

**INFLUENCE OF SYNTHESIS CONDITIONS OF POLYACRYLONITRILE
ON THEIR STRUCTURE AND THERMAL BEHAVIOR**

Julia Kostina¹, Elena Chernikova², Galina Bondarenko¹, Zinaida Poteryaeva²,
Aleksei Cherevan¹, Michael Efimov¹

¹A.V.Topchiev Institute of Petrochemical Synthesis, 29 Leninsky Pr., 119991, Moscow, Russia

²M.V.Lomonosov Moscow State University, Chemistry department,
Leninskie Gory, 1, 119991, Moscow, Russia, Julia@ips.ac.ru

Abstract

Homo- and copolymers based on acrylonitrile were synthesized via different methods of polymerization. The influence of synthesis conditions on the properties of polymers (MWD, microstructure) studied. By DSC and high temperature IR-diffuse reflectance spectroscopy in situ in the range 20-500 °C and IR-microscopy after IR-pyrolysis, investigated the influence of polymer thermal behavior and the condition of polyconjugated systems formation.

Key words: polyacrylonitrile, pseudoliving radical polymerization, IR pyrolysis, DR-FTIR, polyconjugated system

1. INTRODUCTION

Polyacrylonitrile (PAN) and copolymers based on it are widely used to produce fibers for different purposes. When heated above 200 °C (stage "stabilization"), the structure of the main chain of PAN is changing in an inert atmosphere produced only polyconjugated system (PCS) in the air along with the formation of polyconjugated structures of a number of strong oxidation processes take place. Polyconjugated structure has developed surface and high electrical conductivity. In the subsequent high-temperature pyrolysis in an inert atmosphere is formed of graphite carbon matrix (Fig. 1), and the material takes on a new set of properties, which expands the range of its application: based on carbon fibers produce composites for aerospace, automotive, shipbuilding, nuclear industry, construction, etc. Introduction of transition metal salts in polyacrylonitrile matrix promising to create a catalytically active systems.

Physical and mechanical properties of polyacrylonitrile fibers are defined by a set of chemical and technological parameters: the composition of the polymer and the spinning solution, deposition conditions, the orientational drawing, etc. However, such characteristics as the microstructure of the chain, the molecular-mass characteristics are placed on the stage of polymer synthesis and determine the conditions for the formation and composition polyconjugated system (PCS).

Traditionally, the industry PAN and its copolymers are produced in terms of classical free radical polymerization in solution (DMSO, DMF, or aqueous sodium thiocyanate), emulsions or suspensions, using a substantial initiation. For high molecular weight PAN applied radiation polymerization in solution and emulsion, which can be carried out at room temperature. However, these methods in the absence of additional fractionation does not allow you to control the molecular-mass characteristics of polymers, which leads to the formation of products spanning a wide molecular weight distribution

($M_w / M_n > 2-3$). Recently, to solve this problem the authors applied the pseudoliving radical polymerization via the reversible addition-fragmentation chain-transfer mechanism (**RAFT**).

The above methods of polymerization have different effects on the speed of the process, the molecular weight of polymer and its morphology, from this may depend on the behavior of PAN at heating in an inert atmosphere and air and the structure of the resulting PCS. In this context, the objective of this work was to establish the relationship between the synthesis conditions of gomo- and copolymers based on PAN, its thermal behavior in inert and air atmosphere and character of the resulting structure of polyconjugated systems.

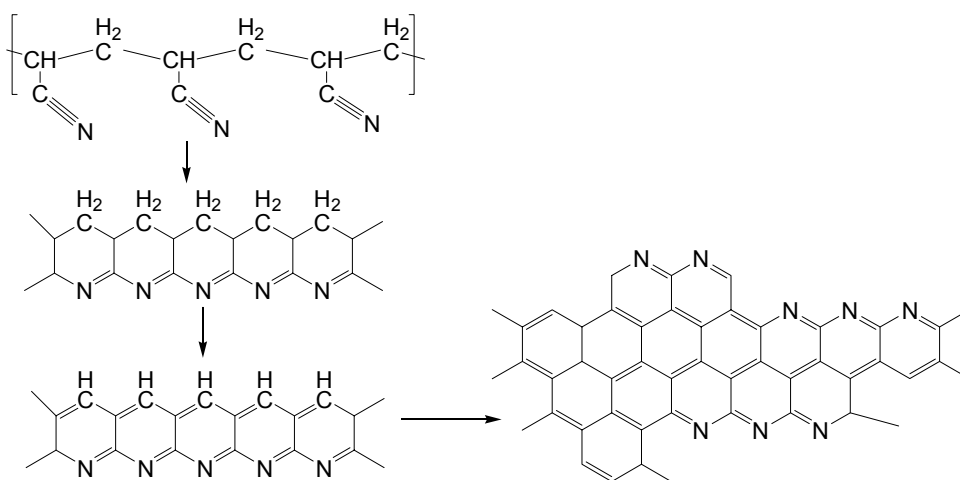


Fig. 1. Structural changes during pyrolysis of PAN

2. EXPERIMENTAL

Acrylonitrile (99%, the firm “Fluka” and “Saratovorgsintez”) before using purified by distillation at atmospheric pressure. DMSO and DMF (99%, the firm “Fluka”) was used without further purification. Azobisisobutyronitrile (**AIBN**) was recrystallized twice from anhydrous ethanol and dried in vacuum to a constant weight. Dibenzyl trithiocarbonate ($R-S-C(=S)-S-R$ (**BTC**), where $R = CH_2C_6H_5$, and characterized by NMR.

Samples for the classical free radical polymerization in a solution of DMSO or DMF were prepared by dissolving the calculated amount of **AIBN** (3.4×10^{-3} mol / L) in a mixture of acrylonitrile and solvent predetermined ratio (20 wt.% Monomer). The polymerization in a solution of DMSO and DMF were carried out at 70°C.

