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# Block Copolymers of Poly(ethylene oxide) Methyl Ether with Acrylonitrile, and with 2-Acrylamide-2-Methylpropane Sulphonic Acid and Acrylonitrile

## Abstract

Block copolymers were prepared by reacting a prepolymer of PEO xanthate with acrylonitrile and ionomeric block copolymers by copolymerisation of the prepolymer with AN and 2-acrylamido-2-methylpropane sulphonic acid (AMPS). The reactions were carried out in an aqueous system containing  $H_2O_2$  and  $H_2SO_4$ . The effects of prepolymer concentration, AMPS, and temperature on yield, composition and intrinsic viscosity were examined. The structure of the obtained block copolymers was confirmed by elementary analysis and  $^1H$ -NMR, FT-IR and GPC measurements.

**Key words:** block copolymers, ionomeric block copolymers, copolymerisation.

## Experimental Data

Block copolymers PEO-PAN and ionomeric block copolymers PEO-b-(AN-co-AMPS) were prepared with the use of PEO methyl ether with molecular weights of  $M_n=2000$  and  $M_n=4000$ . PEO was used in the form of potassium xanthate as a reducing agent in AN polymerisation and AN-AMPS copolymerisation, being simultaneously one of the segments of the block copolymers. The reaction was carried out in an acidic system with hydrogen peroxide as the oxidiser. PEO xanthates, whose characteristics are shown in Table 1, were prepared by reacting PEO with  $CS_2$  and KOH in *m*-xylene (equation 1) according to [10]. The sulphur content of the xanthates was determined by UV spectrophotometry [11] and elementary analysis.

The synthesis of block copolymers was performed in an aqueous system according to [2]. To a three-necked flask fitted with a stirrer, reflux condenser and nitrogen feeding capillary, a suitable amount of redistilled water was poured in and blown through with nitrogen, the whole being thermostated at a specific temperature. Next, during intensive stirring, AN was added in such a quantity as to bring its concentration in the reaction mixture to 1.4 mole/dm<sup>3</sup> followed by

the addition of AMPS,  $H_2O_2$  and PEO xanthate previously dissolved in some water with  $H_2SO_4$ . The process was carried out for 5 h, the precipitated copolymer was then thoroughly washed with water and methanol, and next dried under vacuum at a temperature of 50°C to a constant weight. The intrinsic viscosity of the products was measured by the dilution method in DMF at a temperature of 25°C, using a modified Ubbelohde viscometer. The values of intrinsic viscosity were found by a double extrapolation to zero concentration on the basis of relationships given by Huggins & Heller [13]. The composition of the copolymers obtained was determined by elementary analysis.

The copolymers were also assessed by  $^1H$ -NMR and FT-IR methods. The  $^1H$ -NMR measurements were performed by means of an NMR-Tesla BS-48JA (80 MHz) spectrophotometer. Specimens for analysis were prepared in the form of a 10% deuterated dimethyl sulphoxide,  $(CD_3)_2SO$ . The IR measurements were performed with a FT-IR Mattson spectrophotometer (G.B.). Specimens were prepared in the form of tablets with KBr. GPC analysis was performed using the chromatography system with PL Caliber GPC Software Version 5.1 (Polymer Laboratories Ltd.). 0.05% copolymer solutions in dimethylac-

## Introduction

The valuable properties of polyacrylonitrile (PAN) fibres and their numerous applications in the textile industry are confirmed by a permanent growth in their production. However, PAN fibres are not free from some negative features, and therefore their modification is of significant importance. Recently, syntheses of block copolymers have gained importance, especially thanks to Szwarc's discovery of polymerisation in living system [1]. Processes carried out in such systems make it possible to obtain block copolymers composed of segments of a required length. In block copolymers, each of the block forming components retains its primary properties, while the copolymers themselves gain new properties resulting from the cumulative effect of the components involved. The results of studies on block copolymers of PAN and poly(ethylene oxide) (PEO) are reported in papers [2-9].

