

Studies on the Synthesis of Block Copolymers of Acrylonitrile and Ethylene Oxide

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SYNOPSIS

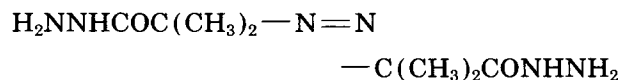
The synthesis of polyacrylonitrile–poly(ethylene oxide) block copolymers was carried out with the use of modified initiator containing azo groups, being a product of reaction between poly(ethylene oxide) (mol wt 6000) with azobisisobutyronitrile. Effects of initiator concentration, temperature, and synthesis time on the yield, composition, and intrinsic viscosity of the copolymers 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. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

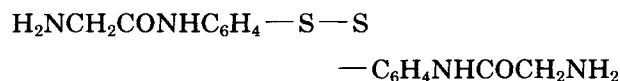
Synthesis of block copolymers is one of the prospective trends in polymer modification. This process allows for the preparation of polymeric products with macromolecules containing segments of various chemical composition and various physicochemical properties. By analogy to the commercially produced high elasticity polyurethanes of segmental structure,^{1–3} it may be expected that the preparation of polyacrylonitrile–poly(ethylene oxide) block copolymers (PAN–PEO) will provide products with modified properties. The synthesis of block copolymers has become of particular importance since Szwarc's finding of living polymers,⁴ which could be prepared so as to obtain a defined segment length.

Polyesters containing azo groups in configuration, such as $[(\text{OR})_n\text{OCOC}(\text{CH}_3)_2\text{—N=N—C}(\text{CH}_3)_2\text{COO}]_m$, were used for the synthesis of poly(ethylene oxide)–polystyrene block copolymers (PEO–PS).⁵ PEO–PS block copolymers containing < 40% of PS blocks are viscous liquids, but they behave like polystyrene when the PS content exceeds 70%. Polyesters with azo groups have been also used to prepare poly(ethylene oxide)–polyacrylamide block copolymers⁶ to be used as emulsifiers, as well as to prepare polystyrene–poly(methyl methacrylate) block copolymers.⁷ The first stage of the synthesis resulted in a prepolymer

of polystyrene with azo groups due to the decomposition of 30% of azo groups. The prepolymer obtained in a heterogeneous system showed higher mol wt than that prepared in homogeneous conditions. In the second stage, azo groups in the prepolymer were decomposed in the presence of methyl methacrylate to form poly(styrene–poly(methyl methacrylate)) block copolymers. The use of similar polyesters for the preparation of polystyrene–polybutadiene block copolymers, as well as polystyrene–polyacrylonitrile copolymers, has been reported.⁸ Articles^{9,10} have described the preparation of prepolymers of styrene and methyl methacrylate with amine or hydrazide terminal groups in the presence of initiator, such as



or



Such prepolymers were used for the synthesis of block copolymers containing polypeptide segments. They are applied to produce biological membranes. Multifunctional initiators with —N=N— or —S—S— groups in their molecules were used to obtain di- and tri-segment block copolymers of methyl methacrylate with peptide segments.¹¹ Similar block

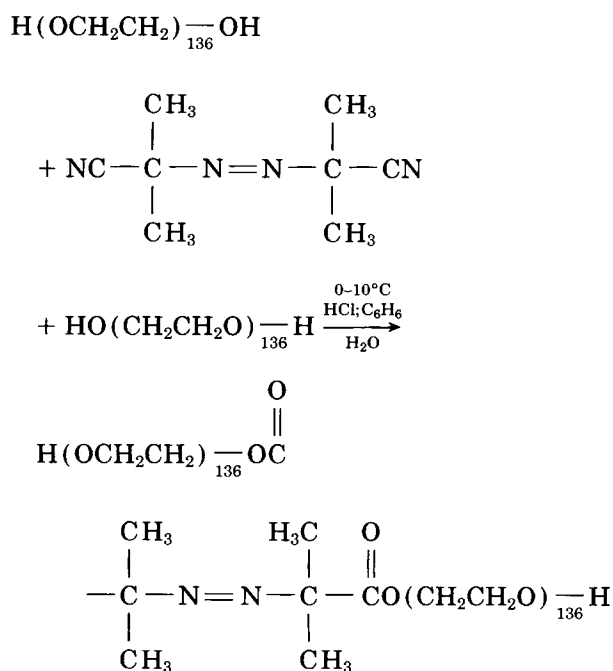
copolymers have been described in literature.^{12,13} The above mentioned copolymers are practically utilized as membranes in medical studies. Block copolymers composed of poly(methyl methacrylate) and poly(butyl acrylate) were obtained by two-stage radical polymerization.¹⁴ Methyl methacrylate prepolymer, containing azo groups, was prepared using $(\text{CH}_3)_3\text{COOCO}(\text{CH}_2)_3\text{CH}(\text{CN})-\text{N}=\text{N}-\text{CH}(\text{CN})(\text{CH}_2)_3\text{COOOC}(\text{CH}_3)_3$ and tetraethylenepentamine $[\text{NH}(\text{CH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{NH}_2)_2]$ at a temperature of 25°C, while the second stage, that is, the polymerization of butyl acrylate initiated by the prepolymer, was carried out in solid, emulsion and solution at 65°C. The obtained copolymers were characterized by microphase separation into distinct domains with glass transition temperatures from -45°C to -38°C and from 113°C to 129°C, respectively. We have reported results of our studies on the preparation of PAN-PEO block copolymers, using a redox system for initiation.^{15,16} PEO xanthate was used as a reductor in this system.