Radiation polymerization of AN in a solution of DMSO and DMF were carried out in a glass reaction vessel, a vessel with the reaction mixture was degassed and irradiated with γ -rays of ^{60}Co with a dose rate 0.072 Gy / s during incubation at 50 and 22°C and stirring with a magnetic stirrer.

Samples for RAFT polymerization were prepared through dissolution of calculated amounts a RAFT agent in a solution of DMSO with **AIBN** initiation and radiolysis. In the first case of preparing a reaction mixture containing **AIBN**, **BTC**, acrylonitrile (31.6 wt.%) and DMSO (68.4 wt.%), which was polymerized for 6 h at 80 °C. In the second case **BTC** mixture contained (5×10^{-3} mol / l), acrylonitrile

(31.6 wt.%) and DMSO, it was irradiated with γ -rays of ^{60}Co with a dose rate 0.029 Gy and 0.024 / s at 25 and 80 °C. The polymer was isolated by the methods described above.

Molecular-mass characteristics of polymers were studied by gel permeation chromatography GPC-120 chromatograph firm "PolymerLabs". Analysis was performed at 50 °C in DMF, for the analysis prepared by the polymer solution in DMF containing LiBr, with the polymer concentration does not exceed 1 mg / ml and less than 0.7 mg / ml. MM calculated using PMMA standards using the known factors from the literature Kuhn-Mark-Houwink for PAN.

Binary copolymers of Acrylonitrile and Methacrylates (MA) were synthesized to determine the effect of small additions of MA at the molecular-mass characteristics, composition and stereoregularity of the polymer. According to literature data, acrylonitrile monomer is more reactive than methyl acrylate, and their copolymerization constants constitute $r_{\text{AN}} = 1.31$ and $= 0.85 r_{\text{MA}}$. We can expect that small additions of MA will have a negligible impact on the regularities of PAN.

For the preparation of the samples calculated from the number of AIBN (3×10^{-3} mol / l) was dissolved in a mixture of AN and MA of given composition, the resulting solution was mixed with DMSO in a volume ratio of monomer: solvent = 3: 7. The reaction mixture was poured into ampoules, degassed on the vacuum system to a residual pressure of 5×10^{-3} mm Hg, and unsolder. The vials were placed in a thermostat heated to 80 °C and polymerized for 12 – 15 hours. At the end of polymerization, the ampoule was cooled with liquid nitrogen, opened and the reaction mixture was poured dropwise into 10–20-fold excess of distilled water with stirring. The polymer was distinguished as a separate phase, it was filtered off, washed thoroughly with the polymer on the filter with distilled water, then with acetone, the precipitate was collected and dried under vacuum to constant weight. The conversion was 60 – 70%, experiments have shown that small additions of MA no effect on the rate of polymerization.

Pyrolysis was carried out in the infrared camera of the laboratory setup of pulsed photon annealing (Fig. 2). The radiation source used halogen lamps, the maximum radiation which occurs in the region 0.9–1.2 microns. The sample in the form of a powder in a graphite tape was fixed on special holders in a cylindrical quartz quartz reactor, at the outer surface of which are 15 lamps. The intensity of the IR radiation temperature was controlled by heating the sample, measured using a thermocouple type L, located directly beneath the sample. The control unit is provided a the rise and lowering the intensity of infrared radiation in a given program. The accuracy of temperature control was 0,25 °C.

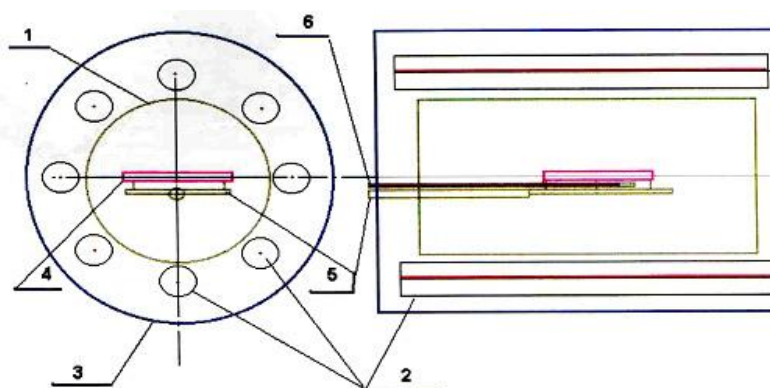


Fig. 2. Scheme of the reactor installation of IR-annealing. 1 - quartz lamp, 2 - halogen lamps 3 - adjustable flap, 4 - semiconductor wafers, 5 - a pedestal, 6 - thermocouple in a quartz tube.

Was found that in case of exposure of IR-radiation to the PAN, the mechanism of formation of conjugated structures not differ from the mechanism of thermal transformations. However, the dynamics of structural transformations of PAN in IR-pyrolysis has specific features compared with the purely thermal process. Drastically reduced the reaction time. Since cyclization of nitrile groups, the stage ends in 10–15 min., while the thermal process, it takes place within 14–16 h.

A sharp increase in the rates of chemical reactions in the IR-pyrolysis is associated with a decrease in activation energy ($E_1 \rightarrow E_2$) of the macromolecules, which are in excited vibrational states as shown in Fig. 3. It is shown that the emission in the IR-spectrum selectively excites the vibration frequencies of chemical bonds, raising their energy state. In IR-pyrolysis of possible selective effects of radiation on the vibrational energy of the individual functional groups of macromolecules, which allows, within certain limits to control the mechanism of structural transformations. Increasing the intensity of IR-pyrolysis of PAN leads to the improvement of graphite-like phases: an increase in the degree of graphitization, increase the size of coherently scattering crystallites, decrease the distance between planes. The degree of graphitization increases with increasing annealing temperature and with increasing degree of graphitization of pyrolyzed PAN.

