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Publisher *Taylor & Francis*

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Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

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To cite this Article Lipatova, T. E. , Kuzmenko, L. S. and Shilov, V. V.(1979) 'Synthesis and Heterogeneous Structure of Anionic Networks of Oligoester Acrylates', *Journal of Macromolecular Science, Part A*, 13: 6, 777 – 787

To link to this Article: DOI: 10.1080/00222337908056688

URL: <http://dx.doi.org/10.1080/00222337908056688>

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Synthesis and Heterogeneous Structure of Anionic Networks of Oligoester Acrylates

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ABSTRACT

Anionic polymerization has been used for the synthesis of polymeric networks based on α,ω -dimethacrylbis(triethylene glycol) phthalate, α,ω -dimethacrylbis(diethylene glycol) phthalate, and α,ω -dimethacrylbis(ethylene glycol) phthalate. The dependence of network polymer yields on catalyst concentration has a maximum. The correlation between the value and position of maxima and the length of the initial oligomeric chain has been established. The network polymers were studied by use of small-angle x-ray scattering. The parameters of heterogeneous structure and their relation to the peculiarities of the polymerization process have been established. It was established that the microheterogeneous structure of the networks is determined by the geometric characteristics of the initial oligomeric chains and the conditions of synthesis.

INTRODUCTION

Unsaturated oligoester acrylates (OEA) are widely used in technological processes. Their hardening proceeds as a rule by radical polymerization. However, their ability to undergo anionic polymerization makes it possible to broaden considerably the feasibility of control of the structure of polymers obtained from a given oligomer [1, 2].

The investigation of networks obtained by anionic polymerization has shown that they are characterized by a great intensity of small-angle scattering. It has been suggested that this scattering is due to the heterogeneous structure of the polymers in question.

It is known that the mechanism of network formation and the molecular structure of the initial oligomer influence the essential structure of the network polymer [1, 3]. Therefore thorough investigation of the networks obtained from OEA with various lengths of the hydrocarbon chain between the polymerizing groups seems to be necessary.

The goal of the present work is the study of regularities of the polymer network by anionic polymerization of α, ω -dimethacrybis-(triethylene glycol) phthalate, α, ω -dimethacrybis(diethylene glycol) phthalate, and α, ω -dimethacrybis(ethylene glycol) phthalate and to find their relation to parameters of heterogeneous structure calculated from the small-angle x-ray diffraction.

EXPERIMENTAL

α, ω -Dimethacrybis(triethylene glycol) phthalate (OEA-1), α, ω -dimethacrybis(diethylene glycol) phthalate (OEA-2), and α, ω -dimethacrybis(ethylene glycol) phthalate (OEA-3) were purified in a chromatographic column filled with activated (calcined) aluminum oxide. Refractive indexes n_D^{20} of the purified OEA-1, OEA-2, and OEA-3 were 1.4920, 1.4998, and 1.5000, respectively. The purified reagents were loaded into a three-sectional vessel filled with argon and were thoroughly degassed. Polymerization was carried out in vacuo. The catalyst (naphthalenesodium) was prepared by the usual technique [4]. Network polymers were obtained from OEA-1, OEA-2, and OEA-3 by the method of "living" anionic polymerization as previously described [4, 5].

The character of the microheterogeneous structure of the polymers has been analyzed by the technique of small-angle x-ray scattering. As is known [6-8], this method makes it possible to determine dimensions of regions of heterogeneity of the value of 10 to 10^3 Å and other parameters.

The x-ray scattering intensities curves were obtained on a small-angle diffractometer with Cu-K α radiation. Primary beam collimation was performed by Kratky's method [9-11], and monochromatization of the beam was performed by the method of total reflection [12]. Scattering radiation was recorded with a scintillation detector controlled by a monitor. The latter recorded fluorescent radiation from the edges of the output slit of the vacuum chamber.

The entire recording unit functioning in accordance with the scheme described previously [13]. Diffractograms were taken in the mode of counter automatic step-by-step scanning.

To reduce the scattering curves to the absolute scale, scattering intensity was measured with the aid of a standard Lupolen specimen which was kindly supplied by Professor O. Kratky. A MIR-1 computer was used to evaluate characteristics of the microheterogeneous structure of the network polymers.

RESULTS AND DISCUSSION

Figure 1 illustrates the dependence of the yields of the network polymers obtained from oligomers of various structures on the catalyst concentration. As is seen, curves 1, 2, and 3 have maxima, and with decreasing chain length between the polymerizing groups, the maximum is shifted towards the region of larger catalyst concentrations and reduced in absolute value.