This article shows the results of the investigations of PAN-PEO block copolymerization initiated by PEO prepolymer containing azo groups. It was aimed at the examination of the effects of temperature, reaction time, and prepolymer content in the reaction mixture on mol wt (intrinsic viscosity), composition, and yield of the synthesis. It was also intended to show the segmental structure of the copolymers.

EXPERIMENTAL

The synthesis of PAN-PEO block copolymers was carried out with the use of a modified initiator pre-

pared by reacting PEO (average mol wt 6000, Merck Schuchardt, Germany) with azobisisobutyronitrile in polar proportion 2 : 1 according to¹⁷



The obtained prepolymer was examined by means of viscosimetric measurements, nitrogen determination by the Kjeldahl method, and gel chromatography, using an apparatus of Knauer (Germany), provided with two detectors: a differential refractometer and a viscosimeter. Water was used as the mobile phase, and the measurements were performed at room temperature. The obtained results of measurements are given in Table I and illustrated in Figure 1.

Table I Characteristics of PEO and Prepolymer

| <i>n</i> | Poly(ethylene oxide) $\text{H}(\text{OCH}_2\text{CH}_2)_n\text{OH}$ | | | <i>M</i> | Prepolymer | | Nitrogen Content (%) | |
|----------|--|----------------------|------------------------------------|----------|--------------------|------------|----------------------|--|
| | (η) in DMF | <i>M_w</i> | <i>M_w/M_n</i> | | (η) in DMF | Calculated | Found | |
| 136 | 0.14 | 6625 | 1.19 | 12166 | 0.32 | 0.22 | 0.20 | |

(*M*) Calculated mol wt; (*M_w*) Weight average mol wt; (*M_n*) Number average mol wt; (η) Intrinsic viscosity, dL/g.

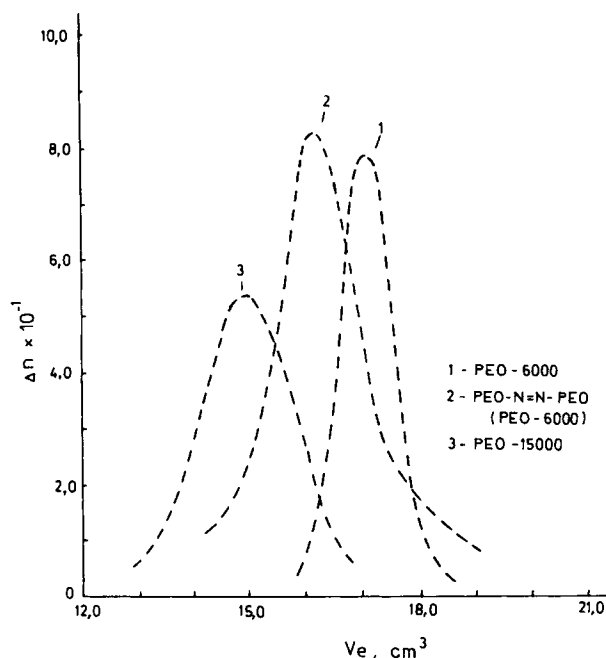


Figure 1 Gel permeation chromatograms of PEO and PEO-N=N-PEO.

The synthesis of PAN-PEO block copolymers was carried out by the solution-precipitation method in aqueous system; the acrylonitrile content was 1.4 mol/dm³. The process was performed under purified nitrogen for 5 h. The precipitated copolymer was thoroughly washed with water and methanol and then was dried to constant weight. The extent of conversion of acrylonitrile and prepolymer was de-

termined gravimetrically and the intrinsic viscosity of copolymers was measured in DMF at a temperature of 20°C, using the dilution technique and an Ubbelohde viscosimeter. Intrinsic viscosity values were obtained by double extrapolation to zero concentration.^{18,19} The composition of the obtained copolymers was determined from nitrogen content.

The block copolymer fractions, which were not precipitated from the reaction mixture during the synthesis nor were dissolved on rinsing with water, were separated by concentration of the filtrate; water and methanol was used for washing, using vacuum distillation. The concentrated solution was then rinsed with benzene to separate unreacted PEO. Table II shows the results of solubility of block copolymer fractions during the synthesis and rinsing.