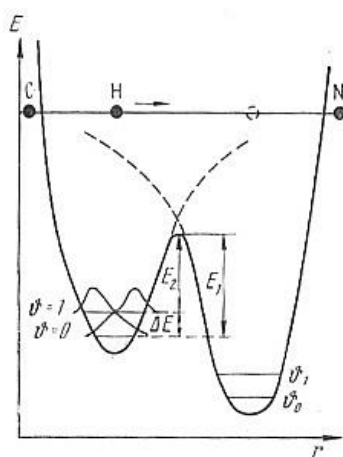


Fig. 3. The energy E of the system depending on the configuration coordinate r ; v - vibrational energy levels; E_1 - an activation barrier of the reaction of the ground vibrational state, E_2 - an activation barrier of the reaction of the excited state

IR-pyrolysis of dry samples of PAN synthesized by the method described above was carried out stepwise for 15 min at temperatures of 50, 80, 100, 120, 140, 160, 180 and 200 °C. IR-spectra were obtained in ATR-FTIR (crystal Ge) in the 4000-600 cm^{-1} in the IR-microscope Hyperion 2000 ("Bruker"), combined with a vacuum infrared spectrometer IFS 66v/s ("Bruker") Processing of the IR-spectra were performed using the software OPUS ("Bruker").

3. RESULTS AND DISCUSSION

3.1. Molecular-mass characteristics of PAN homopolymers.

3.1.1 Classical radical polymerization method, substantial initiation

Were synthesized the samples of PAN in DMSO and DMF use of substantial initiation. The rate of cure in accordance with the literature data decreased from DMSO to DMF. Attention is drawn to the

fact of a significant impact on the nature of the solvent on a molecular weight of polymer. Lowering the MM of the polymer in going from DMSO to DMF may be due to different reasons. For example, non-covalent interactions of the growing polymer chains (complexes with hydrogen bonds) when using DMF. In addition, the chain transfer constant of the solvent DMF for more than DMSO. The value of the polydispersity of the samples selected for the conversion of 60 - 70% of the precipitation of the diluted reaction mixtures in water, relatively low (Tab. 1).

Table 1. Conditions of synthesis of PAN samples and their characteristics

№	Solvent	Initiation	$M_n \times 10^{-3}$	M_w/M_n	The ratio of the intensities of the triads		
					rr	mr	mm
1	DMCO	AIBN	88.2	1.74	1.0 (25.3 %)	2.00 (50.5 %)	0.96 (24.2 %)
2	DMΦA	AIBN	23.1	1.70	1.0 (21.8 %)	2.25 (49.2 %)	1.32 (28.9 %)
3	DMΦA	γ-rays	32.5	1.42	1.0 (23.1 %)	2.18 (50.5 %)	1.14 (26.4 %)
4	DMCO	γ-rays	353.3	1.40	1.0 (23.7 %)	1.94 (50.0 %)	1.28 (30.3 %)
5	DMCO	AIBN – BTC	21.6	1.54	1.0 (21.7%)	2.3 (50.0%)	1.3 (28.3%)
6	DMCO	γ-rays – BTC	39.5	1.58	1.0 (23.9%)	2.13 (50.8%)	1.06 (25.3%)

3.1.2. Classical radical polymerization method, radiolysis initiation

When changing method of initiation on the radiolysis at temperatures above 0 °C the radical mechanism of the process is not changed, and the medium is also homogeneous. Polymerization is characterized by a first-order rate of monomer concentration, the rate increases, and MM decreases with increasing dose rate (in fact, with an increase in the rate of initiation) (Fig. 4).

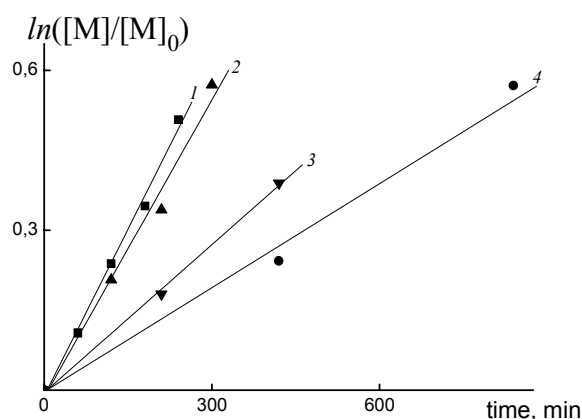


Fig. 4. Dependence of monomer concentration on the time in semi-logarithmic coordinates for the radiation polymerization of acrylonitrile in DMSO at 50 °C at a dose rate of radiation 0.107 (1), 0.075 (2), 0.023 (3), 0.011 (4) Gy/s.

For the PAN samples synthesized at 50 °C radiation polymerization in DMF and DMSO, is characterized by lower values of the polydispersity compared to the PAN, obtained under the action of AIBN. This is probably due to the change in method of selection of samples (repeated reprecipitation),

which led to an additional fractionation of the polymer. This conclusion is consistent with the symmetry of the MWD (Fig. 5) in the coordinates $q_w(M) = f(\lg(M))$. In addition, as in the AIBN-polymerization initiated, PAN which is formed in the presence of DMF is characterized by significantly lower MM than with DMSO.