The aim of the present study was to prepare block copolymers of PEO methyl ether,  $CH_3-(OCH_2)_n-OH$  (PEO), and acrylonitrile (AN), as well as ionomeric block copolymers of PEO methyl ether with 2-acrylamide-2-methylpropane sulphonic acid,  $CH_2=CHCONHC(CH_3)_2CH_2SO_3H$ , (AMPS) and AN.

Table 1. Characteristics of  $CH_3-(OCH_2CH_2)_n-OCSSK$  xanthates.

| PEO  |    | Content %  |       |            |       |            |       |
|------|----|------------|-------|------------|-------|------------|-------|
| Mn   | Pn | Sulphur    |       | Carbon     |       | Hydrogen   |       |
|      |    | Calculated | Found | Calculated | Found | Calculated | Found |
| 2000 | 45 | 3.02       | 3.00  | 49.34      | 48.97 | 8.17       | 7.96  |
| 4000 | 91 | 1.55       | 1.57  | 51.12      | 52.26 | 8.60       | 8.03  |

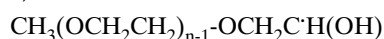
etamide (DMAc) were used for the measurements.

## Results and Discussion

A series of block copolymer syntheses was carried out, examining the effects of the following parameters on the reaction course: a molar oxidiser ( $H_2O_2$ ) to reducer (PEO xanthate) ratio, concentration of PEO xanthate, concentration of 2-acrylamide-2-methylpropane sulphonic, and temperature. Examples of the results of these examinations are given in Tables 2-5. The oxidation of xanthate ion results in the formation of active centres at the sulphur atom, followed by their isomerisation and centre formation at the carbon atom [14,15] according to scheme (2).

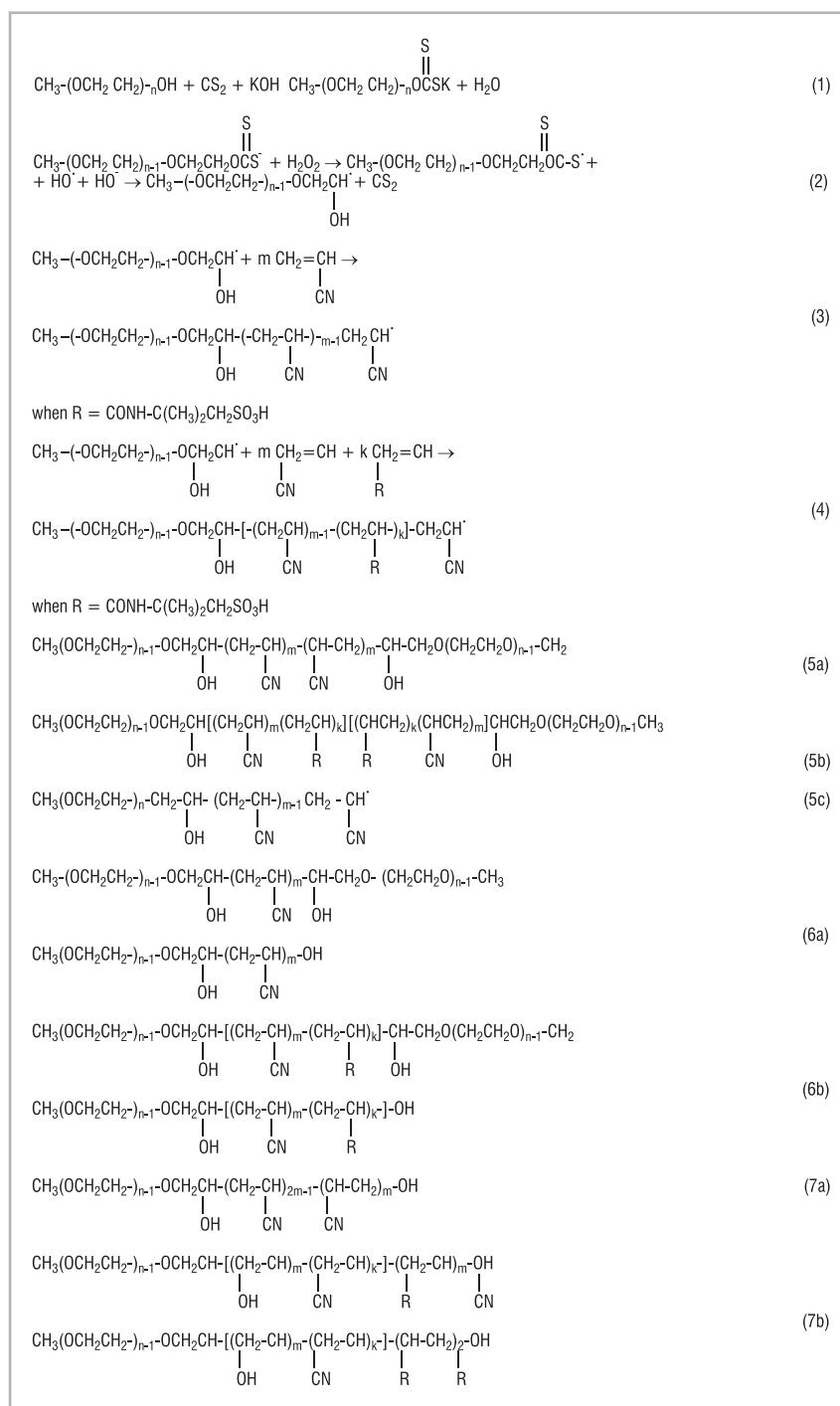
The growth in macromolecules in AN polymerisation can be shown by scheme (3). On the other hand, the growth in macromolecules of ionmeric block copolymers takes the course presented in (4). Data from the literature suggests that as a results of homopolymerisation the macroradical growth is terminated mainly by recombination [16,17], although chain transfer cannot be excluded. The chain termination mechanism by disproportionation is neglected. The recombination of two growing chains results in the formation of block copolymers of the type shown in (5a), or ionmeric in (5b).

