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Mechanism of Polymer Formation in the System Oligoester Acrylate—Sodium Naphthalene

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ABSTRACT

The formation of living soluble and network polymers during anionic polymerization of α, ω-methacrylbis(triethylene glycol) phthalate leads to the two types of the equlibria in the system: the equilibrium distribution of electrons between groups with electron affinity and equilibrium between living soluble and network polymers and oligomer. The equilibrium state can be reached both by direct (polymerization) and reverse (depolymerization) reactions.

A characteristic feature of anionic polymerization of some monomers in aprotic solvents is the absence of chain termination [1]. One of the peculiarities of nonterminating anionic polymerization is the formation of living polymers. Szwarc [2] was the first to investigate the polymerization of styrene in the presence of sodium naphthalene, leading to the formation of living polymers. He suggested an explanation of the reaction mechanism.

Living polymers offer wide possibilities in synthesis of unique block copolymers, polymers of narrow molecular weight distribution and different functional end groups. Papers published during the recent 15 years in the field of anionic polymerization have been devoted primarily to investigation of this process for different monomeric systems under homogeneous conditions. The purpose of these investigations was to study the mechanism of active center formation, their nature, and the kinetic peculiarities of the initiation and chain propagation in anionic polymerization.

Rempp et al. [3] reported methods of synthesizing crosslinked polymers by anionic block copolymerization of two monomers under the action of bifunctional activators in an aprotic medium. The goal of these experiments was to obtain a model network approaching the ideal network with narrow distribution of chain segments between two crosslinks [4-6]. A number of papers have presented results of measurements and calculation of the parameters of such "ideal" networks, the influence of these parameters on the properties being analyzed as well [6, 7].

In 1964 Lipatova and Siderko were the first [8-10] to establish the possibility of anionic polymerization of unsaturated oligomers (oligoester acrylates, OEA), methods of their synthesis having been worked out by Berlin [11].

We found [12] that electrons transferring from catalyst to oligoester acrylate molecules are distributed between phthalate and acrylate groups having different affinities for the electrons. This distribution is a very rapid, equilibrium process. At the very beginning of the process, the electrons move preferentially to the phthalate groups and then to the acrylate ends, initiating in this way the polymerization process. Such an equilibrium electron distribution between functional groups exists all the time the living polymer exists. Thus, in the polymerization of oligoester acrylates, the polymer chain is formed from molecules bearing two like negative charges. This should have an influence on the macromolecule formation during anionic polymerization.

In this study we have made an attempt to find out these characteristic features of the reaction.

EXPERIMENTAL

The oligomer used in this investigation is α, ω-methacrylbis(triethylene glycol) phthalate. Experimental methods and purification of reactants were described earlier [12]. Tetrahydrofuran was used as a solvent for polymerization. The molecular weights of soluble polymer were determined by a sedimentation equilibrium method by using a G-120 ultracentrifuge at 20° C. Glycerine was used as an artificial bottom layer. The network polymer was extracted with acetone for 48 hr to remove soluble products. After extraction, the polymer samples were dried to constant weight in vacuo at 50 C.

IR spectra of network polymer were taken on KBr disks. Hermetically sealed cuvettes were used to obtain IR spectra of living polymer in solution, and NaCl glasses were used for the network polymers.

RESULTS AND DISCUSSION

Formation of Soluble and Network Polymers

As was established previously [8] for the polymerization of OEA in the presence of Na naphthalene, there exists a so-called limiting concentration of catalyst, below which the process practically does not proceed. The ratio of monomer(oligomer) concentration to limiting catalyst concentration C_M/C_{lim} is constant at constant temperature (Table 1). When the concentration of the catalyst is above the limiting catalyst concentration both the soluble and network polymers are fomed in the equilibrium mixture. The overall yield Q of the polymers as a function of the catalyst concentration is presented in Fig. 1. As can be seen, the overall yield has a maximum.