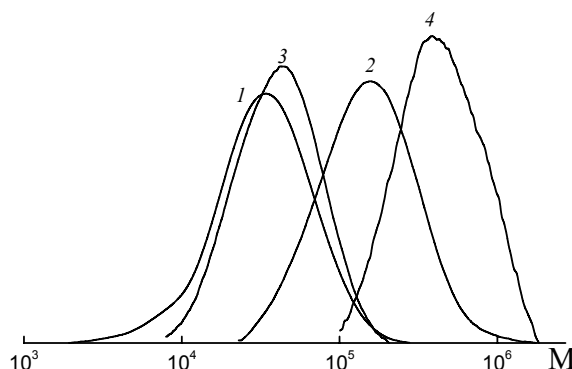


Fig. 5. MWD curves of polymers synthesized by the polymerization of acrylonitrile in DMF solution (1, 3) and DMSO (2, 4) under the action of AIBN (1, 2) and radiolysis (3, 4).

3.1.3. The pseudoliving radical polymerization: the dependence on the nature of initiation. Previously been applied successfully RAFT-polymerization for the controlled synthesis of PAN. In this paper we present the results of comparing the characteristics and thermal behavior of PAN obtained by polymerization of AN in DMSO in the presence of RAFT-agent (BTC), initiated by AIBN or radiolysis.

Radiation polymerization of AN in the presence of BTC (5×10^{-3} mol/l) occurs at relatively high speed and is characterized by a first order reaction rate on monomer concentration (Fig. 6a). That as the temperature decreases the rate of decrease too. As in the case of polymerization initiated by AIBN, the mechanism of this process is pseudoliving. Evidence of this shift of the GPC-curves in the high-MW with increasing conversion, as well as the linear dependence of the conversion of M_n and low values of polydispersity (Fig. 6 b). The effectiveness of BTC in the radiolysis is lower than in the case of a substantial initiation, as indicated by the difference in the values M_n^2 of polymers synthesized at equal concentrations of BTC. The reason for this phenomenon is not yet clear and requires further study.

From the analysis of the intensity ratio of triads rr: mr: mm in the PAN obtained RAFT-polymerization using different types of initiation, it follows that the transition from initiation to the radiolysis of the real proportion of atactic sequences does not change, while the proportion of isotactic triads decreases and is close to the content syndio -triads (Table 1). Thus, by varying the nature of the

² In the process of conversion of pseudoliving radical polymerization relationship is described by

$$M_n = M_{\text{RAFT}} + \frac{q[M]_0}{[RAFT]_0 + f[I]_0(1 - e^{-kit})} M_M [7].$$

solvent and the medium (homogeneous or heterogeneous), as well as the type of initiation (real or radiolysis), were synthesized by six samples of homopolymer PAN, which differ by their molecular mass characteristics.

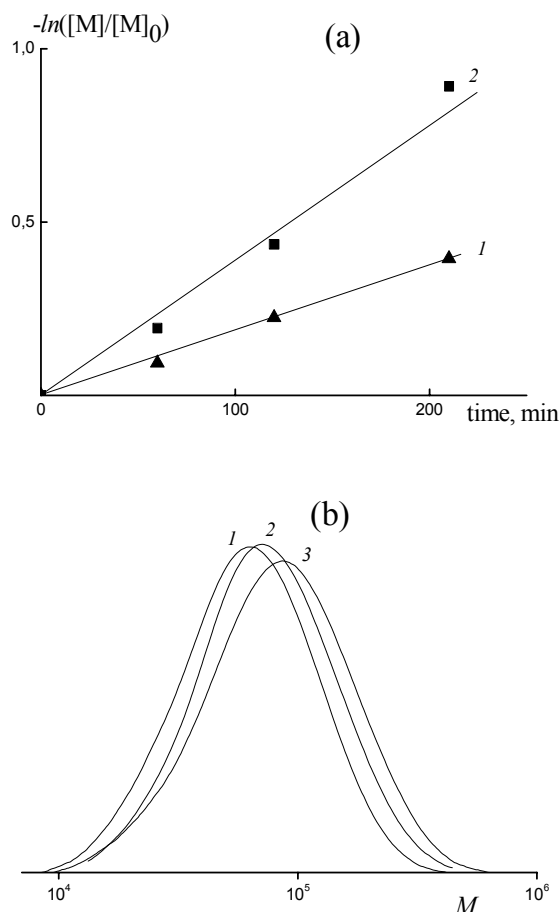


Fig. 6. Results of the study of radiation RAFT-polymerization of acrylonitrile in DMSO in the presence of BTC, $[BTC] = 5 \times 10^{-3} \text{ mol/l}$:

a) the dependence of monomer concentration on the time in the semi-logarithmic coordinates at 25 (1) and 80 °C (2), b) GPC-curves of polymers synthesized at 25 °C in the conversion of 8.9 (1), 20.1 (2) and 32.6% (3)

3.2. The study of the thermal behavior of polymers by DSC.

When heated in the structure of PAN proceeds cyclization reaction of nitrile groups, which leads to the transformation of the linear structure of a flexible polymer in a rigid frame. In an inert atmosphere mainly proceeds strongly exothermic process of cyclization, which is accompanied by the appearance on the DSC curves of the narrow exothermic peak maximum position and the intensity of which depend on the method of obtaining PAN (Fig. 7). For PAN, the synthesized solution-polymerized in the presence of AIBN, before starting for the cyclization of a sample obtained in DMF (curve 2) than in DMSO (curve 1), while for sample 2, the peak is broader and its intensity is lower. When changing the mode of initiation on the radiative processes of cyclization is also used to start in the PAN synthesized in DMF (curve 4), and the maximum peak is shifted by $\sim 15 \text{ }^{\circ}\text{C}$ in comparison with PAN,

formed in the AIBN-initiation, but the process is more exothermic. DSC curve of the sample synthesized in DMSO (curve 5), shifts to lower temperatures by about 20 °C. It can be assumed that the difference in thermal behavior of PAN formed in DMSO and DMF, regardless of the method of initiation due to the difference in their MW.