The copolymers were also examined by ¹H-NMR and IR methods. For the ¹H-NMR characteristics, a Tesla-BS-48JA-80 MHz NMR spectrophotometer was used, the tested samples being prepared in the form of 10% solution of deuterated dimethyl sulphoxide (CD₃)₂SO (Fig. 5). IR spectrophotometric measurements were performed with a H-800 IR spectrophotometer (Hilger-Watts), provided with a NaCl prism, using KBr tablets (Fig. 6).

In order to determine the effects of the prepolymer content in the reaction mixture, temperature, and reaction time on the synthesis of block copolymers, three series of the process were carried out, varying the tested parameter with the remaining conditions being constant. The relationships found are shown in Figures 2-4. To determine the structures of the products obtained, the latter were frac-

Table II Water Solubility of the PAN-PEO Fractions

| Reaction Mixture | | Block Copolymers | | | | | |
|---------------------------|---|------------------------|------|--------------------------|-------|------|---------|
| AN mol/dm ³ | Prepolymer mol/dm ³ × 10 ³ | Water-Soluble Fraction | | Water-Insoluble Fraction | | | |
| | | % | (η) | PAN (%) | % | (η) | PAN (%) |
| 1.4 | 3.95 | 26.56 | 0.80 | 6.58 | 46.72 | 2.90 | 91.59 |
| 1.4 | 9.61 | 30.60 | 0.72 | 12.17 | 42.50 | 1.72 | 88.71 |
| 1.4 | 11.54 | 35.14 | 0.68 | 10.25 | 33.30 | 1.34 | 86.78 |
| Data from the Literature | | | | | | | |
| [22] | 66.7% PAN | 25.70 | — | 19.80 | 74.30 | — | 82.90 |
| [23] | 62.7% PAN | 41.00 | — | 20.90 | 59.00 | — | 91.70 |
| [24] | 44.5% PAN | 32.90 | — | 3.30 | 57.10 | — | 64.70 |

(η) Intrinsic viscosity, dL/g.

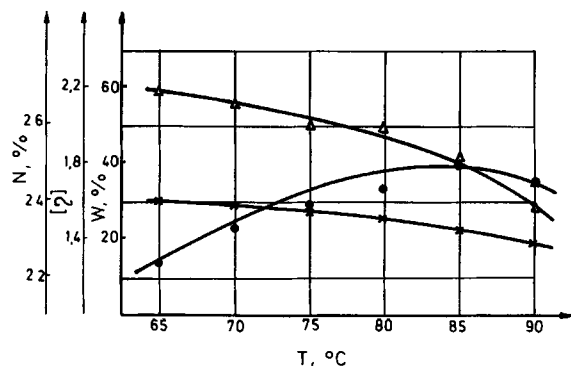


Figure 2 The effect of temperature on yield, intrinsic viscosity, and composition: AN = 1.4 mol/dm^3 , PEO-N=N-PEO = $4.8 \times 10^{-3} \text{ mol/dm}^3$, $\tau = 6 \text{ h}$; (—○—○—○—) yield, (—×—×—×—) nitrogen content, (—△—△—△—) intrinsic viscosity $[\eta]$, dL/g.

tionated by the precipitation method, using 1% DMF solutions at a temperature of 25°C , turpentine being a nonsolvent, as developed at our Institute.²⁰ The fractions were carefully washed with water and methanol, and then were dried under reduced pressure at 50°C to constant weight. Next, weight, intrinsic viscosity (η) and nitrogen content in the fraction were determined. The last fraction contained in the decanted phase, after adding the final portion of turpentine, was obtained by distilling off DMF and turpentine under vacuum and precipitating the copolymer from concentrated solution with methanol. Based on the obtained results, integral and differential viscosity distribution curves were plotted (Fig. 7). GPC examinations were carried out using a liquid chromatograph, type 302 (IChF-PAN,

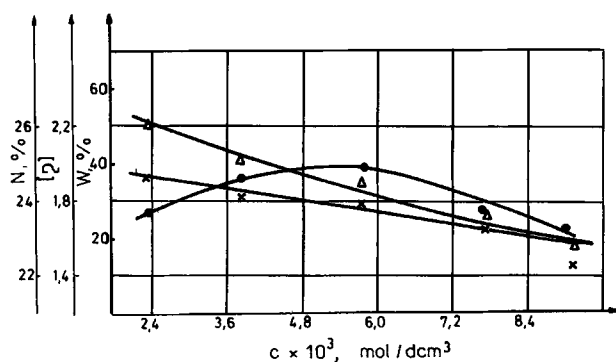


Figure 3 The effect of PEO-N=N-PEO concentration on the yield, intrinsic viscosity and composition. Designations as in Figure 2.

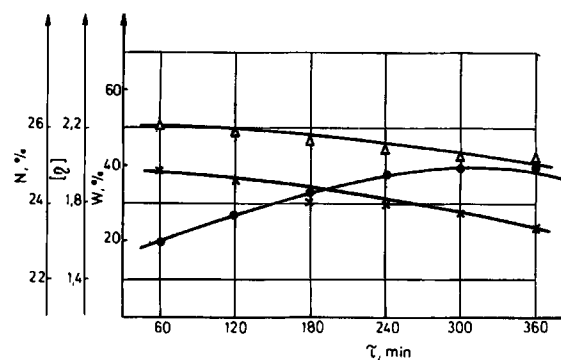


Figure 4 The effect of time on yield, intrinsic viscosity, and composition. Designations as in Figure 2.