TABLE 1. Dependence of C_{lim} on the Coneentration of OEA and Temperature

Reaction temperature (°C)	C_M (mole/liter)	C_c (mole/liter)	(C_M/C_{lim})	Polymer yield (%)
25	0.078	0.0036	21.7	–
	0.6	0.027	22.2	0.21
0	0.066	0.0021	31.4	–
	0.6	0.017	35.2	0.2
-78	0.06	0.00075	80.0	–
	0.327	0.0043	76.3	0.17
	0.6	0.0079	75.9	0.22

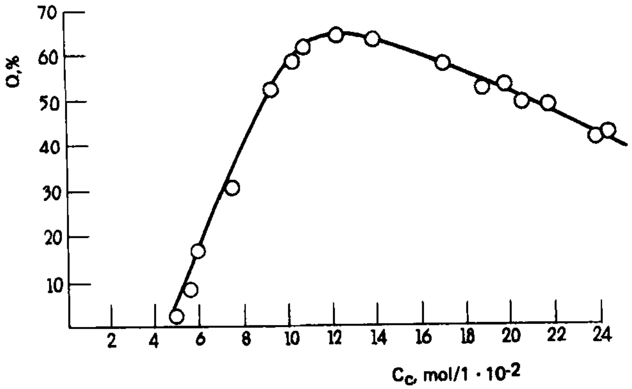

FIG. 1. Dependence of overall yield of polymer on concentration of sodium naphthalene in THF at 25° C.

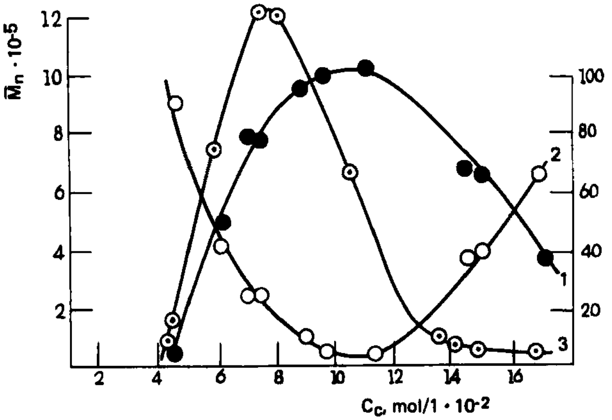

FIG. 2. Dependence of (●) yield of network polymer, (○) yield of soluble polymer, and (⊙) the molecular weight of the soluble polymer on the concentration of sodium naphthalene.

Figure 2 shows that the minimum yield of soluble polymer (curve 2) corresponds to the maximum yield of the network polymer (curve 1). Thus the maximum yield of the polymer is determined by the amount of network polymer.

The molecular weight of the soluble polymer reaches its maximum value 1.2×10^6 (Fig. 2, curve 3) at a catalyst concentration C_C of about 7×10^{-2} mole/liter. The soluble polymer has a sufficiently narrow molecular weight distribution (MWD) (Fig. 3) [14]. The shape of MVD curves is characteristic of "living" polymers obtained at the equilibrium process of the anionic polymerization of monomers [15].

From the Mark-Kuhn-Houwink equation, $[\eta] = kM^{\alpha}$, the value α was determined for the polymer of molecular weight 0.37×10^5 [16] to be 0.39, which indicates that there is considerable branching of the macromolecules. Naturally, a higher molecular product is characterized by a greater branching.

As can be seen, the molecular weight of the soluble polymer obtained from OEA is very high. This is obviously related to the fact that the growing chain of the oligoester carries charges not only at the ends, but also on the phthalate rings which are present as side substituents in each oligomer link.