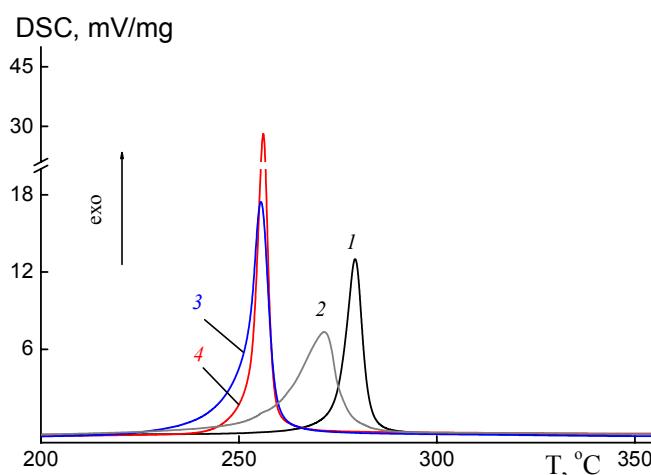


Fig. 7. DSC curves of PAN samples 1-4 (Table 1), obtained by heating the polymer in an inert atmosphere. Numbering of curves corresponds to the numbering of samples in Tab. 1.

3.3. The study of the structure of the PCS by ATR-FTIR.

Analysis of structural changes carried out by the IR spectra of the samples after IR-pyrolysis in the IR-camera.

3.3.1. The classical radical polymerization. The substantial initiation.

For PAN synthesized in DMSO (sample 1, Tab.1), the spectral characteristics of the solvent no registered at 80 °C IR-pyrolysis. The first signs of PCS seen in the IR spectrum is at 140 °C: there are new absorption bands at 1583 and 1490 cm^{-1} of the stretching vibrations of the C=N in the PCS (Fig. 8). With further heating the intensity of these bands increases, the band is strongly broadened. Other than those described above, the recorded absorption bands of stretching vibrations of $\nu_{\text{C}=\text{C}}$ ($\sim 1600 \text{ cm}^{-1}$) and ν_{CH} in the aromatic system (at 3066 cm^{-1}). At the same time observed decrease in the intensity of the absorption band at 1450 cm^{-1} (deformation vibrations of CH_2 -groups of the main chain of PAN), and at 200 °C IR-pyrolysis of the system are left. The absorption band of stretching vibrations of the nitrile group of PAN ($\nu_{\text{C}\equiv\text{N}}$) during the formation of interface is split into two peaks at 2243 cm^{-1} (nitrile group in the original PAN) and at 2200 cm^{-1} (nitrile group, involved in conjugation). At 200 °C IR-pyrolysis the band at 2243 cm^{-1} characteristic of the PAN does not disappear completely, forming a new band at 2200 cm^{-1} common envelope, in addition, there is also an absorption band at 2076 cm^{-1} of the nitrile groups in the conjugated sections of varying lengths.

In the IR-pyrolysis of PAN synthesized in DMF (sample 2), the spectral characteristics of education PCS appear at 160 °C, the absorption band of DMF is no longer registered at the same temperature (160 °C). However, at 200 °C in the IR-spectrum present an absorption band at 1450 cm^{-1} (deformation vibrations of CH_2), which indicates the existence of PCS same “local defect” of structure. In this case the absorption band of the nitrile groups (2243 cm^{-1}) in the same way as for

sample 1 is not fixed. It is known that DMF is quite strongly associated with the proton at the tertiary carbon of the main chain of PAN, resulting in desorption of residual solvent from the film of PAN occurs at a temperature above its boiling point when there is already partly formed by the PCS, in contrast to sample 1, where the disappearance of spectral features of the residual DMSO was observed at a lower temperature infrared pyrolysis and before the formation of the PCS. Probably, with PAN–DMF complex formation and preservation of saturated due to CH_2 -groups between the sites long enough conjugated double bonds. It should be noted that the content of isotactic triads in the chain of sample 2 more than in sample 1 (Tab. 1). Thus, the PCS for the PAN synthesized in DMSO (sample 1), is formed at a lower temperature and has a profound system of conjugation.

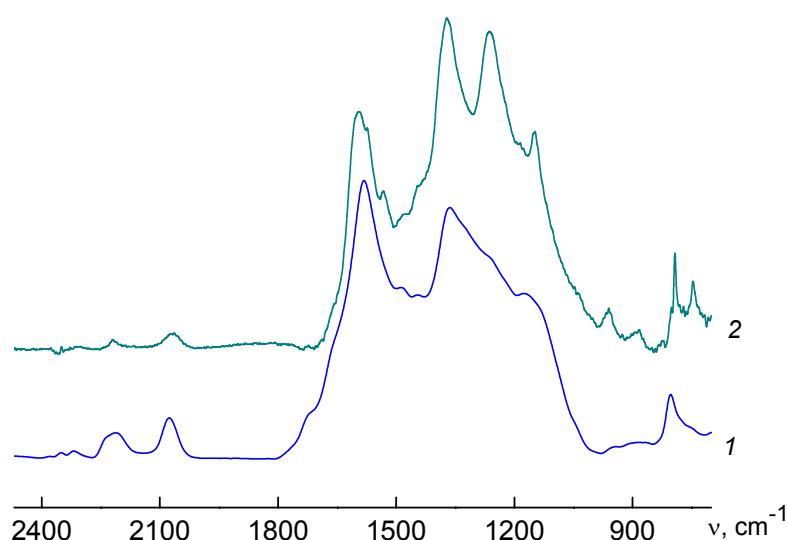


Fig. 8. Fragments of the IR-ATR spectra of samples 1 (curve 2) and 2 (curve 3) at 200 °C

3.3.2. The classical radical polymerization. Initiation of radiation

In Fig. 9 shows the fragments of the IR-spectra of samples 3 and 4, the initiation of radiation received. The beginning of the PCS-formation of PAN samples recorded at 160 °C IR-pyrolysis with the appearance of absorption bands at 1485 cm^{-1} .

