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# Morphology of Polymer of Ethylene Sulfide and Its Block Copolymer with Styrene

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## Synopsis

It has been found that poly(ethylene sulfide) obtained by anionic polymerization in tetrahydrofuran assumes the shapes of platelets, microhedrites, microspherulites, or particles of irregular structure, depending upon the molecular weight of poly(ethylene sulfide). In the case of block copolymers of ethylene sulfide and styrene, the morphological form has been found to be dependent upon the composition of the copolymer.

## INTRODUCTION

Few works on the morphological structure of as-polymerized polymers, i.e., polymers receiving no subsequent treatment have been published. Most studies to date have been concerned with the morphological structure of polymers subjected to various treatments, for example, melting, dissolution, etc., which have a distinct effect on the physical structure of polymers.

Kargin and co-workers[1] have found that in the case of crystalline poly(vinyl chloride) and polyethylene the supramolecular structures are already formed during the polymerization process.

Niegisch[2,3] observed high dendritic crystals in early stages of polymerization of linear polyethylene and spherulites in later stages of polymerization.

Up to now the morphological structure of poly(ethylene sulfide) and its block copolymer with styrene has not been investigated. The copolymers should have an interesting morphological structure, as they are composed of a crystalline poly(ethylene sulfide) and an amorphous polystyrene.

The aim of the present work was to investigate the morphological forms of the polymer of ethylene sulfide and its block copolymer with styrene. The effect of molecular weight on the morphological structure of poly(ethylene sulfide) was studied, as well as the effect of chemical composition of block copolymers of ethylene sulfide and styrene on the morphological structure.

## EXPERIMENTAL

### Polymer Characteristics

Of the polymers under investigation, sample 1 is styrene homopolymer (PS), the samples from 2–6 are poly(ethylene sulfides) (PES) of various

TABLE I
Characteristics of the Polymer Samples

| Sample no. | Polymer | $M_n$ (theoretical)[a] Polymer | $M_n$ (theoretical)[a] PES Segment | PES content, wt.-% | Melting point, °C. | Density, g./cm.$^3$ [b] |
|---|---|---|---|---|---|---|
| 1 | PS | 7200 | | | | |
| 2 | PES | 540 | | 100 | 155[c] | 1.35 |
| 3 | PES | 960 | | 100 | 177[c] | 1.34 |
| 4 | PES | 1440 | | 100 | 184[c] | 1.34 |
| 5 | PES | 5560 | | 100 | 204[c] | 1.35 |
| 6 | PES | 14280 | | 100 | 206[c] | 1.35 |
| 7 | Copolymer | 6850 | 690 | 9.4 | — | 1.06 |
| 8 | Copolymer | 6650 | 1670 | 22.6 | 164[d] | 1.10 |
| 9 | Copolymer | 6480 | 3260 | 44.9 | 215[d] | 1.16 |
| 10 | Copolymer | 6600 | 3960 | 85.7 | 227[d] | 1.31 |

[a] Value calculated according to Szwarc equation: $M_n = [M]/{}^1/_2[C]$, derived for anionic polymerization in the presence of dianions.[6]

[b] Determined by the gradient column method in a system of concentrated aqueous solution of $ZnCl_2$ + water.

[c] Determined by Boetius microscope with heated plate on the principle that a change of shape marks out the melting temperature.

[d] Determined by the DTA method.

molecular weights, and samples 7–10 are block copolymers of styrene and ethylene sulfide of various chemical compositions. The samples were obtained by anionic polymerization in tetrahydrofuran, potassium naphthalene being used as catalyst.[4,5] The characteristics of the investigated samples are given in Table I.

All the polymers characterized in Table I, except polystyrene and its copolymer containing 9.4% of poly(ethylene sulfide), precipitated from the reaction medium as fine powders.[4,5] The powder samples of polymers were rinsed with methanol, dried at 60°C., and used for electron microscope study.

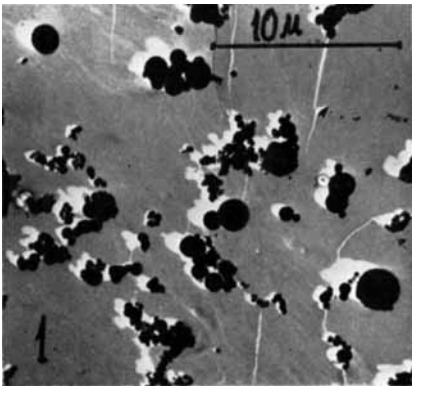


Fig. 1. Polystyrene.