Warsaw) with columns ($250 \times 6 \text{ mm}$) containing silica gel SG-500 and SG-50 of exclusion volumes 500,000 and 50,000, respectively (PS in THF). A differential refractometer RIDK 101 (LW Praha, Czechoslovakia) was used as detector, DMF being the mobile phase at room temperature. The sample was injected with a syringe (IChF-PAN, Warsaw). Figure 8 shows the chromatograms of PEO and of block copolymers.

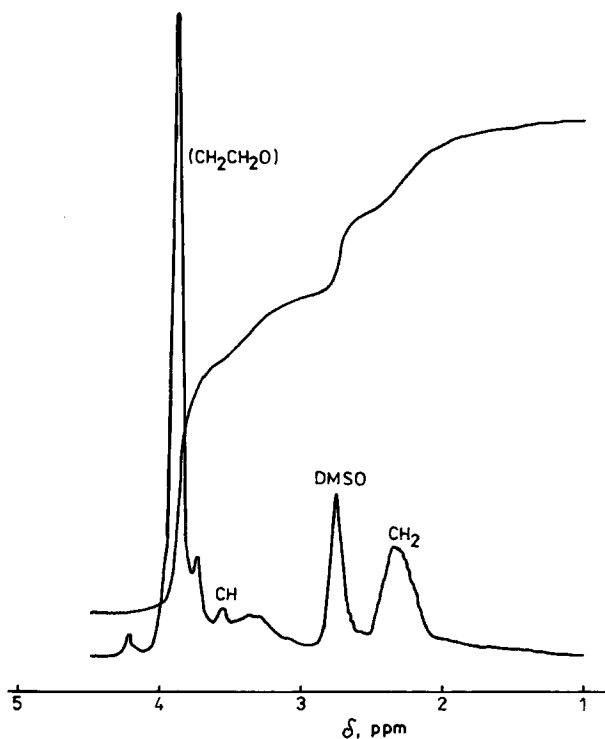


Figure 5 80 MHz $^1\text{H-NMR}$ spectra of PAN-PEO block copolymers.