With increasing temperature up to 180 °C the rapid growth of the absorption bands of conjugated bonds, while in the IR-spectra of PCS present an absorption band of the CH_2 groups (1450 cm^{-1}) is not involved in conjugation. The IR-spectra recorded at 200 °C, is still apparent absorption nitrile groups of the initial PAN (2243 cm^{-1}), however, for sample 4 is almost no absorption band of the CH_2 -groups in contrast to sample 3 (and from a sample 1 described previously), in which the spectrum of this band present. The absorption band at 1600 cm^{-1} in the IR-spectrum of sample 4 is split into two peaks (1611 and 1574 cm^{-1}), the region below 1500 cm^{-1} also differs from the corresponding spectra of sample 3 more pronounced peaks (similar to the sample 2). This could indicate the conjugation sites of different lengths for a sample of 4, separated from each other CH_2 and nitrile groups, and the more

extended conjugation sites in the sample 3. The content of isotactic triads in the chain of the original sample 3 is smaller than in sample 4 (Table 1).

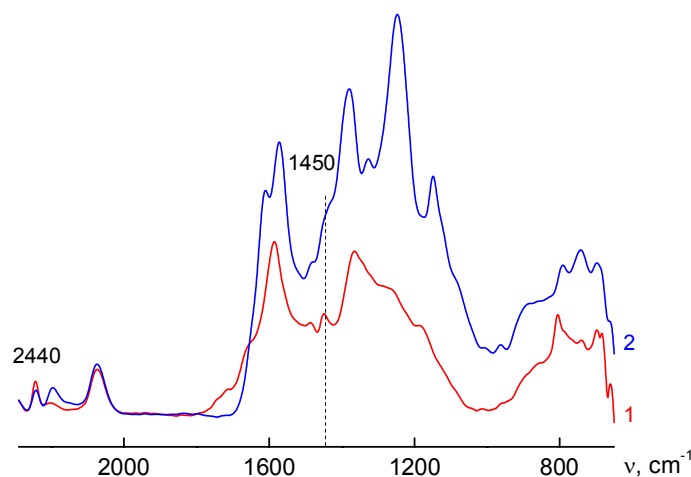


Fig. 9. Fragments ATR-FTIR spectra of samples 3 (curve 1) and 4 (curve 2) after 200 °C IR-pyrolysis

Comparing the conditions of formation and infrared spectra of the PCS for the samples synthesized in one solvent, but with different initiation (1, 4, 2 and 3), we can see that the low MW and broad MWD results in lowering the onset temperature of formation of conjugation. A large fraction of isotactic triads in the polymer chain determines the presence of the conjugation sites of varying length, limited nitrile and CH_2 -groups, resulting in the IR spectra of PCS distinct maxima of the absorption bands of conjugated bonds and the splitting of the absorption band of $\sim 1600 \text{ cm}^{-1}$.

3.3.3. Pseudoliving radical polymerization via the RAFT-mechanism.

PCS with IR-pyrolysis of PAN synthesized with the participation of BTC and AIBN (sample 5), begins to appear already at 120 °C and at 140 °C conjugate well developed (Fig. 10), but the PCS is fully formed in the pyrolysis of the sample in IR camera is much higher than 200 °C. At 180 °C IR-pyrolysis system are present as CN-group (2244 cm^{-1}) and residues of the CH_2 group (1450 cm^{-1}). The nature of the PCS with increasing temperature as a whole does not differ from that described above for the PAN with high content of isotactic triads. The IR-spectrum contains intense absorption bands with distinct maxima at 1380, 1255 and 1153 cm^{-1} and the splitting of the absorption bands of stretching vibrations of nitrile groups into two keeping with the original 2245 cm^{-1} .

When the radiation polymerization of PAN synthesized with BTC (sample 6), the beginning of the formation of PCS recorded between 120 and 140 °C too. Already at 160 °C IR-pyrolysis of absorption bands corresponding to residues of the CH_2 -groups are not registered, the system contains only the nitrile groups, which form the PCS (2218 cm^{-1}). The general background and a slight rise in the intensity maxima of the main absorption bands in the background of the overall envelope in the range $1370\text{--}1000 \text{ cm}^{-1}$ indicate the formation at 180 °C extensive PCS with a lot of rather short paired areas, which is characteristic of polymers with low content of isotactic triads in the chain (fig. 10).

