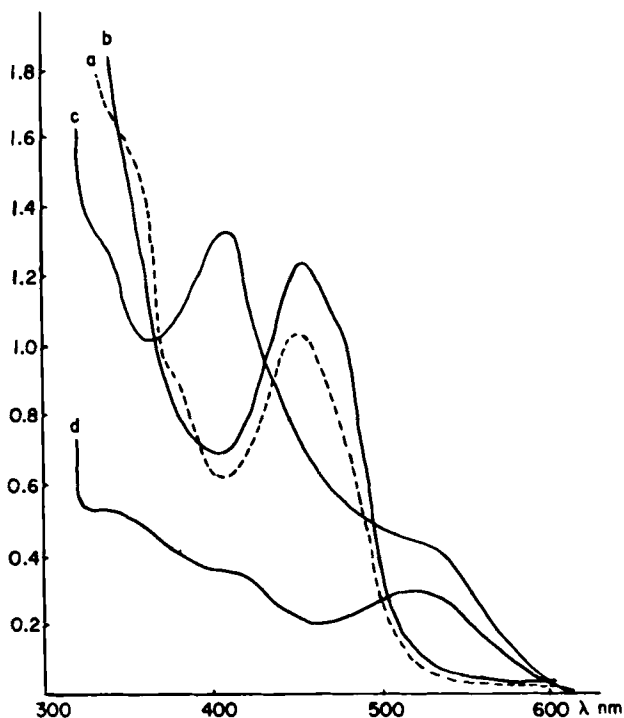
The electron spectrum of such a solution changes during the electrolysis in the following way: first, the intensity of the absorption bands at 420-470 nm increases and then, after the complete reduction of the product, the spectrum contains bands at 325 and 420 nm, a maximum appears at 560 nm, but a maximum at 470 nm disappears (Fig. 3b). Therefore, the distinct differentiation of absorption bands characteristic of ion-radicals and double-charged dimethyl phthalate anion is possible only with the electrochemical generation of ions and radicals. The comparison of the data of electrochemical and spectrophotometric studies allows us to conclude that the double charged anion of dimethyl phthalate has a pink color and can exist only at a definite ratio concentration of monomer and catalyst.

Decreasing or increasing the ratio  $[M]/[J]$  displaces the equilibrium of formation of the ion-radical of dimethyl phthalate or the ion-radical of naphthalene. The color of the solution (Table 1) appears to indicate that the transfer of electron from a catalyst to methyl methacrylate leads to establishment of an equilibrium in the system, this equilibrium being dependent on the  $[M]/[J]$  ratio.

Electrolysis of the methyl methacrylate solution leads both to the development of yellow color and to the appearance of adsorption bands at about 300 and 400 nm (Fig. 3c), the latter being identical to those obtained in a reaction of that monomer with sodium naphthalene. The above results permit one to suggest that the reaction equilibrium at the methyl methacrylate and catalyst concentration ratio of  $[M]/[J] \geq 15$  is almost completely shifted to the right.

The probability of electron transfer from reaction products in Reaction (1') or (2') to the second component was estimated from the experimental data obtained when a product of interaction of one of the components with a catalyst was mixed with another one. The electron spectra of the investigated system before and after the addition of the second monomer are presented in Fig. 4. One can see from Fig. 4 that the addition of dimethyl phthalate to methyl methacrylate causes practically no changes



