Studies on the Synthesis of Fiber-Forming Block Copolymers of Polyacrylonitrile and Poly(ethylene Oxide)

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Synopsis

Modified PEO (MW 6000) containing xanthate groups was used for the synthesis of block copolymers of PAN and PEO. Principal parameters affecting the synthesis were examined. To confirm the segmental structure of the obtained products, precipitation fractionation, gel permeation chromatography, infrared, and ^1H nuclear magnetic resonance methods were used. The fiber-forming properties were investigated by means of rheological examination of concentrated solutions of PAN–PEO and confirmed by spinning the fibers under laboratory conditions. The physical and mechanical properties of the fibers were also determined.

INTRODUCTION

Polyacrylonitrile fibers (PAN) have besides their valuable properties, some drawbacks. These disadvantages include high susceptibility to static electrification, low abrasion resistance, too little elasticity, and low moisture content. In recent years much attention has been paid by many research centers to the modification of the polymer or the resultant fiber in order to eliminate these negative properties. Synthesis of block copolymers of PAN and poly(ethylene oxide) (PAN–PEO) may remedy the situation. Block copolymers have become of particular importance since Szwarc's discovery of living polymers.[1] Reactions in living systems allow preparation of block copolymers with a definite segment length. Konkin and Novitskaya obtained PAN–PEO block copolymers[2,3] using Ce^{4+} salts as oxidizing agents for hydroxyl groups in the PEO prepolymer. Bi-, tri-, or multisegment block copolymers can be formed depending on the number of OH functional groups taking part in redox reactions. Iwakura et al. obtained block copolymers of PAN and polyaminotriazole,[4] using Fe^{3+} ions as oxidizing agents, while the amino groups of polyaminotriazole prepolymer were reductors. A procedure for the preparation of polystyrene and poly(enanth oxide), $HO[(CH_2)_7O]_n - H$ with hydroperoxide terminal groups was also described.[5-7] These prepolymers were used to initiate radical polymerization of acrylinitrile (AN). Finally, polystyrene-polyacrylonitrile and poly(enanthylene oxide)-polyacrylonitrile block copolymers were synthetized by this method. As a result of the two-stage synthesis, polyisobutylene-poly(ethylene oxide) block copolymers[8] and polybutadiene-poly(ethylene oxide) block copolymers[9] were obtained. In both cases,[8,9] the first stage polyisobutylene or polybutadiene with isocyanate terminal groups was formed, which then reacted with OH groups of PEO. Studies on graft

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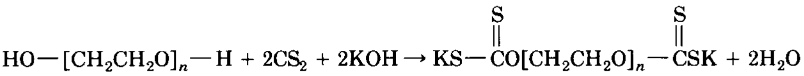
copolymerization of vinyl monomers on viscose fibers were also reported.[10-13] In these processes, xanthate groups played the part of reducing agents, while hydrogen peroxide or metal ions of variable valency were used as oxidizers.

The present study was aimed at the utilization of xanthate groups of the PEO prepolymer for the synthesis of PAN-PEO block copolymers and confirmation of their segmental structure as well as at the preparation of fibers from these copolymers on a laboratory scale.

EXPERIMENTAL

Prepolymer consisting of poly(ethylene oxide) xanthate was obtained from PEO with a molecular weight of 6000 (Merck-Schuchardt, West Germany) in a reaction between PEO, CS_2 and KOH in *m*-xylene system according to:[14]



$$HO{-}[CH_2CH_2O]_n{-}H + 2CS_2 + 2KOH \rightarrow KS{-}\overset{S}{\overset{\|}{C}}O[CH_2CH_2O]_n{-}\overset{S}{\overset{\|}{C}}SK + 2H_2O$$

The sulfur content (determined by ultraviolet spectrophotometry according to Ref. 15 was 2.08% (theoretical value 2.05%).

The synthesis of block copolymers was carried out in aqueous medium according to Wodka et al.[16] To a three-necked flash provided with a stirrer, a reflux condenser, and a capillary supplying nitrogen, redistilled water in a suitable amount was added, which was purged with nitrogen and thermostatted at definite temperature. Then, AN was added in an amount to bring its concentration in the reaction mixture to 1.4 mol/dm^3, also added were H_2O_2, PEO xanthate (dissolved previously in a small amount of water) and H_2SO_4. All substrates were added with vigorous stirring. After the process was completed (within 5 h), the precipitated copolymer was thoroughly washed with water and methanol and dried under reduced pressure at 50°C to constant weight. The extent of reaction of AN and the prepolymer was determined gravimetrically. The intrinsic viscosity of the copolymer was measured in dimethyl formamide (DMF) at 20°C. The measurement was carried out by the dilution method, using a modified Ubbelohde viscometer. The value of $[\eta]$ was found by double extrapolation to zero concentration, based on the relationships given by Huggins[17] and Heller.[18] The composition of the copolymer was determined from the nitrogen content found by the Kjehldahl method.

In order to examine the effects of the oxidizer to reductor molar ratio, PEO xanthate content in the mixture, concentration of hydrogen ions, and temperature on the synthesis of block copolymers, four series of synthesis were carried out varying the examined parameter and maintaining the other ones constant. Figures 1 to 4 are graphic illustrations of the examined relationships.