As shown previously [12, 17], the number of electrons which an OEA molecule can receive varies from one to three, depending upon

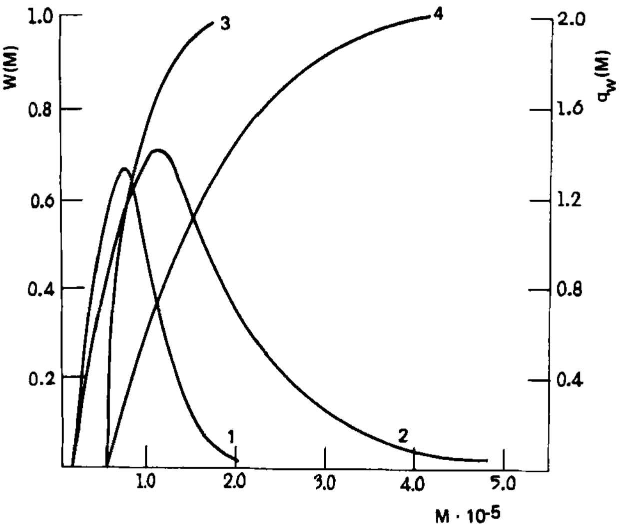

FIG. 3. Differential (1,2) and integral (3,4) curves of molecular weight distribution of the soluble polymer obtained at (1) $C_C = 3.5 \times 10^{-2}$ mole/liter and (2) 1.32×10^{-1} mole/liter.

C_M/C_C. Accordingly, the specific charge e_S of the growing chain changes as well (e_S is the number of electrons per link of the OEA growing chain).

Thus, a macromolecule growing by an anionic mechanism from oligoester fragments is an extended branching molecule which carries identical charges and reaches (due to Coulombic repulsion) great size before joining the network. Apparently, with the increase of catalyst concentration to a definite limit the e_S of the growing chain also increases, and this results from the increase in the Coulombic repulsions between the chains. This creates favorable conditions for the growth of the molecular weight of the soluble polymer (Fig. 2).

Unlike the radical polymerization of oligoester acrylates [11], in our systems the growing polymer chain carrying identical charges has a small possibility of changing its conformation. Therefore the network polymer obtained in the anionic polymerization of unsaturated oligoesters is, apparently, built of extended branched fragments.

If our supposition about the extended and branched character of the polymer chains growing according to the anionic mechanism is correct, then the charges neutralized (deactivation of the polymer) the viscosity of the solution of such polymer must decrease. Table 2 gives the values of the relative viscosities of a living and deactivated polymer at various concentrations of catalyst at 25°C in THF. As is evident from Table 2, the relative viscosity of a living soluble polymer is higher than the relative viscosity of a deactivated polymer.

Because not all the double bonds can be consumed in the formation of a soluble polymer, we have investigated the degree of unsaturation of the polymers obtained at various concentrations of the catalyst.

TABLE 2. Values of Relative Viscosities of Living and Deactivated Soluble Polymer Obtained at Different C_C[a]

C_C (mole/liter)	η_{rel}	
	Living polymer	Deactivated polymer
0.019	2.15	1.85
0.024	2.43	2.21
0.028	2.70	2.56
0.06	2.96	2.64

[a] Reaction temperature, 25°C; $C_M = 6 \times 10^{-1}$ mole/liter.

TABLE 3. Dependence of Degree of Unsaturation of Living Soluble Polymer on C_C

Starting material	C_C (mole/liter)	$D_{C=C_3}/D_{CH_3}$	Remark
α, ω-Methacrylbis-(triethylene glycol) phthalate	–	0.73	n = 1.4928, taken between NaCl glasses
Soluble living polymer	0.028	0.61	Red solution of "living" polymer taken between NaCl glasses
	0.059	0.44	"
	0.08	0.24	"

The degree of unsaturation of the polymer was evaluated by the change in the intensity of the absorption band of valence oscillations of the C=C bond, the absorption band of antisymmetrical oscillations of the CH-bond in the methyl group at a frequency of 1460 cm^{-1} [17, 18] being used as an internal standard. The results are given in Table 3.

As can be seen from Table 3, the unsaturation of the living soluble polymer decreases with increasing concentration of the catalyst. This is quite natural, since at high concentrations of the catalyst a higher molecular weight product is formed. Its molecular weight increases (Fig. 2, curve 3), and, consequently, the degree of branching also increases; as a result, less unsaturated macromolecules are formed. We suppose that the unsaturation of the network polymer must drop also.