The recombination of macroradical (5c) with macroradical



or with the radical  $HO^{\cdot}$  present in the system results in the formation of block copolymers (6a) or ionmeric block copolymers (6b). If a possible homopolymerisation of AN and AMPS due to  $HO^{\cdot}$  is also taken into account in the system under investigation, the chain growth termination may results from the recombination of copolymeric radical with the macroradical of PAN or PAMPS and leads to copolymers such as (7a) or ionmeric block copolymers (7b).

As reported in papers [4,5], the maximum yield of reaction is found when the molar ratio oxidiser:reducer is 1.25:1. Below this value, a low number of centres is formed in the reaction system which is capable of initiating the synthesis of block copolymers. The  $HO^{\cdot}$  radicals present in the system can also participate in the termination of macroradical growth, while above this molar ratio, a high number of active centres are formed in the reaction system; these centres may undergo recombination with the primary radi-



Equations 1-7

cals PEO $^{\cdot}$  or  $HO^{\cdot}$ . In both of the cases considered, a reduced number of PEO $^{\cdot}$  are present which are capable of initiating the polymerisation of AN or the copolymerisation of AN and AMPS.

When the hydrogen ion concentration in the reaction mixture amounts to 0.02 mole/dm<sup>3</sup>, PEO xanthate can be transformed into its acidic form (participating in oxidation), with the highest yield being also obtained with this ion concentration [5]. Above this value of hydrogen ion concentration, the role of side reactions probably

becomes important due to the growth in the reaction rate constants of PEO xanthate decomposition and oxidation resulting in non-reactive combinations. The changes in molecular weight and composition of the obtained block copolymers together with the changes in the oxidiser to reducer ratio and  $H_2SO_4$  can be explained when considering the mechanism of macromolecule growth termination. The synthesis of block copolymers was performed in a heterogeneous system, thus the copolymers were precipitated in a solid phase in which occluded