To elucidate the structure of the products obtained, precipitation fractionation, gel chromatography, and infrared spectrophotometry and ^1H nuclear magnetic resonance (NMR) were used. PAN-PEO block copolymers were fractionated in DMF solution in a concentration of 1% at 20°C, using turpentine as a nonsolvent according to the method developed in our laboratory.[19] The fractions were washed with water and methanol and dried under reduced pressure at 50°C to constant weight. Then, fraction mass, viscosity $[\eta]$, and

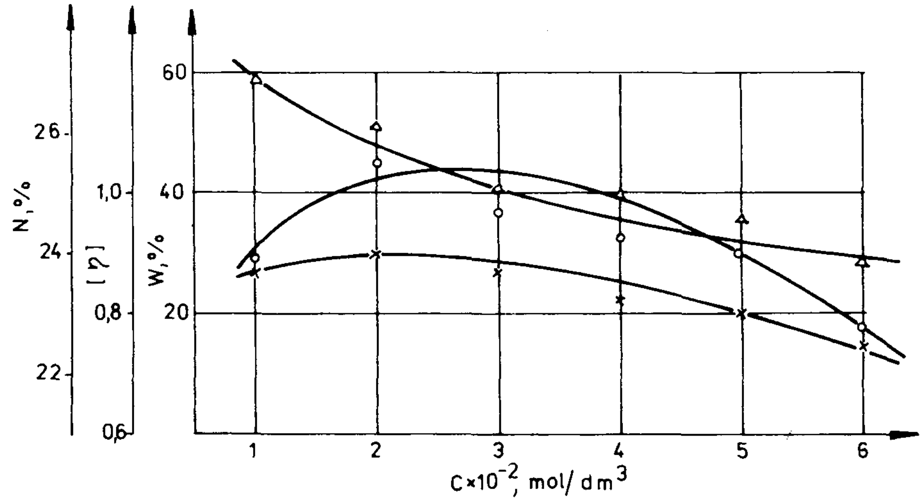


Fig. 1. The effect of H_2SO_4 concentration on the yield intrinsic viscosity and composition. AN = 1.4 mol/dm^3, KSSCOPEOCSSK = 3.8×10^{-3} mol/dm^3, H_2O_2 : KSSCOPEOCSSK = 3 : 1, temp. $-35°C$, $\tau = 5$ h o-o-o- yield, x-x-x- nitrogen content, Δ-Δ-Δ- intrinsic viscosity ([η], dL/g).

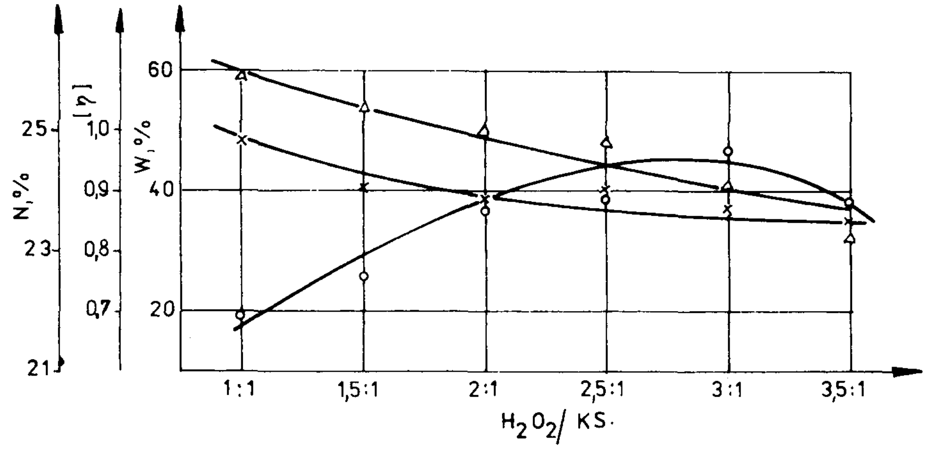


Fig. 2. The effect of molar ratio of oxidizer (H_2O_2) to reductor (KSSCOPEOCSSK) on yield, intrinsic viscosity and composition. Designations as in Fig. 1.

nitrogen content were determined. The last fraction contained in the decanted phase, after addition of final excess of turpentine, was obtained by distilling off DMF and turpentine under vacuum. Then, from the concentrated solution, copolymer was precipitated in methanol. Based on the results obtained, integral and differential curves of copolymer viscosity distribution were plotted (Fig. 5). Gel permeation chromatography (GPC) examinations were carried out by means of a liquid chromatograph, type 302 (Institute of Physical Chemistry, Warsaw). The columns (250 × 6 mm) were filled with silica gel SG 500 and SG 50 with exclusion volumes of 500,000 and 50,000, respectively [polystyrene (PS) in tetrahydrofuran (THF)]. A differential refractometer RJDK 101 (Laboratory Instruments Works, Prague, Czechchoslovakia) was