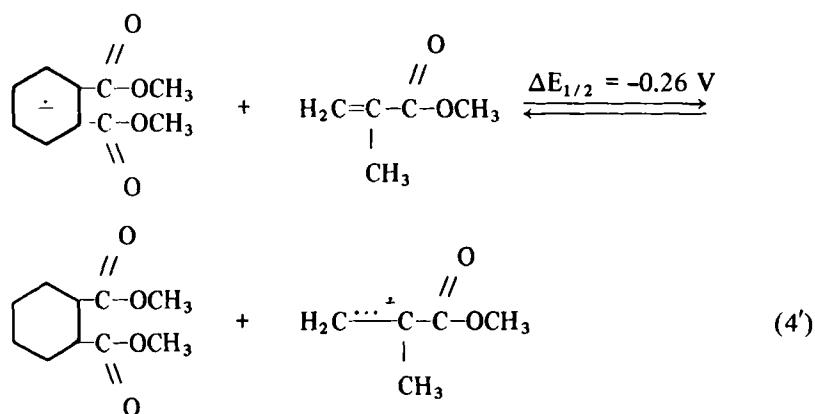
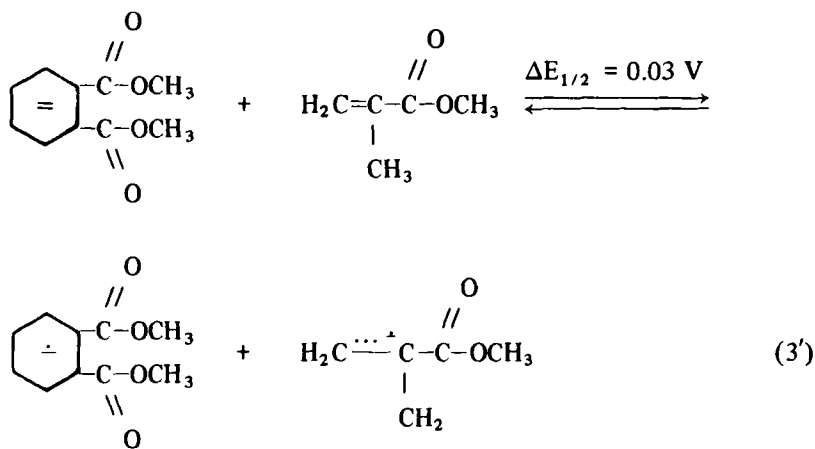


**Fig. 4.** Electron spectra mixtures. a:  $4 \times 10^{-2}$  mole/l methyl methacrylate and  $2.5 \times 10^{-3}$  mole/l sodium naphthalene. b: The same in the presence of  $1.6 \times 10^{-1}$  mole/l dimethyl phthalate. c:  $1 \times 10^{-1}$  mole/l dimethyl phthalate and  $2.6 \times 10^{-3}$  mole/l sodium naphthalene. d: The same in the presence of  $8 \times 10^{-1}$  mole/l methyl methacrylate.

in the spectrum or the color of the solution whereas the addition of methyl methacrylate to the solution of dimethyl phthalate with sodium naphthalene results in the less intensive absorption band at 410 nm, whereas the shoulder at 520 nm changes into a distinct maximum in presence of methyl methacrylate. This indicates that in the model system not only are Reactions (1'), (2'), and (2a') possible, but Reaction (3') and (4') are also.

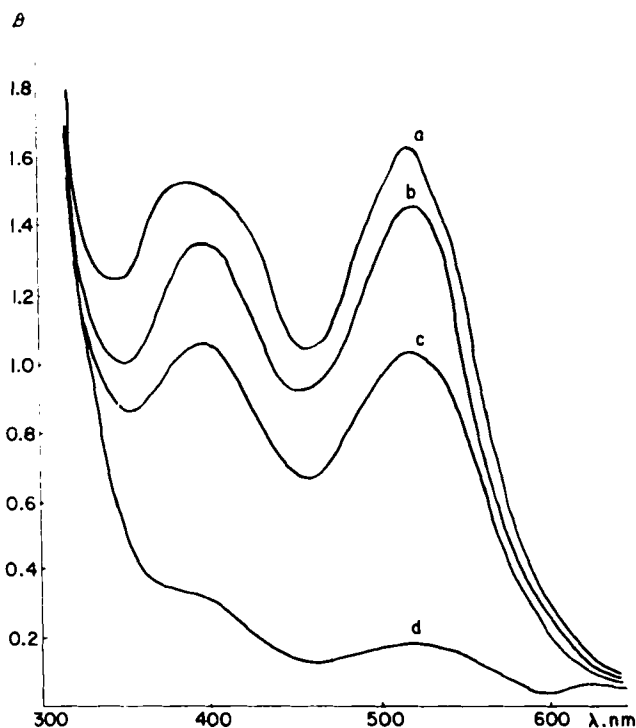
The  $\Delta E_{1/2}$  values show that the possibility of Reaction (4') is negligibly small. The electron spectra of the investigated system illustrate the left to right direction of both reactions.

It is probably that in the OEA-catalyst system, the equilibrium between both single and double charged ions obtained during the electron transfer to phthalate group of OEA exists and depends on the  $[M]/[J]$  ratio.



The most convincing proofs in favor of this suggestion are the electron spectra of a solution of I obtained after the electrolysis at the second wave potential (Fig. 3e). At first, maxima at 320 and 410 nm and a very weak band at 540 nm are observed. In such a system an electron transfer from the OEA phthalate group to methyl methacrylate is also conceivable. Nevertheless, it is likely that the equilibrium established in the OEA-catalyst system is very stable as no change of the ratio of absorption bands intensities was detected during 48 days (Fig. 5), there is only the total lowering of the band intensities.