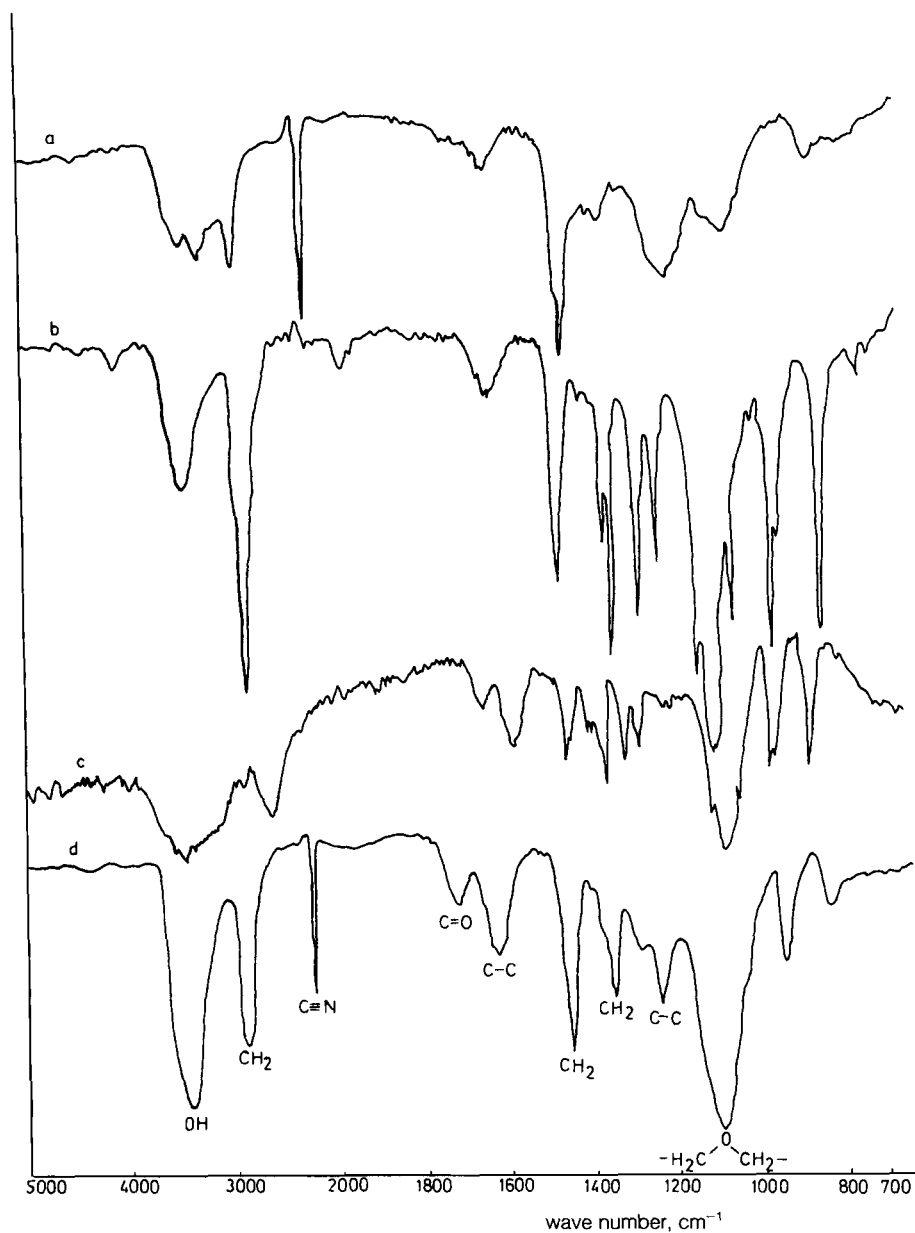


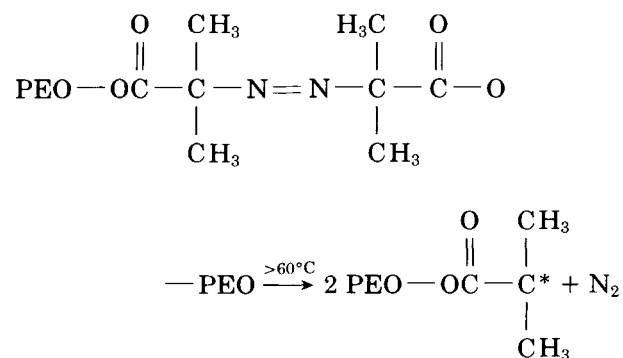
Figure 6 Infrared spectra of PAN (a), PEO (b), PEO-N=N-PEO (c), and PAN-PEO block copolymers (d).

RESULTS AND DISCUSSION

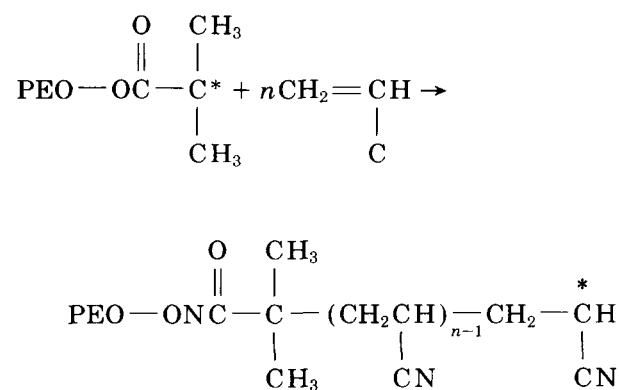
Used for the prepolymer synthesis, PEO was characterized by high mol wt homogeneity, as shown by the value $M_w/M_n = 1.19$. It should be noted that the conditions of synthesis of prepolymer—modified PEO—containing azo groups, such as low reaction temperature, molar reagents ratio 2 : 1, and the reaction medium, make the azoesters formation a preferential process. This is confirmed by the values

of (η) and nitrogen content in the obtained prepolymers. Comparing the chromatograms (Fig. 1) of PEOs with mol wt 6000 and 15,000 (curves 1 and 3) and those of the obtained product, it is seen that the shape of the chromatographic curve and position of its maximum are evidence of its high homogeneity (Fig. 1).

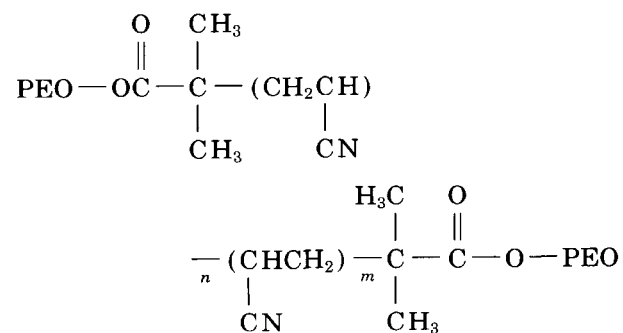
The formation of active centers in the synthesis of block copolymers can be shown by the following scheme:



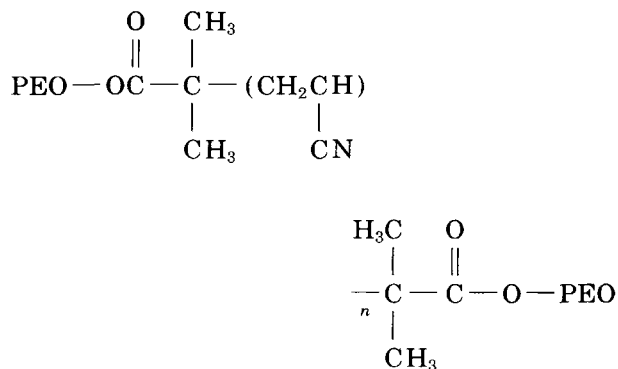
The growth of PAN segments can be illustrated as follows:



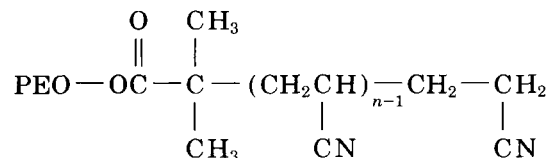
The macroradical resulted from the termination of kinetic chain form block copolymers. Bamford et al. found that, in the case of AN polymerization, the macroradical growth termination takes place via the recombination process.²¹ However, one can not exclude a possible chain transfer, but the mechanism of termination by disproportionation is negligible. The growth termination process by recombination can proceed via recombination of two growing macroradicals:



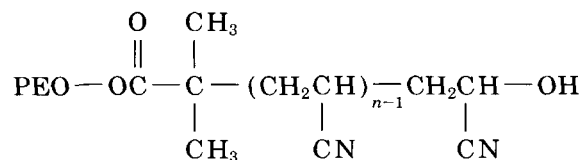
or recombination of macroradical with the primary radical:



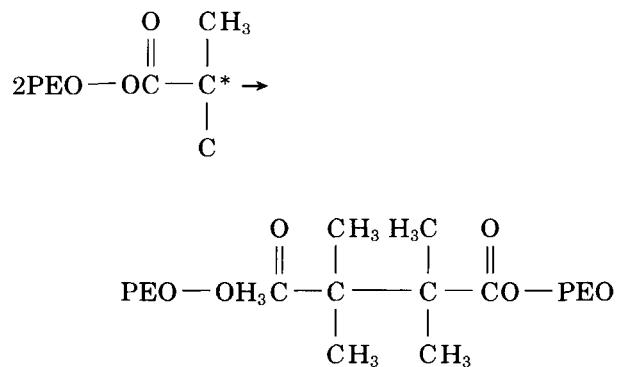
Taking into account a possibility of kinetic chain transfer onto monomer or solvent (water), one should also expect that two types of macromolecules may be formed:



or



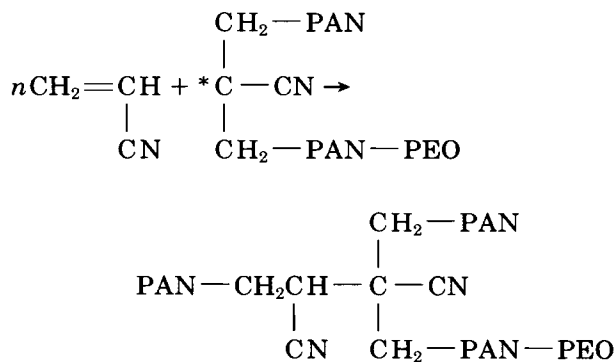
It is worth mentioning that the primary radical can also be recombined:



Such a possibility of recombination does not affect the character of the block copolymers being formed. The products resulted from the latter reaction, as water soluble, are removed during rinsing the copolymers with water and methanol. The results of the chain termination mechanism presented were that the block copolymer under investigation may consist of two- or three-segment macromolecules (PEO-PAN, PEO-PAN-PEO).

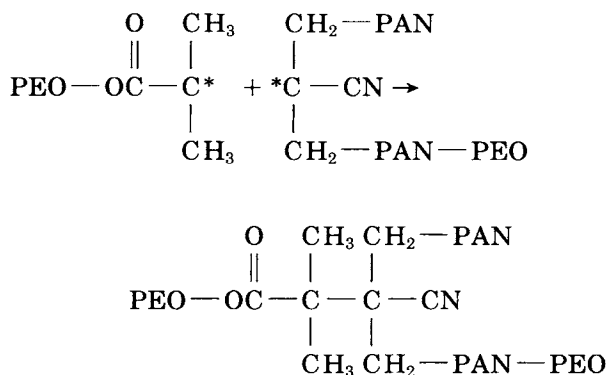
Figures 2-4 show that the synthesis of PAN-PEO block copolymers is affected by temperature, reaction time, and prepolymer content. The dependence of the extent of reaction on temperature, prepolymer content in the reaction mixture, and reaction time is typical for general relationships of polymerization. Reaction temperature is one of the more important factors affecting the synthesis. Its increase brings about a greater number of active centers and, consequently, a greater number of macroradicals. Raising the temperature also causes the termination rate constants to increase. When temperature exceeds 75-80°C, and initiator concentration is above 4.8×10^{-3} mol/dm³, a slight decrease in the extent of the reaction is observed. As can be seen from Figure 2, the increase in temperature and in the prepolymer concentration in the reaction mixture bring about a decrease in the intrinsic viscosity (η) of PAN-PEO copolymers. This means that under these conditions, PAN-PEO block copolymers with shorter PAN segments are formed. This is also confirmed by lowered nitrogen content in the products obtained with increasing temperature and prepolymer concentration in the reaction mixture. Such a poly-molecular block copolymer may contain fractions with short PAN segments (especially in the case of three-segment block copolymers PEO-PAN-PEO), which cannot be separated from the reaction medium or are dissolved during rinsing with water and methanol. Dissolution of PAN-PEO block copolymer fractions with short PAN segments was confirmed by experimental data. Figure 3 shows the dependence of yield, composition, and intrinsic viscosity on the prepolymer content in the reaction mixture. The yield curve shows a parabolic shape with a maximum at 4.8×10^{-3} mol/dm³ of the prepolymer and then is decreased considerably. This is an unusual phenomenon since the increase of the prepolymer content in the reaction mixture should bring about higher yield and increased PEO quantity in the copolymers obtained. It should be pointed out that a PEO segment in PAN-PEO block copolymers is soluble in water. In order to obtain more information about the effect of length of PAN segments