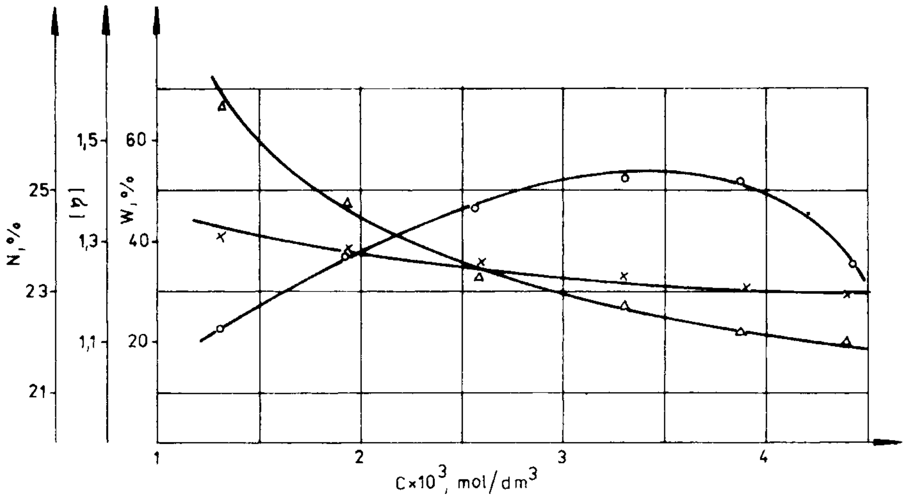


Fig. 3. The effect of concentration of PEO xanthate on yield, intrinsic viscosity, and composition. Designations as in Fig. 1.

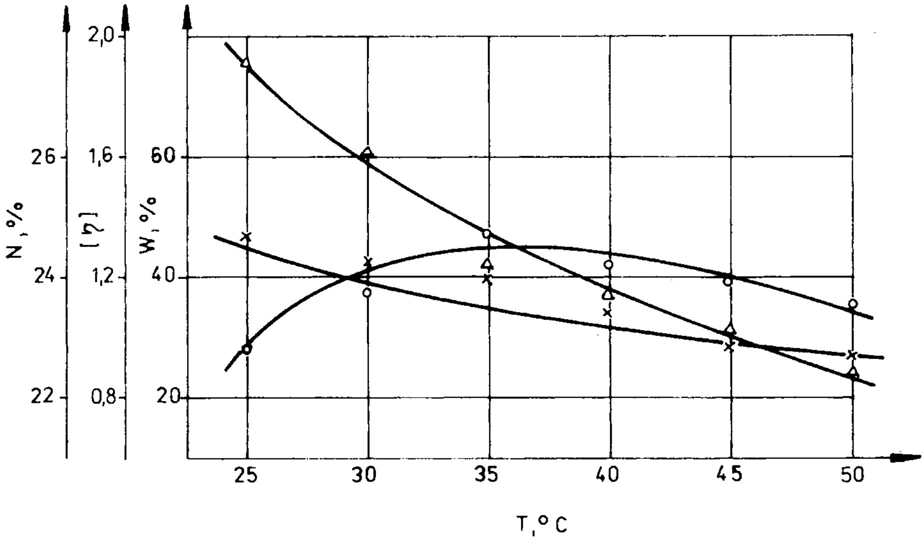


Fig. 4. The effect of temperature on yield intrinsic viscosity and composition. Designations as in Fig. 1.

used as a detector. DMF was the mobile phase at ambient temperature. Samples were introduced with an injector (Institute of Physical Chemistry, Warsaw). Figure 6 shows chromatograms of the PEO and block copolymers.

In order to confirm the structure of the block copolymers obtained, IR spectrophotometric studies of both homo- and copolymers of PAN and PEO were carried out with aid of a H-800 spectrophotometer containing a NaCl prism (Hilger-Watts, UK). The test samples were made in the form of pellets with KBr. Spectra of the products are shown in Figure 7. ^{1}H-NMR analyses were carried out with a BS-48JA NMR-Tesla spectroscope. Samples for this

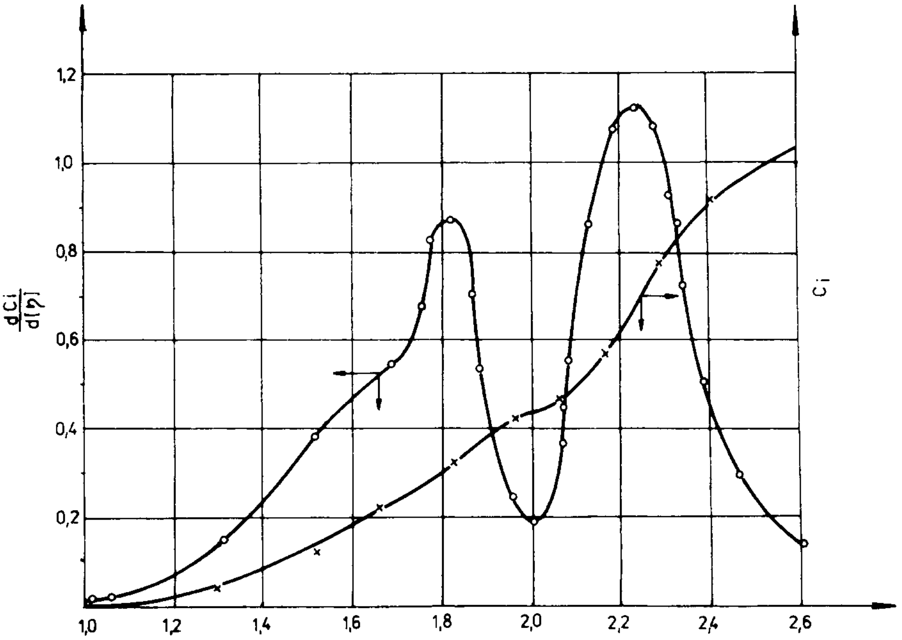


Fig. 5. Integral and differential curves of the intrinsic viscosity ([η], dL/g) distribution of PAN–PEO block copolymers.