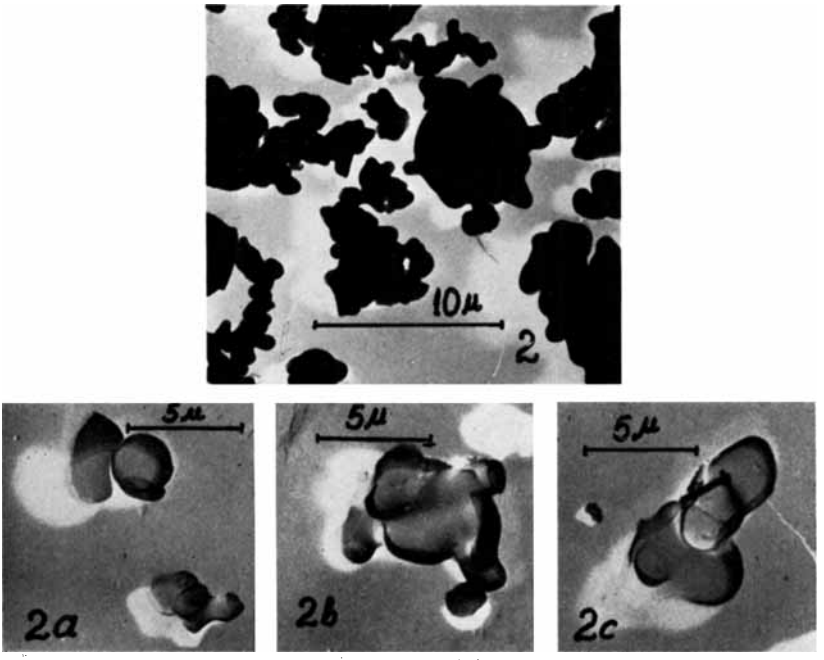


Fig. 2. Copolymer containing 9.4% PES.

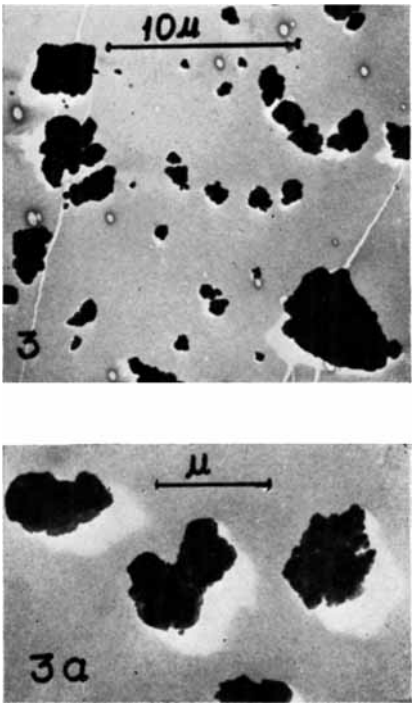


Fig. 3. Copolymer containing 22.6% PES.

Polystyrene and its copolymer containing 9.4% poly(ethylene sulfide) were precipitated with methanol. The powders obtained were dried and used for investigation.

### Preparation of Specimens for Electron Microscopy

The powder specimens were spread over a net covered with a film of poly(vinyl acetate). An excess of powder was shaken or blown off, and this was repeated several times. The two sides of the carrier films, which were formed by evaporation of a drop of 0.2% poly(vinyl acetate) solution in benzene from a water surface, are not the same. It has been found that the water side of the film has much better adhesion to the test specimens than

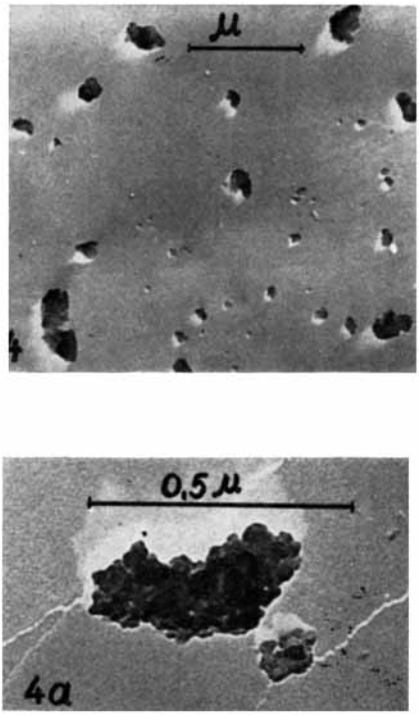


Fig. 4. Copolymer containing 44.9% PES.

the air side of the film. It is, therefore, much easier to work on the water side of the film.