**Table 2.** The effect of PEO xanthate on the synthesis of block copolymers (PAN-PEO); ([AN]=1.42 mol/dm<sup>3</sup>, [H<sub>2</sub>SO<sub>4</sub>]=0.02 mol/dm<sup>3</sup>, oxidizer to reducer ratio 1.25:1, temp. 40°C, time 5h).

| [KS] x 10 <sup>3</sup><br>mol/dm <sup>3</sup> | KS-PEO-2000 |              |                           |                          |      | KS-PEO-4000 |              |                           |                          |       |
|-----------------------------------------------|-------------|--------------|---------------------------|--------------------------|------|-------------|--------------|---------------------------|--------------------------|-------|
|                                               | Yield,<br>% | [η],<br>dl/g | Nitrogen<br>content,<br>% | Copolymer composition, % |      | Yield,<br>% | [η],<br>dl/g | Nitrogen<br>content,<br>% | Copolymer composition, % |       |
|                                               |             |              |                           | PAN                      | PEO  |             |              |                           | PAN                      | PEO   |
| 7.18                                          | 22.56       | 2.18         | 25.40                     | 96.18                    | 3.82 | 28.80       | 1.92         | 24.75                     | 93.71                    | 6.29  |
| 8.98                                          | 32.16       | 2.15         | 25.20                     | 95.42                    | 4.58 | 33.80       | 1.62         | 24.36                     | 92.24                    | 7.76  |
| 10.78                                         | 38.47       | 1.98         | 25.04                     | 94.81                    | 5.19 | 34.80       | 1.40         | 23.85                     | 90.31                    | 9.69  |
| 12.56                                         | 40.08       | 1.78         | 24.83                     | 94.04                    | 5.96 | 39.32       | 1.35         | 23.80                     | 90.12                    | 9.88  |
| 14.36                                         | 38.56       | 1.64         | 24.70                     | 93.87                    | 6.13 | 36.25       | 1.31         | 23.60                     | 89.36                    | 10.64 |

**Table 3.** The effect of AMPS concentration on synthesis of ionomeric block copolymers PEO-b-(AN-co-AMPS); ([AN]=1.42 mol/dm<sup>3</sup>; [KS-PEO (2000)]=10.2x10<sup>-3</sup> mol/dm<sup>3</sup>; [H<sub>2</sub>SO<sub>4</sub>]=0.02 mol/dm<sup>3</sup>; U:R=1.25:1; temp. 40°C; time 5h).

| [AMPS] x10 <sup>2</sup><br>mol/dm <sup>3</sup> | Conversion,<br>% | [η], dl/g | Nitrogen<br>content, % | Sulphur<br>content, % | Copolymer composition, % |       |       |
|------------------------------------------------|------------------|-----------|------------------------|-----------------------|--------------------------|-------|-------|
|                                                |                  |           |                        |                       | PEO                      | PAN   | PAMPS |
| 1.54                                           | 25.60            | 1.67      | 23.51                  | 0.32                  | 10.06                    | 87.36 | 2.58  |
| 2.31                                           | 27.58            | 1.52      | 23.71                  | 0.54                  | 10.20                    | 86.31 | 3.49  |
| 3.08                                           | 35.00            | 1.35      | 24.02                  | 0.88                  | 9.16                     | 85.12 | 5.72  |
| 3.86                                           | 37.88            | 1.33      | 23.68                  | 1.06                  | 9.12                     | 84.02 | 6.86  |
| 4.63                                           | 36.88            | 1.27      | 24.18                  | 1.51                  | 8.12                     | 82.00 | 9.78  |

**Table 4.** The effect of AMPS concentration on the synthesis of ionomeric block copolymers PEO-b-(AN-co-AMPS); ([AN]=1.42 mol/dm<sup>3</sup>; [KS-PEO (4000)]=5.7x10<sup>-3</sup> mol/dm<sup>3</sup>; [H<sub>2</sub>SO<sub>4</sub>]=0.02 mol/dm<sup>3</sup>; U:R=1.25:1; temp. 40°C; time 5h).