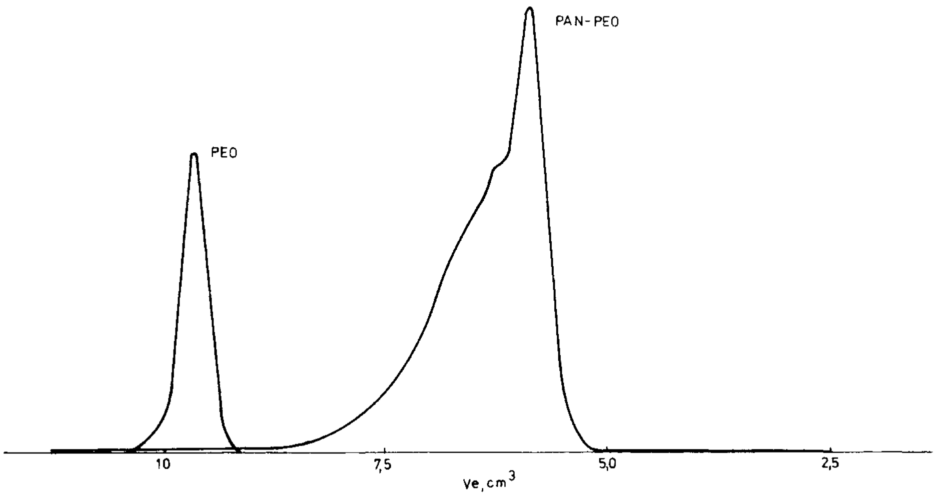


Fig. 6. Gel permeation chromatograms of PEO (MW 6000) and PAN–PEO block copolymers.

analysis were prepared in the form of 10% solution in $(CD_3)_2SO$. The ^{1}H-NMR spectra are shown in Figure 8.

Rheological examinations of concentrated solutions of PAN–PEO block copolymers were carried out with a "Reotest" viscometer at shearing stresses 0.1–10^4 Pa. Solutions in DMF with concentrations of 15.0%, 17.5%, and 20% were used.

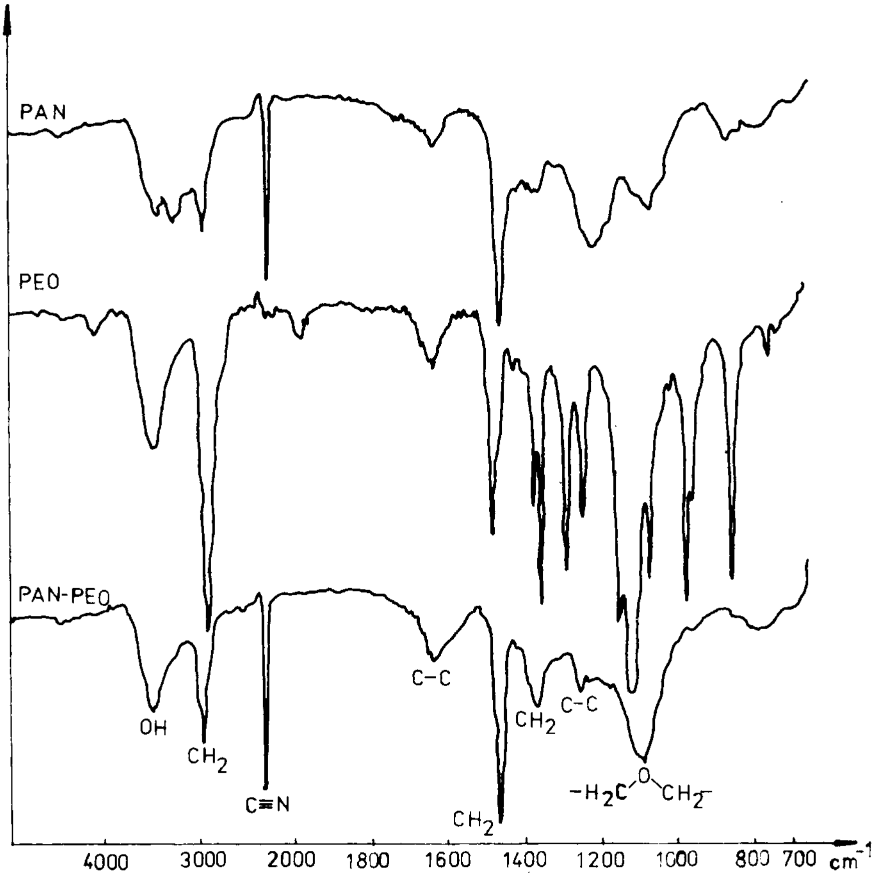


Fig. 7. Infrared spectra of PAN, PEO, and PAN–PEO block copolymers.