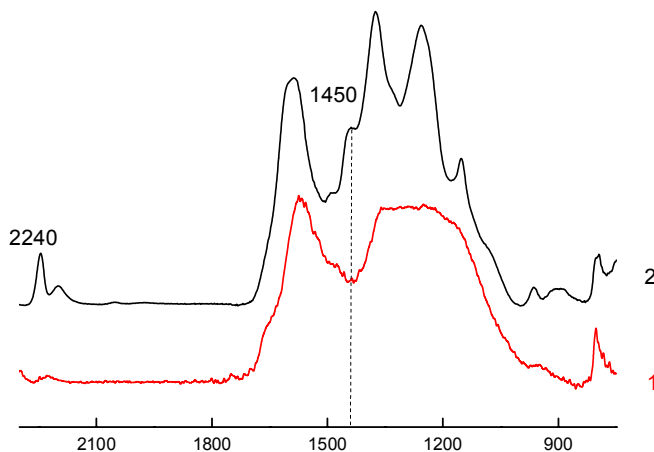
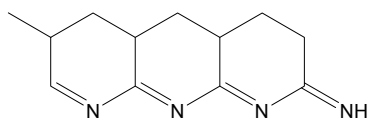
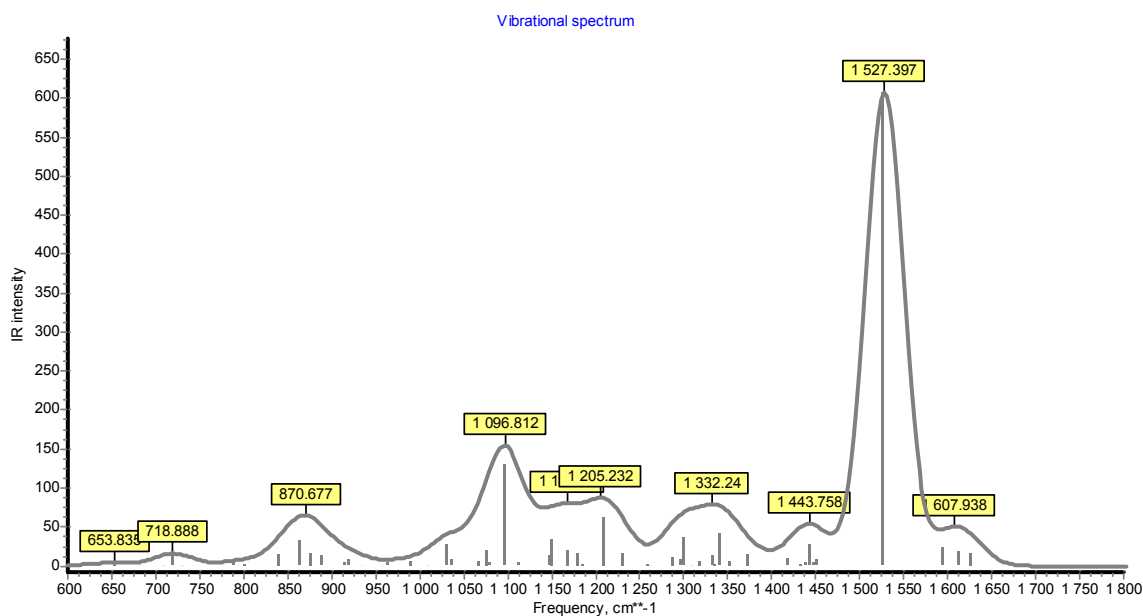


Fig. 10. Fragments ATR-FTIR spectra of samples 6 (curve 1) and 5 (curve 2) after IR-pyrolysis



(a)



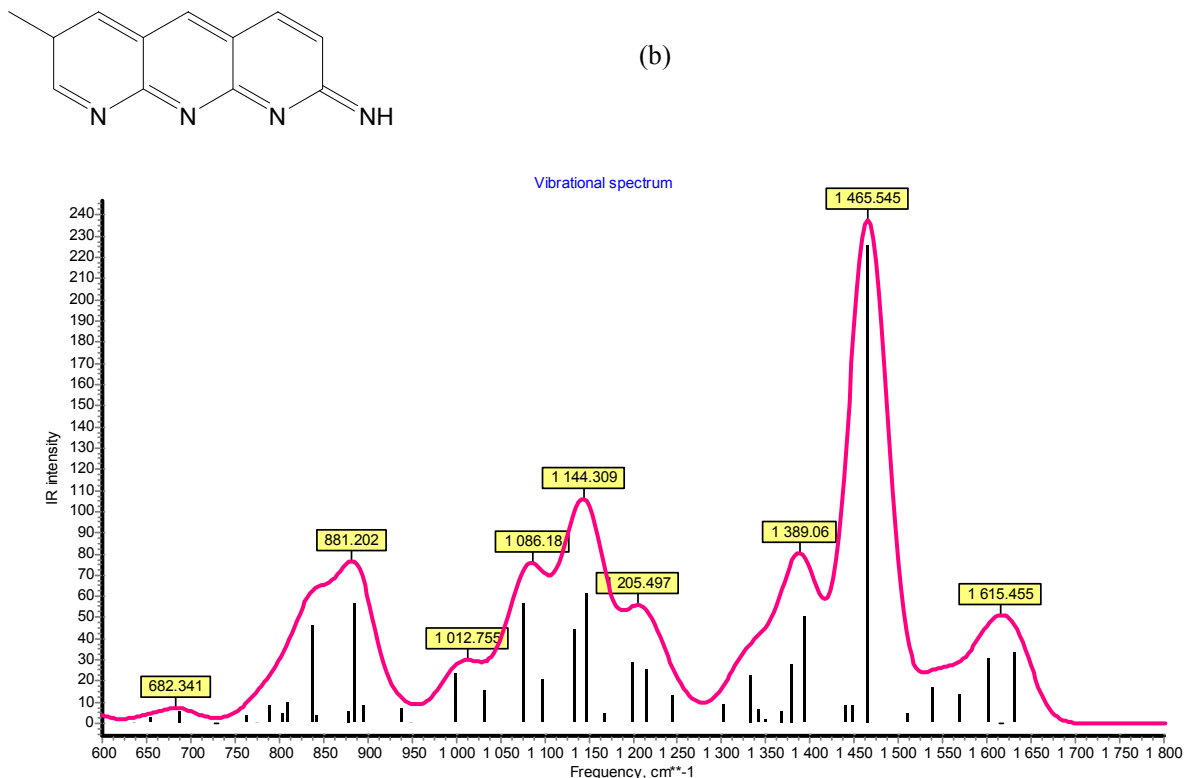


Fig. 11. The calculated vibrational spectrum of models

It is known that during high-temperature pyrolysis (above 750 °C) for a range of wave numbers of absorption bands of functional groups is broadened to longer wavelengths as well as to shorter wavelengths and is characterized by a common envelope without distinct maxima. According to Fig. 1, in the early formation of PCS formed C=N links, and only if there are deeper of conjugation C=C bond take pace.