Investigations of the polymer by IR spectroscopy shows that, with the increase of the catalyst concentration to a definite limit, the degree of unsaturation of the polymer drops (Fig. 4). The degree of unsaturation was calculated in a way similar to the soluble polymer. As is evident from Fig. 4, the minimum degree of unsaturation of the network polymer lies in the region of the catalyst concentrations in which the maximum yield of the polymer is obtained.

Anionic polymerization of OEA was investigated over a wide range of catalyst concentrations (Fig. 1 and 2) which made it possible to reveal regularities of the process more completely. Network polymer appears only beginning with $C_C = 4 \times 10^{-2}$ mole/liter and its

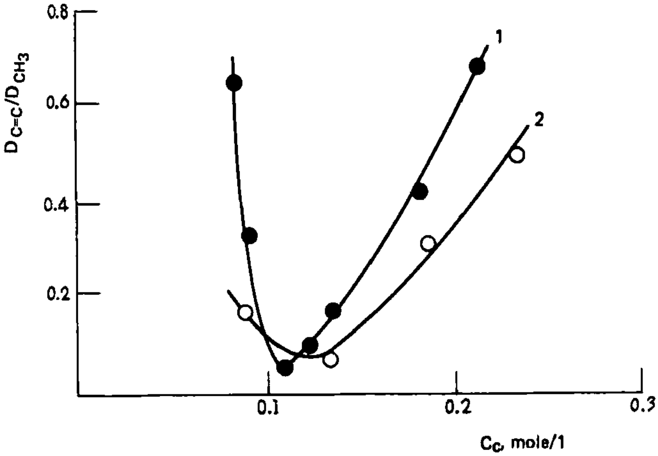

FIG. 4. Dependence of the degree of unsaturation of the network polymer on the concentration of sodium naphthalene and on temperature: (1) at 25° C; (2) at -78° C.

yield rises with catalyst concentration, reaching 65% at $C_C = 1.2 \times 10^{-1}$ mole/liter. Further increase in the catalyst concentration leads to a drop of the polymer yield. An increase of catalyst concentration leads to a decrease in both the molecular weight of the polymer and the yield of the network polymer and to an increase in the fraction of the soluble polymer. The drop in the molecular weight is caused, apparently, by the attainment of the limiting e_S of the growing chain at a definite catalyst concentration. Further increase of C_C leads to an increase in number of the initial active centers. Such a dependence is observed in the anionic polymerization of ordinary monomers [20].

However, it would be insufficient to explain the drop in the overall polymer yield and in the yield of the network polymer and the increase of the fraction of the soluble polymer at large C_C only by the accumulation of charged particles in the system.

Before discussing the reasons for the changes in the systems, depending on the catalyst concentration, we must consider some properties of the oligoester acrylate–sodium naphthalene system. The nature of groups capable to polymerization, catalyst, solvent, MVD of soluble polymer, and the color of the reaction mixture lead to the conclusion that the polymerization process proceeds with formation of living polymers [13]. This is of importance in explaining the influence of the catalyst concentration on the molecular weight of the soluble polymer. The living polymer formation is an equilibrium process. Therefore at each stage of reaction both direct (polymerization) and reverse (depolymerization) reactions are in process. Due to this, the decrease in overall yield of polymer, including yield of the network polymer, at large catalyst concentration should be explained not only by increase of the number of active centers, but also by an increase of the role of depolymerization when the oligomer/catalyst ratio decreases.

The many investigations of anionic polymerization indicate that the main factor which determines the equilibrium in the system is temperature. General considerations and experimental results presented in this paper lead to the conclusion that, besides temperature, next most important determining factor in the equilibrium in the system is the ratio of the oligomer (monomer) and the catalyst.