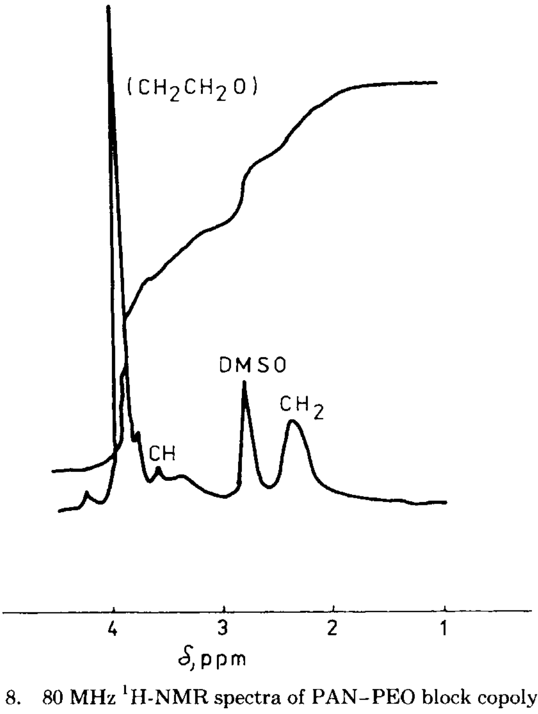


Fig. 8. 80 MHz ^{1}H-NMR spectra of PAN–PEO block copolymers.

TABLE I
Rheological Examinations of Solutions of Block Copolymers

Composition (%)		Intrinsic viscosity $[\eta]$ (dL/g)	Temperature (°C)				E (KJ/mol)
			Viscosity (Pa · s)				
PAN	PEO		25	40	55	70	
91.5	8.5	1.19	16.30	10.05	5.70	1.35	28.24

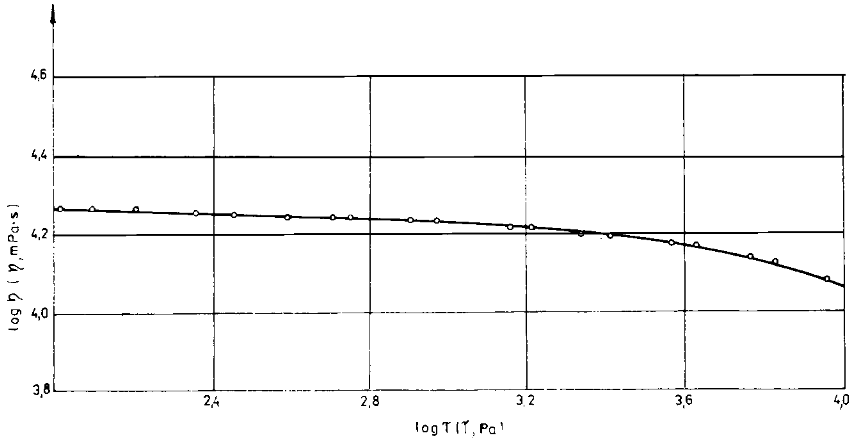


Fig. 9. Flow curve for the concentrated solution of PAN–PEO block copolymers.

The effects of temperature on viscosity and activation energy of viscous flow of PAN–PEO solution are shown in Table I. Figure 9 illustrates graphically the changes of viscosity with increasing shearing stress.

Fibers from the block copolymers were formed in laboratory spinning equipment provided with a piston-feeding system, using 17.5% solutions in DMF. The solidification bath consisted of aqueous DMF solution at 8–10°C. The feeding rate was 4.35 m/min. Spinerettes with 60 holes of 0.07 mm diameter were used. The path in the solidification bath was 100 cm in length. Next, the fibers were introduced to a plasticizing bath consisting of 30% aqueous DMF solution at 85–90°C, the path length being 50 cm and finally to a boiling water bath using 600% drawing and the fibers were stabilized at 120°C for 60 min. Properties of the fibers obtained and of PAN fibers produced under analogous conditions are given in Table II.

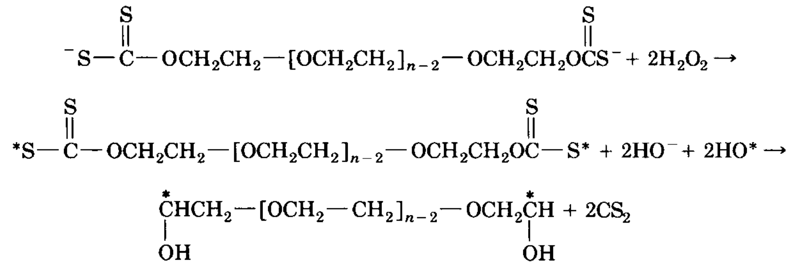
RESULTS AND DISCUSSION

It can be seen from the results (Figs. 1–4) that the conditions of the synthesis of block copolymers affect their yield, intrinsic viscosity (molecular weight), and composition. The oxidation of xanthate ions results in the formation of active centers on sulfur atoms, which then undergo isomeriza-