in block copolymers on the solubility in aqueous medium, we carried out experiments with the synthesis of copolymers of varied lengths of PAN. As seen in Table II, an increase of water-soluble fractions accompanies an augmentation of the prepolymer content in the reaction mixture. No doubt, this result is caused by the formation of block copolymers containing shorter PAN segments. With a constant length of the PEO segment, the mol wt of the copolymers is dependent on the length of the PAN segment. The formation of copolymers containing shorter PAN segments, due to the increased amounts of the prepolymer in the reaction mixture, is evident because of the intrinsic viscosities of the fractions of PAN-PEO block copolymers isolated by concentrating the filtrates as well as the viscosities of aqueous and ethanol washings. Table II also shows some data from the literature²²⁻²⁴ about the solubilities of PAN-PEO copolymer fractions obtained by ion-type reactions. It can be observed that these solubilities are of a similar order of magnitude as those of our fractions mentioned above. Besides, as shown by Galin,²⁵ PAN-PEO block copolymers, synthesized via ionic reactions with PEO contents higher than 60% by weight, are water-soluble. On the other hand, the interpretation of the results of the water soluble fractions of PAN-PEO block copolymers, obtained by free-radical processes, is more complex. In this case, a mixture of copolymers of two- and three-segment (PAN-PEO; PEO-PAN-PEO; PEO-PAN-PAN-PEO) structure is obtained. Therefore, in addition to the segment length (weight content), the solubility is also affected by the segmental structure as well as by the presence of branched macromolecules, which are likely to occur since the chain transfer to the block copolymer macromolecule can not be excluded. The branched segment can be PAN chain:



Neither can be excluded the PEO segment branching

as a result of recombination with primary radical $\text{PEO-OC(O)C}^*(\text{CH}_3)_2$:



As is seen from Figure 4, the prolongation of the reaction time is accompanied by a slight decrease in the intrinsic viscosity (η). This decrease, however, is not as distinct as in the case of the prepolymer concentration increase or the temperature rise when the decrease of (η) is undoubtedly due to the drop of polymerization degree of the PAN segment.

$^1\text{H-NMR}$ spectra of PAN-PEO block copolymers (Fig. 5) contain three groups of signals. The signal within the range 3.8–4.0 ppm results from four protons of the polyoxyethylene group $[-\text{CH}_2-\text{CH}_2-\text{O}-]_n$; the signal within 2.0–2.5 δ from $-\text{CH}_2-$ group and that within 3.5–3.7 δ from $-\text{CH}-$ protons. The results of IR spectrophotometry confirm the structure ascribed to the obtained products. In the spectra of these copolymers, characteristic bands of both segments are observed. In the spectrum of PAN [Fig. 6(a)], there is a characteristic band of $-\text{CN}$ group at a wavelength of 2240 cm^{-1} and that of $-\text{CH}_2-$ at 2940 cm^{-1} and at 1440 cm^{-1} . The absorption band of either group $-\text{C}-\text{O}-\text{C}-$ is observed in the PEO spectrum [Fig. 6(b)] at the wavelength 1150 cm^{-1} ; there are also bands of $-\text{CH}_2-$ and $\text{C}-\text{C}$ at 2940 cm^{-1} and 1440 cm^{-1} .

All the bands characteristic for the segments of block copolymer under investigation can be observed in the spectra along with a new one at a wavelength of 1720 cm^{-1} , due to the carbonyl group [Fig. 6(c) and (d)].