Therefore, one may think that to obtain a shift in equilibrium in such a system it is necessary to change the ratio of concentration of the groups



**Fig. 5.** Electron spectra of  $8 \times 10^{-2}$  mole/l in the presence of  $3.5 \times 10^{-3}$  sodium naphthalene dissolved in tetrahydrofuran. a: 80 min after mixing. b: 24 hr after mixing. c: 120 hr after mixing. d: 48 days after mixing.

taking part in electron transfer. In fact, the experimental data have shown that the addition of methyl methacrylate to the living polymer in an ampoule leads to the gradual (in 5 days) yellowing of formerly red polymer and to a 25 wt % increase in polymer. The addition of dimethyl phthalate causes no changes whereas the addition of OEA results in a yellowing of polymer surface but no experimentally measurable polymer weight increase is observed. The above experimental data allowed us, first, to specify the equilibrium condition during the initiation of the OEA polymerization, and second, to prove that during polymerization there is no chain transfer or chain rupture reaction caused by electron transfer from the OEA-methyl methacrylate group on the growing end to the dimethyl phthalate group.

The results described lead to the conclusion that in anionic

polymerization of unsaturated oligoesters containing functional groups with different affinities to electrons the polymer chain is formed from the molecules bearing at least two like negative charges. In consequence the molecules forming a polymer network should be extended as much as possible, which might be of great importance for the formation of the network polymer. This should influence the first change in the network structure and the reaction kinetics.

### CONCLUSIONS

1. Spectrophotometric investigations of OEA and model systems have shown that in the course of interaction of sodium naphthalene with OEA electron transfer both to the phthalate and to the methyl methacrylate group of oligomer molecules takes place.

2. The separate stages of the electron transfer process were studied using polarographic methods.

3. Based on the differences of electron affinity of the catalyst and those of the reducible groups of OEA and of the model compounds, reaction schemes were proposed which describe the separate stages of electron transfer to OEA molecules.

4. It was found that in the OEA-catalyst system there is an equilibrium, the conditions of which are determined by the ratio of concentrations of catalyst and electron attracting groups as well as by the possibility of electron exchange between the phthalate and methyl methacrylate group of the OEA oligomer.

5. By means of spectrophotometry, ESR, and electrolysis at a controlled potential, it was shown that electron transfer is from the phthalate group of OEA to the methyl methacrylate group, whereas the reverse process does not take place. This shows the impossibility of chain ending and chain transfer because of the existence of two electron attracting groups in the OEA molecule.

### REFERENCES

- [1] T. E. Lipatova and W. M. Siderko, *Dokl. Akad. Nauk SSSR*, **178**, 856 (1968).
- [2] A. A. Berlin, T. Ja. Kefely, and G. W. Korolev, *Polyesteracrylates*, Nauka, Moscow, 1967, p. 54.

- [3] A. A. Arest-Yakubovich, *Uspechi Chimii Polimerov*, Chimia, Moscos, 1966, p. 5.
- [4] L. Silverman and W. G. Brandshow, *Anal. Chem.*, **31**, 1672 (1959).
- [5] J. Jovtscheff and F. Falk, *J. Prakt. Chem.*, **13**, 265 (1961).
- [6] Yu. K. Yurjev, *Practical Works on Organic Chemistry*, Moscow University, Moscow, 1967, pp. 47, 59.
- [7] Yu. L. Spirin, A. P. Hantmacher, and S. S. Medvedev, *Vysokomol. Soedin.*, **1**(8), 1258 (1959).
- [8] M. Murphy, M. J. Carangelo, M. B. Ginaina, and N. C. Marhan, *J. Polym. Sci.*, **54**, 107 (1961).
- [9] J. J. Hoijtink, *Rec. Trav. Chim. Pays-Bas*, **76**, 885 (1957).
- [10] M. Szwarc, *Makromol. Chem.*, **35**, 132, (1960). M. Szwarc, *Chim. Technol. Polim.*, **5**, 3 (1965).
- [11] J. J. Hoijtink, E. der Boer, P. H. van der Mei, and W. R. Weijland, *Rec. Trav. Chim. Pays-Bas*, **75**, 487 (1956).
- [12] E. A. Moelwyn-Hughes, *Physical Chemistry*, Pergamon, London-New York-Paris, 1961.
- [13] A. W. Iljasov, Yu. M. Kargin, A. Ya. Levin, I. D. Morozova, and N. N. Sotnikova, *Izv. Akad. Nauk SSSR, Chem. Ser.*, **5**, 1030 (1968).

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