The decrease in the network polymer maximum yield in the series OEA-1, OEA-2, OEA-3 can be attributed to the diminution of the critical molecular mass of the branched soluble macromolecular fragments of which the network is built [1]. Obviously, this fact may be explained by a decreased conformer number for shorter chains and correspondingly with more adverse conditions for the formation of network structures.

The shift of the maximum yield towards larger concentrations of the catalyst can be explained by an increase of the specific charge of growing branched fragments.

It should be noted that a distinguishing feature of these systems is the presence in the initial OEA of two types of groups (phthalate and methacrylate), able to accept an electron which are characterized by a different affinity to electrons and then separated by a system of σ -bonds of various lengths. Earlier [4] it was shown that the phthalate ring has a greater affinity for electrons than methacrylate groups. Hence, the distribution of charges in oligomers under polymerization is shifted appreciably towards preferential position of electrons on the phthalate rings. The number of phthalate rings in a volume unit of OEA-3 is substantially greater than for OEA-1; consequently the magnitude of a specific charge is much greater in the first case.

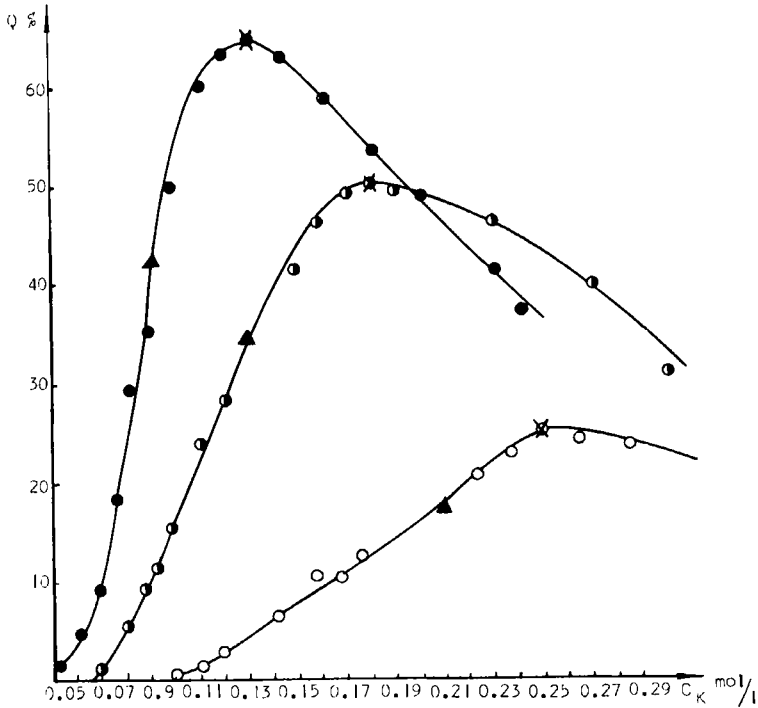


FIG. 1. Network yield - catalysis concentration plots: (●) OEA-1; (●) OEA-2; (○) OEA-3.

This, together with a restricted conformation set (inherent in the shorter chains) brings about greater coulombic and steric hindrances in the formation of the polymer network, an increase in the content of the catalyst required being therefore necessary to obtain a maximum in the yield of the polymer.

Figure 2 illustrates the curves for small-angle scattering of x-rays in the polymers under investigation. These curves were obtained for materials which correspond to maximum yield of network polymer (crosses in Fig. 1) and maximum yield of soluble polymer (triangles in Fig. 1) and for a network based on OEA-2, which was prepared by the electrochemical initiation method.

It will be seen that an exceptionally high level of scattering is characteristic of all the examined networks. These curves can be arbitrarily divided into three groups: OEA-3 (two curves); OEA-2