The fractionation of PAN-PEO block copolymers was carried out by the precipitation method, allowing the division of the copolymer into two liquid phases. Separation of the fraction precipitated in the form of concentrated solution allowed equilibrium to be reached faster during fractionation. The copolymer

fractions precipitated in succession were characterized by lower values of intrinsic viscosity (η) and different chemical compositions. Determining (η) of particular fractions, it was found that the experimental straight lines showing the relationship $\eta_{\text{red}} = f(c)$ of successive fractions are not intersected. This means that the determined value of (η) expresses mol wts and fractionation proceeds selectively in respect to mol wt (fractionation losses were about 3.5%). The distribution of (η) is two-modal (Fig. 7). In the differential curve of (η) distribution there are two maxima: at (η) = 1.75 dL/g and [η] = 2.15 dL/g. Such a distribution of the copolymer intrinsic viscosity may suggest a possible chain termination by recombination of two growing macroradicals or a growing macroradical with the primary radical. Such a mechanism of termination leads to the formation of two- and three-segment copolymers. Under the given synthesis conditions, that is, at specified chain growth rate, the statistically shorter and longer macromolecules were assumed to have two-segment and three-segment structures, respectively. None of the precipitated fractions was homopolymeric, though the presence of PAN macromolecules in the separated fractions can not be excluded.

Gel chromatography was used to separate the macromolecules of the obtained block copolymers according to their size. As can be seen from Figure 8, the shape of the PEO chromatogram (in DMF) gives evidence of a high homogeneity of mol wt, but the chromatogram of the PAN-PEO block copolymer is characterized by a multimodal distribution. The formation of a mixture of block copolymer fractions with different segmental structure and differ-

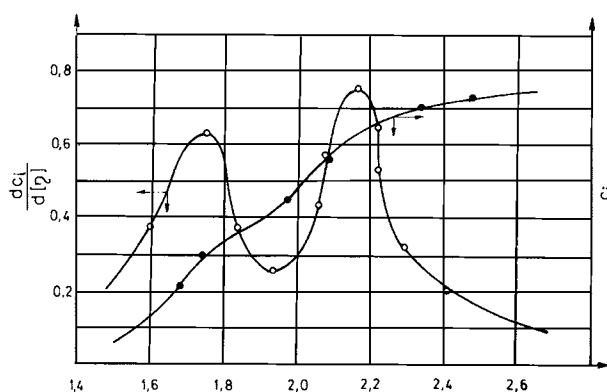


Figure 7 Integral and differential curves of the intrinsic viscosity [η], dL/g] distribution of PAN-PEO block copolymers.

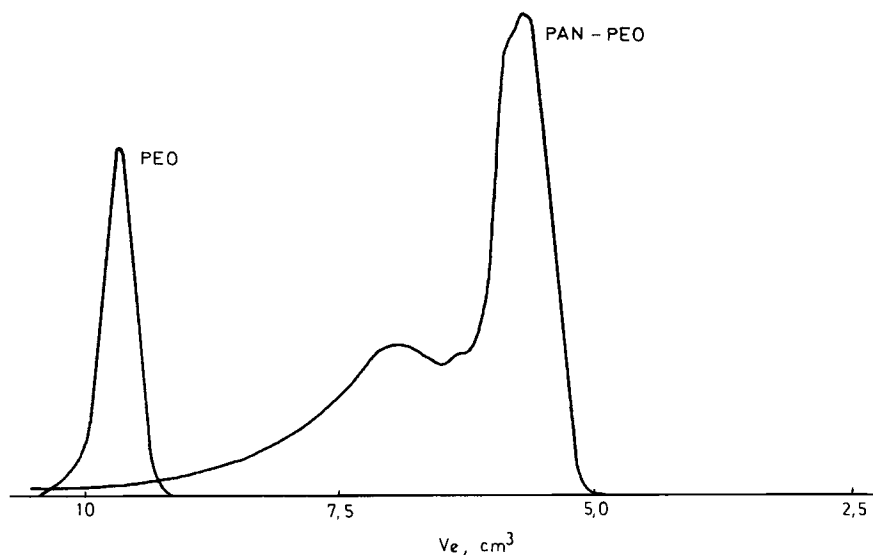


Figure 8 Gel permeation chromatograms of PEO (MW 6000) and PAN-PEO block copolymers.

ent mol wt is confirmed by the shape of chromatographic curve.

The whole area of the chromatographic curve can be divided into three ranges of mol wt. Within the range of lower mol wts, there occurs a peak corresponding to the exclusion volume of the system of columns used (mol wt of standard PS in THF 50,000). As was previously mentioned, fractions of block copolymers with two-segment structure can occur in this region. A distinct peak within the range of higher mol wts, corresponding to the exclusion volume of the column system used (mol wt above 500,000 for PS in THF), may be ascribed to the presence of fractions with high mol wts. There may occur block copolymer fractions of two-segment PAN-PEO and three-segment PAN-PEO-PAN structures. The shape of the chromatographic curve in the part beyond maximum, corresponding to the exclusion volume for standard PS above 500,000, may be due to the fact that in copolymer mixture, fractions with high mol wts can occur, which can be excluded from the column. These fractions can undoubtedly be formed as a result of recombination, giving PEO-PAN-PAN-PEO copolymers. In all the discussed cases, the length of the PAN segment depends mainly on the termination mechanism, and this length, in turn, at a constant PEO segment length (mol wt 6000) is decisive with regard to the mol wt of the copolymers.

Based on the results obtained, it can be concluded

that the discussed syntheses lead to the formation of PAN-PEO block copolymers.

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