| [AMPS]x10 <sup>2</sup><br>mol/dm <sup>3</sup> | Conversion,<br>% | [η],<br>dl/g | Nitrogen<br>content,<br>% | Sulphur<br>content,<br>% | Copolymer composition, % |       |       |
|-----------------------------------------------|------------------|--------------|---------------------------|--------------------------|--------------------------|-------|-------|
|                                               |                  |              |                           |                          | PEO                      | PAN   | PAMPS |
| 1.54                                          | 25.60            | 1.79         | 23.02                     | 0.32                     | 12.04                    | 85.88 | 2.580 |
| 2.31                                          | 27.58            | 1.82         | 23.00                     | 0.55                     | 12.07                    | 84.33 | 3.60  |
| 3.08                                          | 35.20            | 1.45         | 24.10                     | 0.88                     | 10.97                    | 83.32 | 5.71  |
| 3.86                                          | 37.88            | 1.30         | 23.12                     | 1.07                     | 9.56                     | 83.48 | 6.96  |
| 4.63                                          | 36.62            | 1.26         | 22.80                     | 1.51                     | 9.40                     | 80.79 | 9.81  |

**Table 5.** The effect of temperature on the synthesis of ionomeric block copolymers PEO-b-(AN-co-AMPS); ([AN]=1.42 mol/dm<sup>3</sup>; [KS-PEO (2000)]=10.46x10<sup>-3</sup> mol/dm<sup>3</sup>; [AMPS]=3.86x10<sup>-2</sup> mol/dm<sup>3</sup>; [H<sub>2</sub>SO<sub>4</sub>] = 0.02 mol/dm<sup>3</sup>; time 5h).

| Temperature,<br>°C | Yield,<br>% | [η],<br>dl/g | Nitrogen<br>content,<br>% | Sulphur<br>content,<br>% | Copolymer composition, % |       |       |
|--------------------|-------------|--------------|---------------------------|--------------------------|--------------------------|-------|-------|
|                    |             |              |                           |                          | PEO                      | PAN   | PAMPS |
| 30                 | 30.10       | 2.06         | 23.69                     | 1.23                     | 10.29                    | 81.75 | 7.96  |
| 35                 | 39.20       | 1.92         | 23.38                     | 1.25                     | 9.21                     | 82.67 | 8.12  |
| 40                 | 40.08       | 1.78         | 23.42                     | 1.33                     | 7.54                     | 83.84 | 8.62  |
| 45                 | 39.20       | 1.68         | 23.60                     | 1.32                     | 6.86                     | 84.60 | 8.54  |
| 50                 | 36.50       | 1.52         | 24.00                     | 1.28                     | 5.34                     | 86.34 | 8.32  |

**Table 6.** Characteristics of block copolymers PEO-PAN.

| Copolymerisation                                                                                                                                                                  | Conversion,<br>% | [η], dl/g | Nitrogen<br>content,<br>% | Copolymer<br>composition, % |       | Mn     | Mw     | Mw/Mn |
|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------------------|-----------|---------------------------|-----------------------------|-------|--------|--------|-------|
|                                                                                                                                                                                   |                  |           |                           | PEO                         | PAN   |        |        |       |
| [AN]=1.42 mol/dm <sup>3</sup><br>[POE-KS]=3.8x10 <sup>-3</sup> mol/dm <sup>3</sup><br>[H <sub>2</sub> SO <sub>4</sub> ]=0.02 mol/dm <sup>3</sup><br>U:R = 1.25:1<br>T=30°C, t=5 h | 52.16            | 2.60      | 23.85                     | 9.64                        | 90.36 | 306000 | 712000 | 2.32  |

macroradicals were present. In such a system, a two-molecule termination mechanism is assumed to take place [15]. The termination rate then clearly depends on the degree of occlusion associated with the convolution of macromolecules and their aggregation. The high degree of macroradical occlusion by the macromolecules formed makes the AN and AMPS diffusion difficult, and therefore the reaction growth rate decreases. This decreases the polymerisation degree of the PAN segment and the AN-AMPS copolymer, while the occlusion degree decreases the reaction termination rate.