Conditions of Equilibrium in the Oligoester Acrylate Catalyst System

To be sure that the anionic polymerization of OEA involves equilibrium processes at the formation of living polymer as well as at the stage of electron distribution among the functional groups [12], we investigated the formation of polymer from OEA under the influence of sodium naphthalene as a function of time [20-22]. It was found that upon contact with the catalyst, the oligomer instantly acquires a peculiar color. The viscosity of this solution increases rather quickly, but the flocky network polymer appears in the form of a residue only after a long time (approximately several hours at 25°C). As can be seen from Fig. 5 in the first 30 min the degree of conversion reaches 5%, and in 2 hr it is somewhat more than 10%, which conforms with the results of previous investigations [8]. Apparently, at the initial instant of reaction, the rate is at the maximum (in relative units, equal to 0.2 relative unit/min). Thereafter, the process slows down, and during the time interval from 6 to 20 hr (curve 1, Fig. 5) the rate reaches 0.04 relative unit/min. After 24 hr of reaction at 25°C, equilibrium is reached, and the yield of the polymer practically does not change. Thus, it can be seen that for the oligomer systems reaching equilibrium in the formation of living polymers is a rather lengthy process.

As equilibrium is reached in the system, the molecular weight must remain constant. Our investigations of the molecular weight

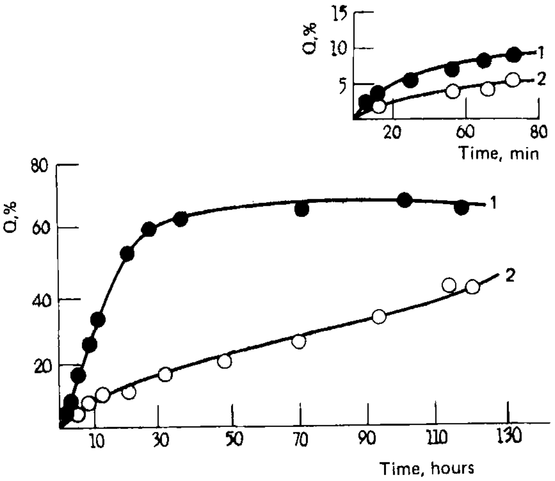

FIG. 5. Dependence of the overall yield of the polymer on the polymerization time of samples obtained (1) at 25° C; (2) at -78° C $C_C = 8 \times 10^{-2}$ mole/liter.

of a soluble polymer depending on time are presented in Fig. 6. It is seen that a marked increase in molecular weight takes place in the initial stage of the process, which conforms with the values of relative rates. After 5 hr of reaction the increase in the molecular weight is slower, and towards 24 hr of reaction the molecular weight reaches its equilibrium value. Generally, the molecular weight of the soluble polymer from the initial stage of the reaction (10 min) to the state of equilibrium (24 hr) changes approximately 20-fold.

After 24 hr of reaction, the system reaches equilibrium; the yield of the polymer does not change for a long time (observations conducted at 25° C for 5 days). However, at -78° C (Fig. 5, curve 2) the system does not reach equilibrium during the time of study, while at 25° C equilibrium is attained.

It is evident from the above results that the polymer chain of the soluble polymer grows sufficiently quickly, and, as it approaches the equilibrium state, the rate of growth drops sharply, which may be related to the increased probability of depolymerization. Besides, the reaction system contains a network polymer; therefore the

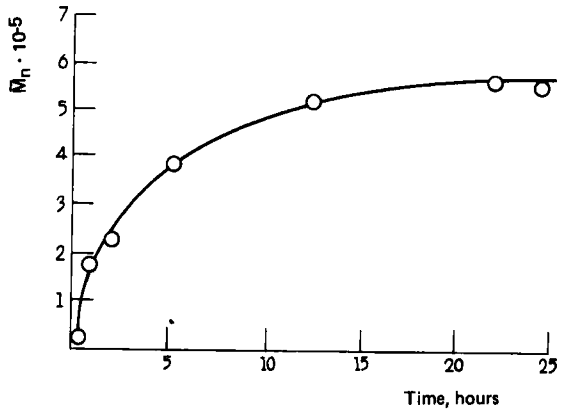

FIG. 6. Dependence of the molecular weight of the soluble polymer on the polymerization time at $C_C = 5.6 \times 10^{-2}$ mole/liter: (1) at 25° C; (2) at -78° C.

overall rate is probably determined by the diffusion rate of the reactants to the active centers of the network. This probably accounts for the sharp retardation of the process at low temperatures.