TABLE II
Properties of PAN–PEO Fibers

Polymer	Composition (%)		Intrinsic viscosity [η] (dL/g)	Fiber thickness (tex)	Tensile strength (cN/tex)	Elongation (%)	Cycle number to break		Volume resistivity ρ^* (Ω cm)
	PAN	PEO					Bending	Abrasion	
PAN–PEO	91.5	8.5	1.19	23.0	32.92	9.0	2803	735	3×10^{10}
PAN	100	—	1.98	20.5	34.35	8.0	1050	376	1×10^{14}

tion, bringing about active centers on carbon atoms.[10, 11]

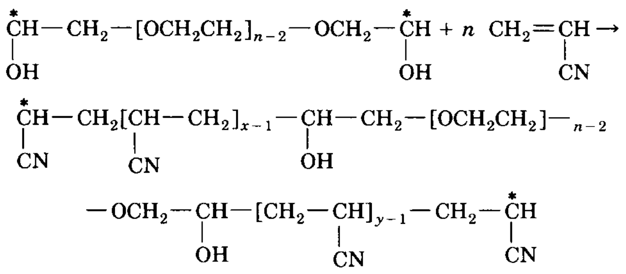


$$^{-}S-\overset{\overset{S}{\|}}{C}-OCH_2CH_2-[OCH_2CH_2]_{n-2}-OCH_2CH_2O\overset{\overset{S}{\|}}{C}S^{-} + 2H_2O_2 \rightarrow$$

$$^{*}S-\overset{\overset{S}{\|}}{C}-OCH_2CH_2-[OCH_2CH_2]_{n-2}-OCH_2CH_2O\overset{\overset{S}{\|}}{C}-S^{*} + 2HO^{-} + 2HO^{*} \rightarrow$$

$$\underset{\underset{OH}{|}}{\overset{*}{C}H}CH_2-[OCH_2-CH_2]_{n-2}-OCH_2\underset{\underset{OH}{|}}{\overset{*}{C}H} + 2CS_2$$

The propagation of macromolecules can be illustrated by the following scheme:



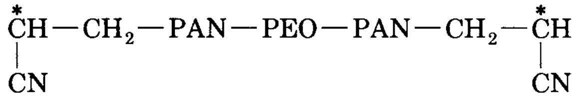
$$\underset{\underset{OH}{|}}{\overset{*}{C}H}-CH_2-[OCH_2CH_2]_{n-2}-OCH_2-\underset{\underset{OH}{|}}{\overset{*}{C}H} + n\ CH_2{=}\underset{\underset{CN}{|}}{CH} \rightarrow$$

$$\underset{\underset{CN}{|}}{\overset{*}{C}H}-CH_2[\underset{\underset{CN}{|}}{CH}-CH_2]_{x-1}-\underset{\underset{OH}{|}}{CH}-CH_2-[OCH_2CH_2]-_{n-2}$$

$$-OCH_2-\underset{\underset{OH}{|}}{CH}-[CH_2-\underset{\underset{CN}{|}}{CH}]_{y-1}-CH_2-\underset{\underset{CN}{|}}{\overset{*}{C}H}$$

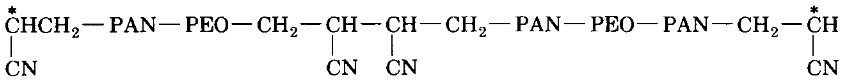
where $x + y = n$.

Designating the polyacrylonitrile segment with PAN and the poly(ethylene oxide) segment with PEO, the latter formula may be expressed by the symbols:



$$\underset{\underset{CN}{|}}{\overset{*}{C}H}-CH_2-\mathrm{PAN}-\mathrm{PEO}-\mathrm{PAN}-CH_2-\underset{\underset{CN}{|}}{\overset{*}{C}H}$$

According to the literature, the termination of chain in homopolymerization of AN takes place mainly by recombination.[20] The recombination of two growing macromolecules leads to the formation of block copolymers of the following type:



$$\underset{\underset{CN}{|}}{\overset{*}{C}H}CH_2-\mathrm{PAN}-\mathrm{PEO}-CH_2-\underset{\underset{CN}{|}}{CH}-\underset{\underset{CN}{|}}{CH}-CH_2-\mathrm{PAN}-\mathrm{PEO}-\mathrm{PAN}-CH_2-\underset{\underset{CN}{|}}{\overset{*}{C}H}$$

Recombination of macroradical with the PEO radical or with HO* radical present in the system gives rise to the formation of

PEO-PAN-PEO-PAN-PEO or

HO-PAN-PEO-PAN-OH

Taking into account that PEO xanthate with one functional group (the other group may be decomposed or oxidized to unreactive unit) possibly may be present in the reaction system, block copolymers of the following type can be formed:

PEO-PAN-PEO

or

PEO-PAN-PAN-PEO

Suitable concentration of hydrogen ions in the reaction mixture allows the xanthate to change to acidic form, and at the same time the highest yield of the synthesis of block copolymers was obtained when the concentration of H_2SO_4 in the reaction mixture was 0.02 mol/dm^3 (Fig. 1). At higher concentration of H_2SO_4, there is an increase in the decomposition rate and oxidation of PEO xanthate, leading to the formation of unreactive compounds.[21,22]

As can be seen from Figure 2, the maximum yield of the synthesis of block copolymers was obtained when the molar ratio of oxidizer to reductor was 3 : 1. Below this value fewer active centers are formed to initiate the reaction, whereas above this ratio a great number of active centers form which can be recombined with PEO* radicals or with HO* present in the system. In both cases, a decreased number of PEO* radicals appear, able to initiate the AN polymerization, which consequently leads to decreased extent of reacted AN.