The specimens for smaller magnification were shadowed with gold and those for greater magnification were shadowed with germanium at an angle of 45 ±3°.

Replicas of block copolymer specimens containing 9.4% poly(ethylene sulfide) were made of germanium as described above. The study was carried out on an electron microscope, type VEMW-100 (Soviet Union).

## RESULTS

Results of observations are given in Figures 1–10. Neither polystyrene nor the copolymer containing 9.4% poly(ethylene sulfide) precipitates during polymerization. On addition of methanol they precipitate from the reaction solution as powder particles of different shapes. Polystyrene precipitates in form of spherical particles of different sizes (Fig. 1). The copolymer particles are in the form of lumps stuck together or aggregates of smaller elements (Fig. 2). It can be seen from the replicas (Figs. 2*a*,*b*,*c*) that these lumps are mostly separate particles of irregular shape.

Under low magnification the particles of copolymer containing 22.6% poly(ethylene sulfide) appear to be aggregates with deckle edges (Fig. 3), but at higher magnifications (Fig. 3*a*) one can perceive their granular structure. At higher poly(ethylene sulfide) content, namely, at 44.9% and 85.7% (Figs. 4 and 5), the structure of particles appears to be a type of laminar platelet. In addition, fine plates are also observed (Fig. 5).

Poly(ethylene sulfide) particles of molecular weight about 500 have a pronounced platelet structure (Fig. 6), the size of platelets being quite considerable. Their thickness varies over a considerable range. In Figure 6*b* the thickness is from 50 to 300 A. Larger particles (Fig. 6*c*) consist of small platelet elements. With an increase in molecular weight increase to

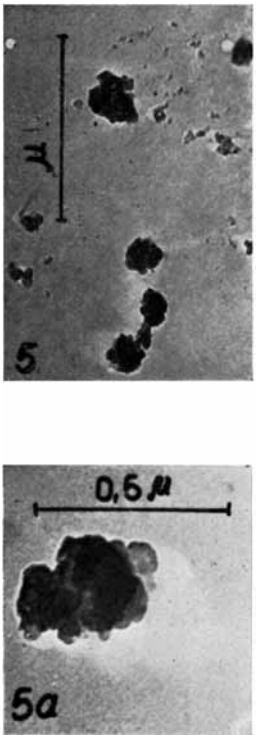


Fig. 5. Copolymer containing 85.7% PES.

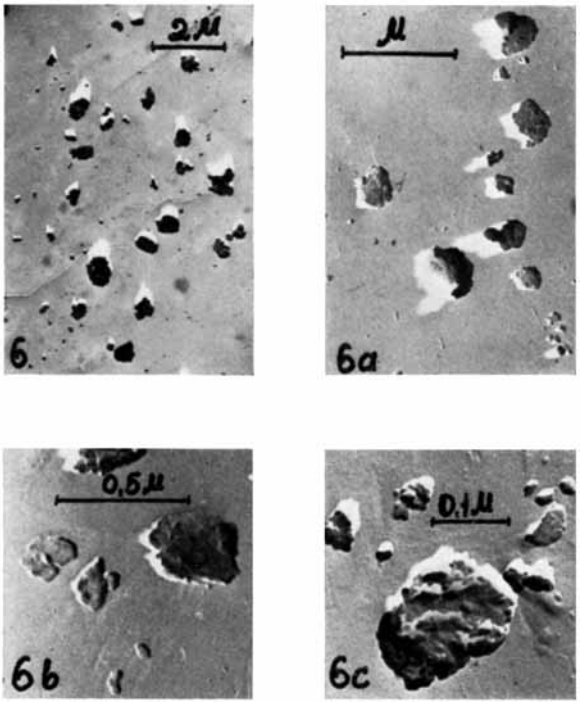


Fig. 6. PES of molecular weight 540.

about 1000 one can observe an interesting phenomenon. Besides the platelet forms (Fig. 7) one can perceive microspherulites (Fig. 7*a*, arrow) having branches developed in one plane. These morphological forms develop more distinctly at molecular weights of about 1500 (Fig. 8). At a molecular weight of about 5600, the poly(ethylene sulfide) particles are mostly flat and consist of smaller elements (Fig. 9), primarily microhedrites and microspherulites. One can also observe platelet forms (Fig. 9*d*).

In case of polymer having a molecular weight of 14,280 one can observe a diminution of the regularity of morphological structure as compared with the polymer of molecular weight 5560; in this case microspherulites and platelets appear rarely (Fig. 10*b*, 10*c*). The polymer particles mostly irregular in shape and have a tattered surface. The appearance of whiskers developing from particles can be considered as an interesting detail of morphological structure of polymer having molecular weight 14,280 (Fig. 10, 10*a*).