The increase in the concentration of PEO xanthate in the reaction mixture results in the formation of a higher number of active centres and consequently a higher number of growing macromolecules, but the latter contain shorter segments of PAN or AN-AMPS copolymers, as confirmed by the drop in intrinsic viscosity and nitrogen content. The decrease in the block copolymer yield when the concentration of PEO xanthate with Mn=2000 in the reaction mixture exceeds 10.46 x 10<sup>-3</sup> mol/dm<sup>3</sup> may be apparent. This would mean that the higher number of active centres present under these conditions leads to the formation of block copolymers with very short segments of PAN and AN-AMPS. Copolymer fractions of such short segments may be removed while washing the precipitated copolymers with water.

One of the major factors affecting the synthesis of block copolymers is temperature. As follows from Table 5, the increase in temperature within the range of 30-45°C causes the block copolymer synthesis yield to increase, while further temperature raising results in a decrease in this value. At the same time, as follows from Table 5, the increase in the synthesis temperature causes the polymer intrinsic viscosity to decrease. This is probably due

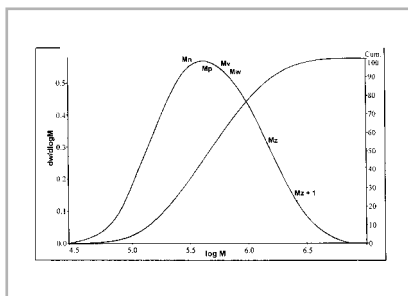


Figure 1. The integral and differential molecular weight distribution curves of POE-PAN block copolymer.

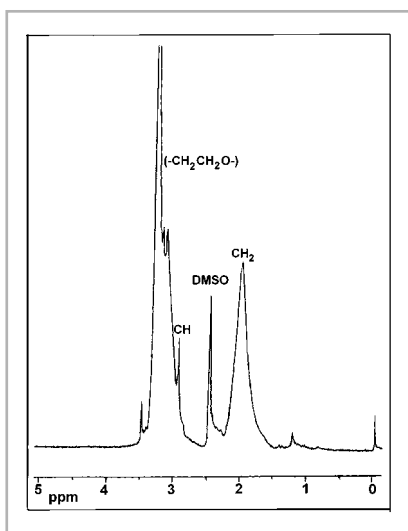


Figure 2. <sup>1</sup>H-NMR spectrum of PEO-PAN block copolymer.

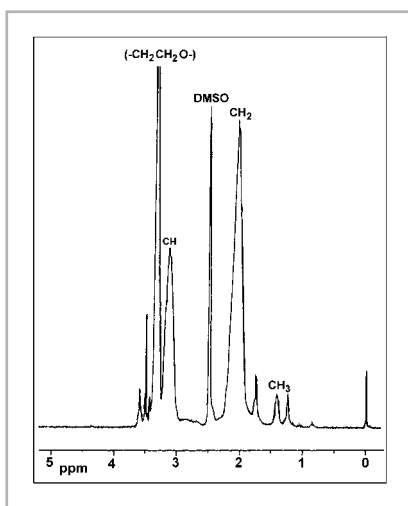


Figure 3. <sup>1</sup>H-NMR spectrum of PEO-b-(AN-co-AMPS) ionomeric block copolymer.

to greater effects of xanthate oxidation and primary radical recombination proceeding more intensively at higher temperatures.