If the above suggestions of the equilibrium is correct, then in the reaction mixture an equilibrium amount of the oligomer must also exist [21]. As can be seen from Fig. 7 the minimum equilibrium concentration of the oligomer corresponds to the maximum overall yield of the polymer.

In a closed system, the living polymer coexists with the free catalyst and with a monomer [1], due to the depolymerization which goes on simultaneously with the growth of the chain. Therefore it may be concluded that in an equilibrium system where living polymers (soluble and network) are formed they ought to be present in equilibrium amounts. That means an equilibrium between free oligomer, soluble living polymer and network living polymer and catalyst must exist [21, 22].

If the system is in equilibrium, then, naturally, a question arises whether it is possible to approach the state of equilibrium from another point, i.e., to activate ("revive") the deactivated polymer, bringing it into contact with the catalyst under the same conditions, when a living polymer is formed from the corresponding monomer. Only two reports [23, 24] are known to indicate that the color

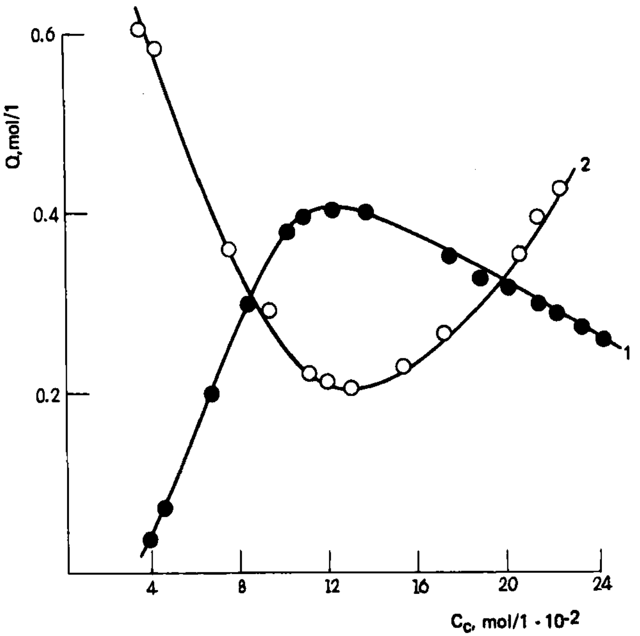

FIG. 7. Dependence of (1) the overall yield of the polymer and (2) the equilibrium concentration of the oligomer on C_C.

characteristic of the living polymer which takes place at the contact of inactive polymer with the catalyst is restored. However, the processes of attaining equilibrium in the system of living polymers which may be achieved both at polymerization and at depolymerization have not been studied. We considered it possible to reactivate the deactivated network polymer obtained in the anionic polymerization of the oligoester.

As an example of the investigation in this line we carried out the "revival" or "reactivation" of a deactivated (extracted by means of the solvent and dried) network polymer from α, ω-methacrylbis(triethylene glycol) phthalate, for which purpose the network polymer swollen in THF was subjected to the action of sodium naphthalene. In this case the polymer and the solution above it acquired a red coloration. After 24 hr of contact of the network polymer with the catalyst the weight of the network polymer decreased and both soluble polymer and oligomer appeared in the system. The latter was