## DISCUSSION

Poly(ethylene sulfides) do not dissolve completely in a reaction medium consisting of tetrahydrofuran. Due to this it is hardly likely that free macromolecules could be formed first in nonsolvent medium involving a saturation of solution followed by a very fast formation of morphological

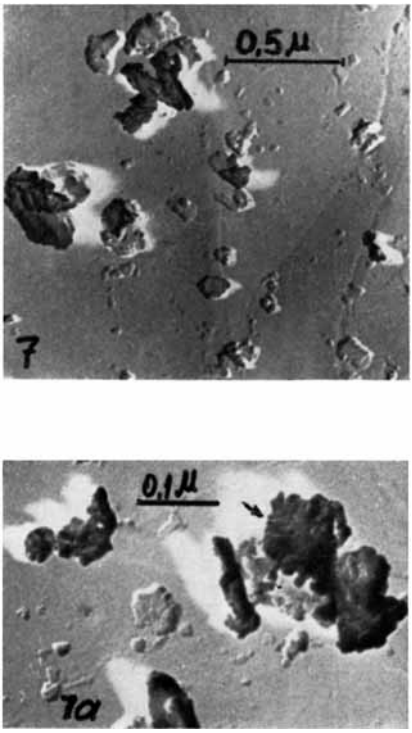


Fig. 7. PES of molecular weight 940.

structure consisting of platelets or microspherulites typical of high crystalline state of polymers. Hence one might believe that the poly(ethylene sulfide) structures described are formed during the propagation phase of the polymerization process. This would mean that macromolecules are arranged in the observed morphological forms within their growth during polymerization.

It may be concluded that the ordered supramolecular structures can be formed directly during the polymerization process. The observed forms depend distinctly upon the molecular weight. At low molecular weight (about 500–1000) one can observe the platelet form, and at higher molecular weight (about 1500–5600), microhedrites and microspherulites. At a molecular weight of 14,280 particles of irregular structure are formed. The reason for this is not clear on the basis of the present data.

As far as the copolymers are concerned, the presence of the polystyrene segment in the macromolecule has a distinct modifying effect upon the form of the products formed. This can be clearly seen in case of copolymers containing 22.6 and 44.9% poly(ethylene sulfide); the molecular weights of the poly(ethylene sulfide) segments are about 800, 1600, and 3000 (Table I), but the copolymer is in the form of microplatelet aggregates, while the poly(ethylene sulfides) of similar molecular weight are either of distinctly developed platelets or microhedrites or microspherulites.

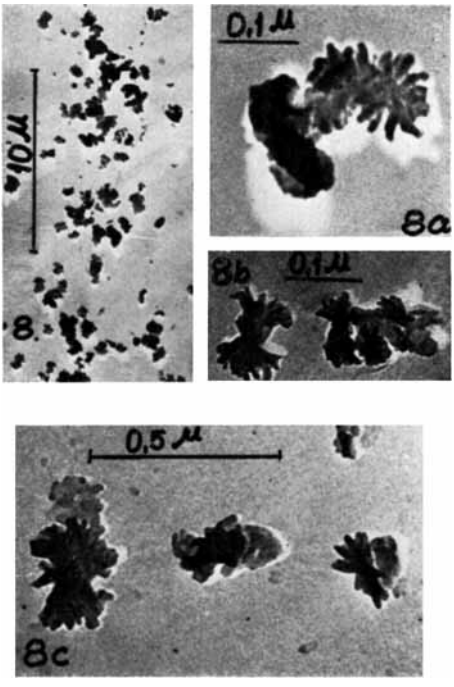


Fig. 8. PES of molecular weight 1440.