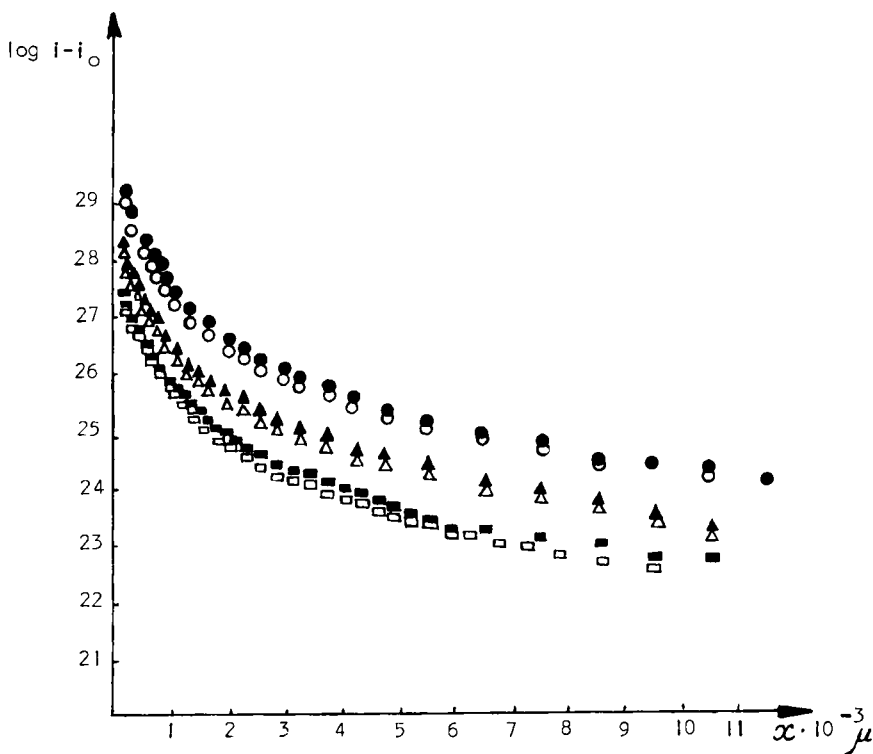


FIG. 2. Plots of $\log I$ vs. scattering angle for series of anionic networks: (1) (●) OEA-3, maximum yield of network; (2) (○) OEA-3, maximum yield of soluble polymer; (3) (▲) OEA-2, maximum yield of network; (4) (△) OEA-2, maximum yield of soluble polymer; (5) (●) OEA-2, electrochemical initiation; (6) (□) OEA-1, maximum yield of network.

(two curves); OEA-1 and OEA-2 prepared by the method of electrochemical initiation.

The absence of the effect of interparticle interference is characteristic of all the curves of Fig. 2.

The high level of scattering in the system is indicative of an exceptionally well developed heterogeneity of the polymer. This can be explained by the presence of regions with sharply differing electron densities. Amorphous polymers produced in block are characterized by insignificant fluctuations of electron density of supermolecular

formations [14-19]. Consequently, it is impossible to explain the sharp increase of the scattering ability of the networks by the fluctuation of electron density caused by the presence of more or less orderly regions. There are indications that small-angle scattering can increase appreciably due to the embedding of foreign particles [15], including in this case, fragments of catalyst. However, virtually the same level of scattering as for the rest of the specimens is observed for the polymer prepared by the method of electrochemical initiation of anionic polymerization.

On the other hand, we have compared the small-angle scattering for networks based on OEA immediately after polymerization and the same materials extracted by the usual method. In the first case, the scattering level was very low and increased after extraction. This may be explained by the formation of micropores due to removal of solvent, oligomer, and soluble polymer from the network bulk.

It is a known fact that networks prepared in a solvent can be characterized by microporosity [20]. The presence of micropores results in great local differences in electron density, hence, in a sharp increase of material scattering.

As seen in Fig. 2, the heterogeneous structure of networks formed in this type of polymerization is to a considerable degree dependent on the structure of oligomer molecules, and to a much lesser degree, on the anionic polymerization conditions. However, a sudden change in the technique of polymer production leads to a considerable change in the polymer heterogeneous structure. Thus the curve characterizing the network polymer prepared from OEA-2, by the method of electrochemical initiation (curve 5), differs appreciably from the two curves characterizing OEA-2 obtained by the method of chemical initiation (curves 3 and 4).

A more or less compact packing of microregions of a heterogeneous structure commonly leads to interference peaks on small-angle scattering curves [6]. The absence of such effects indicates a diluted character of the heterogeneous structure, i. e., a considerable excess of distances between heterogeneity regions over the sizes of those regions.

After processing the small-angle scattering curves of Fig. 2, the following quantitative characteristics of the microheterogeneous structure have been obtained: distance of heterogeneity l_c [6, 21, 22]; average sizes of regions on nonhomogeneous structure l_p [19, 21-23]; average radii of heterogeneous structure regions [6-8, 19, 24, 25]; specific surface of heterogeneity S/V [6, 26]; average square of fluctuation of the electron density, $\langle \eta^2 \rangle$ [26]; thickness of the transition layer between phases found in accordance with Fonk's program [27]; volume fraction of micropores, $\varphi_1(1 - \varphi_1)$ calculated on the basis of the relation $\langle \eta^2 \rangle = \varphi_1(1 - \varphi_1)(\rho_1 - \rho_2)^2$ [19]. For pores $\rho_2 = 0$, and therefore $\varphi_1(1 - \varphi_1) = \langle \eta^2 \rangle / \rho_1^2$.