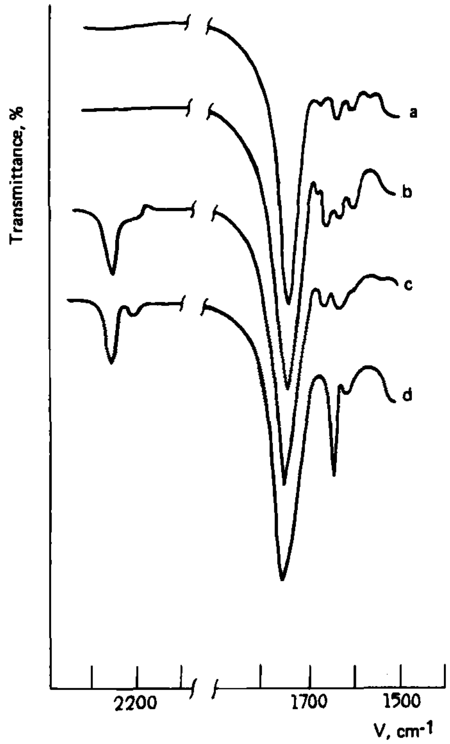

FIG. 8. IR spectra of polymers: (a) network polymer; (b) network polymer after activation; (c) activated network polymer after interaction with AN; (d) activated soluble polymer after interaction with AN.

ascertained polarographically by the appearance of the three waves which are characteristic for OEA. In this case, the relationship of the concentration of the equilibrium system components was similar to that for the direct reaction of OEA and catalyst at the corresponding ratio. In the reactivation of the network polymer an increase in the degree of unsaturation was observed by the increase in the intensity of the absorption band of the C=C bond in the region 1640 cm^{-1}, Fig. 8).

The fact that the addition of monomers [acrylonitrile (AN) or methyl methacrylate (MMA)] causes a change in the coloration and in the increase of the polymer weight proves that the "revived" (activated) polymer is active. In addition, appearance of a band characteristic of the CN group in the 2260 cm^{-1} region (Fig. 8c), in the IR spectrum of the "activated" network polymer after the contact with AN is further confirmation.

The results which were obtained during the investigation of polymer lead to the conclusion that for such an activation the mechanism by which polymer is obtained is of no importance, only it should be built of monomers (oligomers) capable of forming living polymers. To confirm this conclusion, the interaction with sodium naphthalene of the network polymer swollen in THF and obtained from OEA according to the radical mechanism was studied. The results were fully analogous to the results given above of the "revival" (activation) of the network anionic polymer.

On the basis of the results obtained we suppose that the means of reaching equilibrium in the system may also be characteristic of the usual linear polymers which are built of monomers able to form living polymers according to the anionic mechanism.

CONCLUSION

On the basis of the results the mechanism of formation of living network polymers and soluble polymers from oligoester acrylates, containing two types of functional groups can be pictured as follows. At the initial moment of reaction (just after the contact with the catalyst) an equilibrium distribution of electrons takes place among the functional groups of OEA, which have different affinity to the electron.

Apart from this kind of equilibrium, another kind of equilibrium exists in the system: living soluble polymer, living network polymer, and free oligomer. There is marked dependence of the amount of each product on the catalyst concentration, due to the fact that both the polymerization and depolymerization reactions take place in the reaction system.

The equilibrium of the process of living polymer formation from OEA enabled us to suppose that the state of equilibrium can be reached both by direct (polymerization) and reverse (depolymerization) reactions. We succeeded in showing that, on contact of deactivated polymer of network structure with catalyst, depolymerization takes place, and equilibrium amounts of the living soluble and network polymers and free oligomer arise in the system.

The equilibrium may be presented schematically [Eqs. (1)].

Oligomer + catalyst — initial system

↓

living soluble polymer + living network polymer + oligomer + catalyst — equilibrium system

↑

nonactive network polymer + catalyst — initial system (1)

The network living polymer is formed from extended branched fragments carrying identical charges and reaching critical values. The critical (equilibrium) value of the molecular weight of the fragment is determined by the oligomer/catalyst ratio and the temperature.

In our opinion, the availability of reaction-capable (living) ends in network polymers opens wide possibilities for introducing functional groups of various types into the network and imparting definite properties to the polymer.

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