From the considerations on the synthesis of block PEO-PAN copolymers

and ionomeric PEO-b-(AN-co-AMPS) copolymers, it results that the mechanism of macroradical termination decides the different segmental structure and chemical composition. With the use of PEO xanthate for the synthesis of PEO-PAN block copolymers and PEO-b-(AN-co-AMPS) ionomeric copolymers, one can obtain two- and three-segment copolymers with PAN and AN-AMPS segments of different lengths and different chemical compositions. However, the contribution of the PAN homopolymer and the AN-AMPS copolymer cannot be excluded.

To confirm the two- and three-segmental copolymer structures, PEO-PAN block copolymers of high molecular weight were prepared (intrinsic viscosity 2.6 dl/g; Table 6). The block copolymers obtained were examined by gel chromatography, and the results are shown in Figure 1 presenting the integral and differential functions of the distribution of PEO-PAN molecular weights. From Figure 1 it follows that the differential function of PEO-PAN molecular weights is characterised by a mono-modal maximum. Such a distribution indicates the formation of PEO-PAN block copolymers with two- and three-segmental structures, but with different lengths of the PAN segments.

The <sup>1</sup>H-NMR spectrum of PEO-PAN block copolymer obtained (Figure 2) contains three groups of signals. The signal within 3.2-3.5 ppm is derived from four protons of the polyoxyethylene group,  $(-\text{CH}_2\text{CH}_2\text{O}-)_n$ , signal within 1.8-2.0 ppm of  $-\text{CH}_2-$ , while that within 3.1-3.2 ppm is derived from protons of  $-\text{CH}-$ . On the other hand, in the spectrum of ionomeric block copolymer (Figure 3), in addition to signals of PEO and AN protons, there are also signals derived from AMPS protons, namely, within 1.2-1.4 ppm from  $-\text{CH}_3$  protons, within 3.5-3.6 ppm from  $-\text{CH}_2-$  and within 3.1-3.2 ppm from  $-\text{CH}_2-\text{SO}_3^-$  protons.

In the FT-IR spectra of PEO-PAN block copolymers and ionomeric PEO-b-(AN-co-AMPS) block copolymers (Figure 4), one can observe characteristic bands of the nitrile group ( $-\text{CN}$ ) at  $2240\text{ cm}^{-1}$ , the ether group ( $-\text{C}-\text{O}-\text{C}-$ ) at  $1100\text{ cm}^{-1}$ , the amide group ( $-\text{NHCO}-$ ) at  $1650-1670\text{ cm}^{-1}$  (amide I) and at  $1523-1560\text{ cm}^{-1}$  (amide II) and the sulphonic group ( $-\text{SO}_3^-$ ) at  $1050\text{ cm}^{-1}$ . The results of <sup>1</sup>H-NMR and FT-IR measurements are consistent with data from the literature [18,19].

The findings of <sup>1</sup>H-NMR, FT-IR and GPC examinations, as well as those of

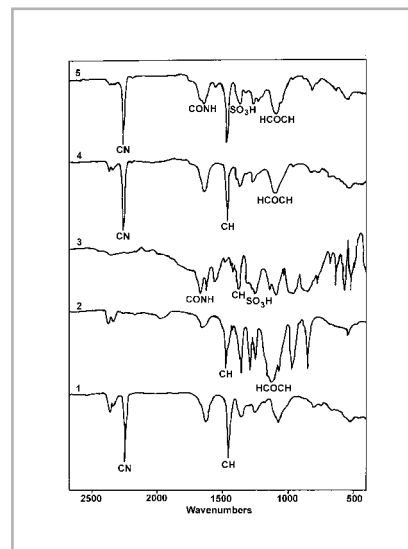


Figure 4. FT-IR spectra of: 1 - PAN; 2 - POE; 3 - AMPS; 4 - POE-PAN; 5 - POE-b-(AN-co-AMPS).

elementary analysis, indicate that the PEO-PAN block copolymers and ionomeric PEO-b-(AN-co-AMPS) block copolymers obtained have segmental structures. Fibre-forming properties of the obtained block copolymers will be the object of further studies.

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