TABLE 1. Structural Parameters for Anionic Networks Obtained by Small-Angle Scattering

Network	Curve in Fig. 2	l_p (Å)	l_c (Å)	R_1 (Å)	R_2 (Å)	S/V (m^2/g)	Porosity (%)	$\langle \eta^2 \rangle \times 10^2$ (dl-mole/cm ³) ²
OEA-1	6	895	-	60	580	0.07	0.27	0.12
OEA-2	5	965	725	60	580	0.13	0.31	0.13
OEA-2	4	710	450	55	420	0.52	0.74	0.33
OEA-2	3	690	450	55	420	0.52	0.74	0.33
OEA-3	2	635	280	60	460	2.8	2.5	1.1
OEA-3	1	650	400	60	460	3.8	4.7	2.1

The respective quantitative characteristics of the microheterogeneous structure of the networks are given in Table 1. Table 1 shows that in the range OEA-3, OEA-2, OEA-1, l_c increases from 600 to 900 Å. For OEA-2 obtained by the method of electrochemical initiation, l_c is the greatest (960 Å). Hence, for all networks obtained by the same initiation method a correlation is shown between l_c and the chain length in the polymerizing groups. However, there is a deviation from this relationship for the network obtained by a substantially different method.

The l_p values were determined by the asymptotic path of the small-angle scattering curves at maximum angles. In accordance with this, it should be noted that the presence of micropores different in size should lead to a difference in the values l_c and l_p , since l_c is an integral criterion and the l_p value is materially affected by the availability of smaller regions of heterogeneity. Therefore, by analyzing the differences between l_c and l_p , a conclusion can be made about differences in the sizes of the heterogeneity regions available in the system. These differences are the greatest for the OEA-3 specimen (specimen 2), 635 to 280 Å. They are the smallest for the OEA-2 specimen obtained by the method of electrochemical initiation i. e., 960 to 725 Å. Hence, a narrower distribution of pores by the sizes is characteristic of a latter specimen.

Figure 3 illustrates the dependence of the natural logarithm of scattering intensity on the square of the scattering angle. In compliance with the existent theory these dependences for a fully dispersed

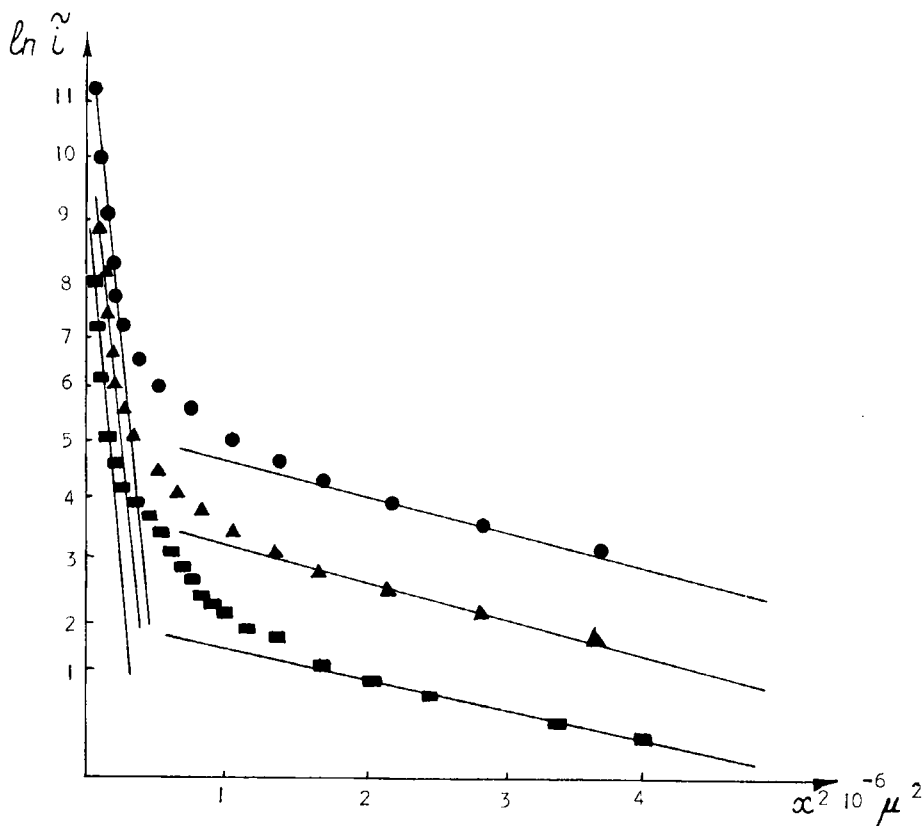


FIG. 3. Plots of $\ln i$ vs. square of scattering angle for series of anionic networks: (●) OEA-3; (▲) OEA-2; (■) OEA-1.

system must be rectilinear [6-8]. In the case when a system has several regions of heterogeneity of certain sizes, their radii can be determined by plotting a number of tangents [6].