Changes in $[\eta]$ and in nitrogen content in the PAN-PEO block copolymers with variations of the oxidizer to reductor ratio and of H_2SO_4 concentration, can be explained in terms of the termination mechanism. The synthesis of block copolymers was carried out in an heterogeneous system. Thus, the block copolymers were precipitated as a solid phase in which occluded macromolecules were present. It is assumed that in such a system a mechanism of two-molecule termination takes place.[23] The rate of termination depends then distinctly on the occlusion extent which is associated with the coiling aggregation of macromolecules.[24-27]

High degrees of occlusion make AN diffusion difficult, and consequently the propagation rate decreases, resulting in a decreased degree of polymerization of the PAN block. The increased concentration of PEO xanthate in the reaction mixture leads to the formation of a higher number of active centers. For this reason in the reaction system, more growing macromolecules are formed, but they have shorter PAN segments, which is confirmed by a decrease in $[\eta]$ and in nitrogen content (Fig. 3). The decrease in the copolymer yield when the concentration of PEO xanthate in the reaction mixture exceeds the value 3.85×10^{-3} mol/dm^3, may be only an apparent one. As follows from the measurements of $[\eta]$ and nitrogen content, the increase in xanthate content in the reaction mixture, brings about a drop of these values. This means that the active centers appearing under these conditions in a greater number lead to the formation of block copolymers with very short PAN blocks. Such polymolecular block copolymers PAN-PEO can contain a small amount of macromolecules (fractions) of short PAN blocks which cannot be precipitated from the reaction mixture, or can be removed when washing the products with water and methanol. As found by Galin et al.,[28] the fractions of PAN-PEO block copolymers, in which the content of PEO exceeds 60% by wt, are water soluble.

One of the most important factors affecting the synthesis of block copolymers is temperature. As follows from Figure 4, increase in temperature within the range 25-35°C induces an increase in the reaction yield. Further rises of temperature result in decreased yield. This is associated with extension of side processes (decomposition and oxidation of xanthates to unreactive compounds) occurring more intensively at elevated temperatures.

The ^{1}H-NMR spectra (Fig. 8) of block copolymers contain three groups of signals. The signal within the range 3.8-4.0 ppm arises from the four protons of the polyoxyethylene group $\mathrm{+CH_2—CH_2—O+}_n$, and that within 2.0–2.5δ from $—CH_2—$ and finally the signal within the range 3.5–3.7δ from protons of $—CH—$.

The results of infrared spectrophotometry confirm the structure assumed for the PAN-PEO block copolymers obtained. In these spectra characteristic bands for segments are observed. Characteristic bands of the $—CN$ group can be seen in the PAN spectrum [Fig. 7(a)] at 2240 cm^{-1} and that of $—CH_2—$ at 2940 cm^{-1} and at 1440 cm^{-1}. In the PEO spectrum [Fig. 7(b)], the band of $—C—O—C$ is observed at 1150 cm^{-1}. Besides the other band, the bands of the $—CH_2—$ and $C—C$ groups are observed at 2940 cm^{-1} and 1440 cm^{-1}, respectively.

In the spectra of block copolymers, all the above-mentioned bands characteristic for the components of the block copolymer are observed.

Fractionation of PAN-PEO was carried out by the precipitation method which allows division of the copolymer into two liquid phases. Separation of the precipitated phase in the form of concentrated solution allowed for faster equilibrium during fractionation. Subsequently precipitated fractions of the copolymer were characterized by lower values of intrinsic viscosity $[\eta]$ and different chemical compositions. It was found in the determination of $[\eta]$ for particular fractions that the experimental straight lines, showing $\eta_{\text{red}} = f(c)$ of fractions with various compositions, do not intersect. This gives evidence that the determined values of $[\eta]$ are a measure of molecular weights, and fractionation occurs selectively in relation to molecular weight (losses in fractionation were about 3%). The distribution of $[\eta]$ (Fig. 5) of the investigated copolymer is a two-block distribution. In the differential curve two maxima are observed at $[\eta] = 1.80$ dL/g and $[\eta] = 2.30$ dL/g. The value $[\eta] = 2.0$ dL/g corresponds to the inflection point in the integral curve and to the minimum in the differential curve. Such a distribution of $[\eta]$ may suggest a possible chain termination, which, in turn, may lead to the formation of bi-, tri-, and multisegment copolymers. Bi- and trisegment macromolecules can be formed by recombination of PEO–PAN* or $\dot{\text{P}}$AN–PEO–PA$\dot{\text{N}}$ with HO* radical. Multisegment macromolecules can be formed by recombination of two growing macroradicals $\dot{\text{P}}$AN PEO–PA$\dot{\text{N}}$ and $\dot{\text{P}}$AN PEO–PA$\dot{\text{N}}$ under the given conditions of synthesis, that is, at definite chain propagation rate, it was assumed that the statistically shorter macromolecules had bi- and trisegment structure and the longer ones multisegment structure. None of the separated fractions was PAN homopolymer (based on elementary analysis and infrared spectrophotometry), although the presence of PAN macromolecules in the separated fractions cannot be excluded.