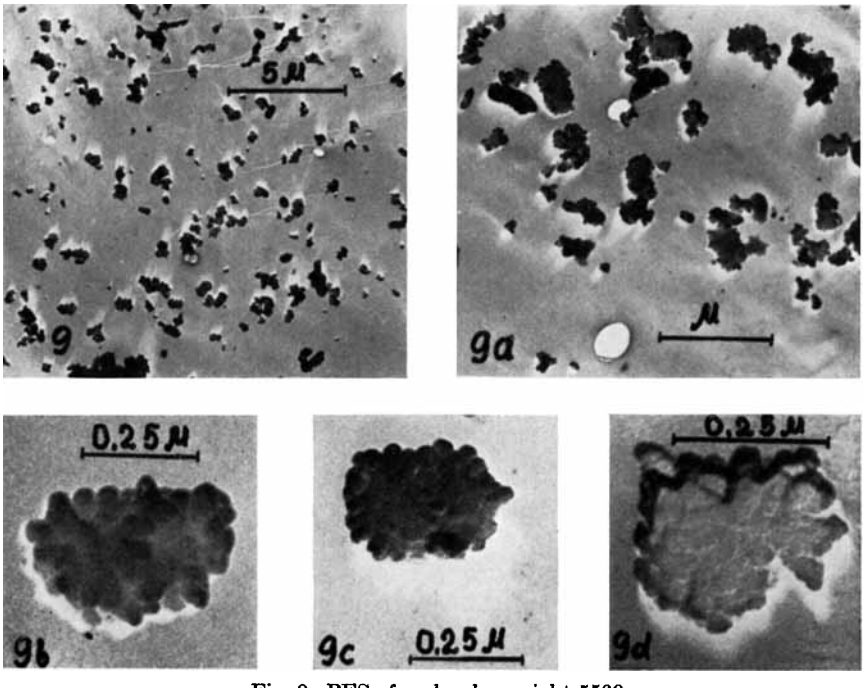


Fig. 9. PES of molecular weight 5560.

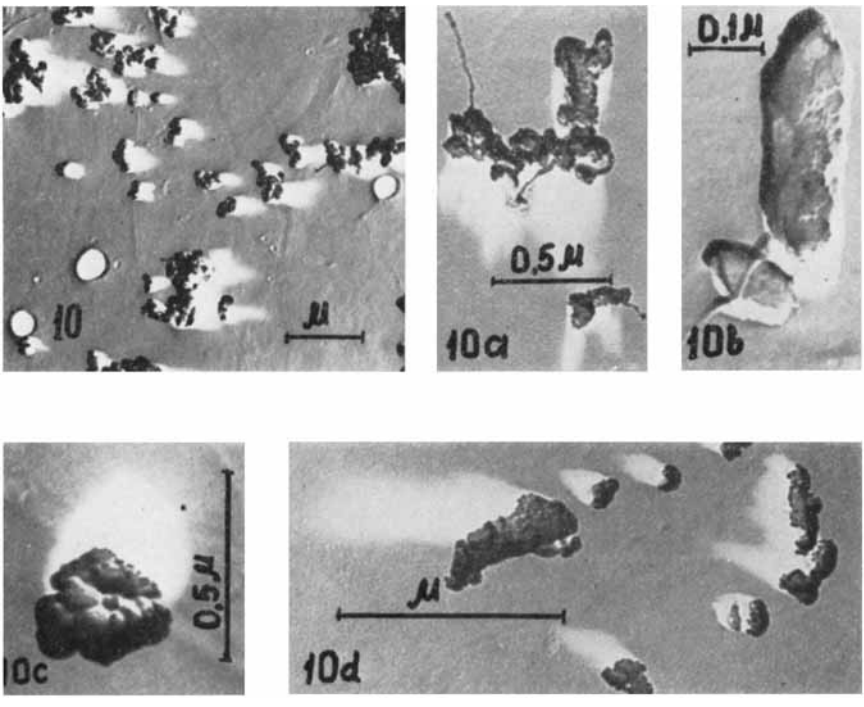


Fig. 10. PES of molecular weight 14,280.

The copolymer containing 9.4% poly(ethylene sulfide), although it can be dissolved in the reaction medium like polystyrene, precipitates as particles different in form from polystyrene particles.

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## Résumé

On a trouvé que les formes morphologiques du sulfure de polyéthylène obtenu par polymérisation anionique dans le tétrahydrofurane, étaient des plaquettes, des microhédrites, des microsphérulites ou des particules présentant une structure irrégulière fonction du poids moléculaire du sulfure de polyéthylène utilisé. Dans le cas de copolymères séquencés de sulfure d'éthylène et de styrène la forme morphologique dépendait de la composition du copolymère.

## Zusammenfassung

Es wurde gefunden, dass die morphologischen Formen des durch anionische Polymerisation in Tetrahydrofuran erhaltenen Polyäthylensulfids in Abhängigkeit vom Molekulargewicht die Gestalt von Plättchen, Mikrohedriten, Mikrosphärolithen oder Teilchen mit unregelmässiger Struktur besitzen. Im Falle der Blockcopolymeren von Äthylensulfid und Styrol hängt die morphologische Form von der Zusammensetzung des Copolymeren ab.

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