Usually it is achieved by rectifying portions of the curve. In our case the character of the curves of Fig. 3 makes it impossible to rectify their individual portions. It shows that the systems are perhaps characterized by a high degree of polydispersion of the particles [28].

For this reason we have determined only the minimum and maximum sizes of the regions of heterogeneity corresponding to the outer and inner sections of the curves (Fig. 3).

The minimum radii of micropores for all the networks are on the average 60 Å. The maximum radii are from 400 to 600 Å.

The volume fraction of micropores increases suddenly in passing from OEA-1 to OEA-2 and OEA-3 (from 0.3 to 5%). The specific surface of heterogeneity for the specimens obtained on the basis of OEA-3 is also the greatest.

Fluctuation of electron density also increases by one order of magnitude in passing over from the networks based on OEA-1 to the networks based on OEA-3. The latter values S/V , ϕ , $\langle \eta^2 \rangle$, indicate a material increase in the total volume of micropores and heterogeneity of the networks with the reduction in the length of the oligomeric molecule. It should be noted that with comparatively large regions of heterogeneity the thickness of the transition layer is relatively small (of the order of 10 Å). This fact points to the presence of sharp phase borders between the polymeric matrix and micropores and to virtually ideal two-phase structure of the networks. (The observable thickness of the boundary layer corresponds in length to not more than one molecule of the oligomer).

It should be noted that the principal feature of the networks based on OEA-1, OEA-2, and OEA-3 is that the concentration of catalyst required for a maximum yield of the network polymer is at maximum for the case of OEA-3.

Perhaps, in the initial oligomer-solvent system electrons are uniformly distributed in the microspaces. In polymerization, a microstratification occurs usually during the formation of a network polymer in the presence of a solvent [29]. In such a case, the specific charge of microregions of the network structure increases, which causes local inhibitions of the process of polymerization. Since in oligomers with shorter chains the magnitudes of specific charges are greater, the feasibility of such a process for the resulting networks increases. This leads to the emergence of a large number of weakened (less crosslinked) regions. Upon removal of the solvent the gel volume diminishes suddenly (decreases sharply). Fragments of the polymeric network strive to assume a more compact packing so as to have a minimum of free energy. This leads, probably, to the onset of a great number of internal stresses and their irregular distribution in the network. Owing to this, areas of polymer with a comparatively small quantity of crosslinks become places where origination of micropores is highly probable.

Obviously, the networks based on OEA-1 are characterized by lesser local heterogeneity; hence, the number of weakened areas in the networks is smaller. Additionally, after removal of the solvent, microstresses should be smaller, due to a wider conformation selection. All this leads to a comparatively smaller quantity of micropores on the OEA-1 basis.

Those networks are characterized by a smaller polydispersity of the heterogeneous system which also points to a more uniform course of the polymerization processes.

The comparison of the characteristics of microheterogeneous structure of the networks obtained by the methods of chemical and electrochemical initiation shows that in the latter case the microheterogeneity of the network is less expressed: $\langle \eta^2 \rangle = 0.33 \times 10^{-2}$ and 0.13×10^{-2} , respectively. This is related to peculiarities of the reaction of growth of polymeric molecules near the electrode.

CONCLUSION

Networks based on OEA obtained by the method of anionic polymerization in the oligomer-solvent system are characterized by a marked heterogeneous structure. Microheterogeneity is peculiar to all cellular polymers, especially to those obtained in a solvent. In contrast to polymerization in the absence of charges in anionic networks, the formation of micropores is determined by a coulombic interaction of charged fragments of the polymeric network being formed.

Besides, the processes of polymerization of the polymer-oligomer-solvent systems studied are characterized by a local heterogeneity associated with the molecular structure of the initial oligomers, so that a greater heterogeneity of the system is characteristic of shorter and more rigid oligomeric molecules.

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Accepted by editor October 6, 1978

Received for publication December 11, 1978