The macromolecules of the obtained block copolymers were separated according to size by means of gel permeation chromatography (GPC). The obtained GPC characteristics allowed comparison with the results of precipitation fractionation. As seen from Figure 6, the shape of the PEO chromatogram confirms high homogeneity of molecular weight, but the chromatogram of the PAN–PEO block copolymer is characterized by multiblock distribution.

It should be noted that the oxidation of xanthate groups results in two active centers capable of initiating the PAN segment propagation. This leads to the formation of copolymers with various segmental structures depending on the mode of termination. The formation of a mixture of block copolymer fractions with various structures and molecular weights is confirmed by the shape of the chromatographic curve changing toward lower molecular weights (Fig. 6). Within this region, no clearly developed maxima are observed corresponding to various types of block copolymers, and the curve shape may suggest superposition of maxima. The distinct peak corresponding to the exclusion volume of the column system used (molecular weight over 500 000 for PS in THF) may suggest that fractions of high molecular weights occur in the mixture of copolymers.

As was already mentioned, during the synthesis bi-, tri-, and multisegment block copolymers can be formed. In all cases, the length of the PAN block depends mainly on the termination mechanism; at the same time this length at constant length of the PEO block (or blocks) controls the molecular weight of the copolymer macromolecule.

The structure of fibers being formed depends to great extent on the rheological properties of concentrated spinning solutions. Therefore, it was expedient to examine the rheological properties of block copolymer solutions with concentrations used in fiber formation. Figure 9 shows the relationship between the viscosity of concentrated solution of block copolymer and shearing stress. As can be seen from this figure, at low shearing stress (up to 1 KPa) one observes small variations in viscosity. Above this value, considerable changes in viscosity of the concentrated copolymer solutions can be observed. This may be associated with structure variations of the block copolymer solutions. According to Kirgizbaeva et al.,[29] concentrated solutions of statistic copolymers (acrylonitrile, methyl acrylate, and itaconic acid) form a structure of loose tridimensional (space) network, in which macromolecules solvated with the solvent may occur, their packing density and interactions being dependent on their chemical composition.

It is worth mentioning that in concentrated solutions of block copolymers, an additional phenomenon may take place, namely a division of microphases into separate domains. As reported by Meier,[30] in the case of examination of definite block copolymers the domains contain only one of the components. Only on their surface, diffusion layers may occur, in which segments of both polymers are present. Taking into account the above remarks concerning the formation of loose network and other block copolymers forming domains, it should be stated that the considerable drops in viscosity due to higher shearing stresses may be associated with destruction of the structures formed. One should remember that the examined solutions are not stable with time. Considerable increase of viscosity of these solutions suggests that gel formation takes place. The increased viscosity may be associated with selective action of solvent on the domains. DMF is a good solvent for PAN segments, but at the same time, a poor solvent for the PEO segments.[31]

The increase in temperature as seen from Table I, brings about a decrease in the viscosity of the concentrated solution of block copolymers. The activation energy of the viscous flow of the examined solution may be a measure of the intensity of intermolecular (interdomain) interaction.

The dynamics of structure propagation during fiber formation depends mainly on the elastic properties of macromolecules of fiber-forming polymers.[32,33] The propagation depends on the initial structure of macromolecules and on the physical and chemical properties of the polymer-solvent system and of the nonsolvent. The formation of PAN–PEO fibers was based on the conditions of formation of polyacrylonitrile and its statistic copolymers. As found in the examination of rheological properties, the stability of concentrated solutions of block copolymers differs considerably from that of concentrated solutions of PAN and its statistic copolymers. A characteristic feature of the structure of PAN fibers and PAN statistic copolymers is the porous structure of the freshly spun fibers. Decrease in the temperature of the solidification bath generally brings about the formation of small capillaries in great quantity, but a decrease in the concentration of solvent in the solidification bath causes the formation of large capillaries. Drawing of the obtained fibers was carried out in an aqueous medium containing the solvent. Such a bath plasticizes the fiber structure. During drawing partial straightening of macromolecules of block copolymer occurs as well as their orientation along the fiber axis. During deformation, displacement of domains may also take place. The data discussed show that on increasing the degree of deformation of fiber, the principal physical and mechanical parameters are changed according to general rules for manmade fibers. As can be seen from Table II, the strength parameters of fibers produced from PAN–PEO block copolymers under laboratory conditions are comparable with those of fibers from PAN homopolymer prepared under analogous conditions. Increased bending and abrasion strengths of the PAN–PEO fibers result undoubtedly from the elastic PEO segment present in the copolymer macromolecules. In the performance properties of textile fabrics, besides strength and aesthetic properties, a basic quality is comfort during use. Manmade fibers, including PAN fibers, show a high propensity for electrostatic build-up, which presents a nuisance for the user. It is seen that the obtained PAN–PEO fibers show much lower volume resistivity than that of fibers from homopolymer PAN and its copolymers. Thus a great decrease in the resistivity is associated with the structure of block copolymers, mainly with the possibility of forming separate domains of PAN and PEO, since copolymers with similar composition (content of the other component) do not show such great changes in resistivity.

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