In addition, quantum chemical calculations of models of conjugated structures containing only the C=N bond (Fig. 11a) and C=N and C=C bond together (Fig. 11b), confirmed the broadening of the spectral region with maxima shift to longer wavelengths for deeper of conjugation. Hence, in systems 1, 3 and 6, we see a deeper conjugation compared with the systems 2, 4 and 5

In Table 2 summarize the comparative features of educational and analyze the structure of the PCS in the IR-pyrolysis of PAN samples synthesized under different conditions.

Summarizing the analysis of thermal behavior and structure of the PCS in the IR pyrolysis of PAN samples with different history, we can make some general conclusions. For samples containing isotactic triads > 28% (systems 2, 4 and 5) in the IR-spectra after IR-pyrolysis observed a number of distinct bands of conjugated C=N and C=C bonds, while almost always remain the absorption band of the CH₂- and nitrile group, characteristic of the initial PAN. For these samples in terms of IR-pyrolysis are easily formed short segments of conjugated double bonds of different lengths separated by a saturated CH₂-groups. For samples containing the isotactic triads ≤ 26.5% (samples 1, 3 and 6) in the IR-spectra are observed after the IR-pyrolysis of broad, shifted to longer wavelengths of the absorption band of the conjugated double bonds, while the absorption bands of CH₂ and nitrile groups,

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characteristic of the original PAN no. That is, for these samples should expect more formed and more extended of conjugation system.

Table 2. Comparative analysis of the effect of synthesis conditions on the formation conditions of PAN and the structure of the PCS

System	T of the beginning of the PCS formation, °C	CH ₂ -groups	ν_{CN} in the PCS, cm ⁻¹	-C=C- and -C=N- groups in the PCS
1	140	–	2240 2200 2070	1721(shoulder) 1650(sh) 1581(intensive) 1370–1000 (int)
2	160	+	– 2219 2067	1650(sh) 1611 (int) 1580(int) 1530(low) 1370 (int) 1260 (int) 1150 (int)
3	160	+	2243 2200 (low) 2070	1721 (sh) 1650 (sh) 1580 (int) 1370–1000(int)
4	160	–	2243 2200 2070	1611 (int) 1580 (int) 1370 (int) 1250 (int) 1150 (int)
5	120-140	+	2244 2200	1650(sh) 1611 (int) 1580(int) 1530(low) 1370 (int) 1260 (int) 1150 (int)
6	120-140	-	- 2218	1721(sh) 1650(sh) 1581(int) 1370–1000(int)

Thus, we can divide all the samples of PAN into two groups, forming a deep PCS conjugation (samples 1, 3 and 6) and forming a PCS with short conjugated segments separated by a nitrile, and CH_2 -groups (samples 2, 4 and 5). Based on the data set, the most perfect system of defect-free and fully conjugated bonds is characteristic for the system 6.

3.3.4. Copolymers of acrylonitrile and methyl acrylate, the synthesis and thermal behavior. Parameters for the stereoregularity of copolymers with the introduction of small additions of MA did not change compared to the PAN obtained in DMSO, and comprise: rr: mr: mm = 1.00: 2.22: 1.04 (23.5%: 52.1%: 24.4%). In Fig. 12 shows the normalized GPC-curves of the synthesized samples.

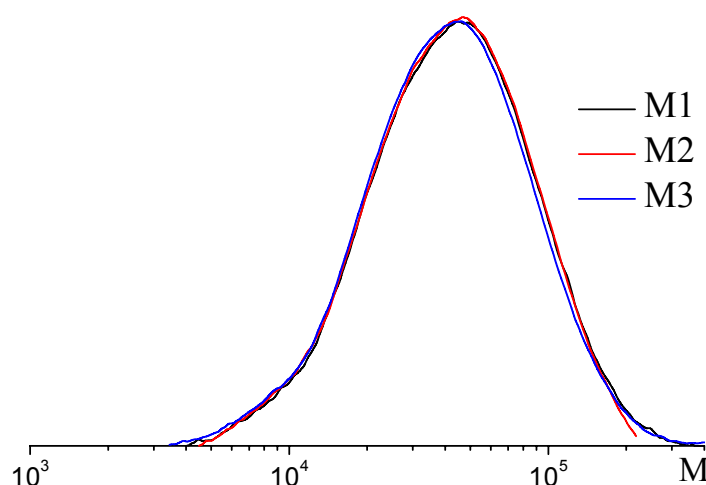


Fig. 12. Normalized to unit area GPC curves of binary copolymers of AN / MA, received a classical radical polymerization

Table 3 shows the results of calculations of molecular-mass characteristics of binary copolymers. It is seen that the addition of 1 – 5 mol.% of MA to the reaction mixture AN/DMSO/AIBN has virtually no effect on the MW and the width of the MWD.

Table 3. Molecular-mass characteristics of the copolymers

№	composition, the molar %		M_n	M_w	M_w/M_n
	AN	MA			
M1	95	5	33600	51400	1.52
M2	97	3	29900	49200	1.64
M3	99	1	30000	48800	1.62

Investigation of the thermal behavior of the copolymer of MA and AN by DSC showed that the introduction of MA does not affect the PCS-formation in an inert atmosphere: the temperature interval and the position of the maximum on the DSC curve does not change compared to the homopolymer PAN obtained in DMSO, but decreased the intensity of heat. Transformations in the copolymer, the heated air to occur in a narrower temperature range than in the homopolymer, and the maximum heat release is shifted to 30 °C to lower temperatures.

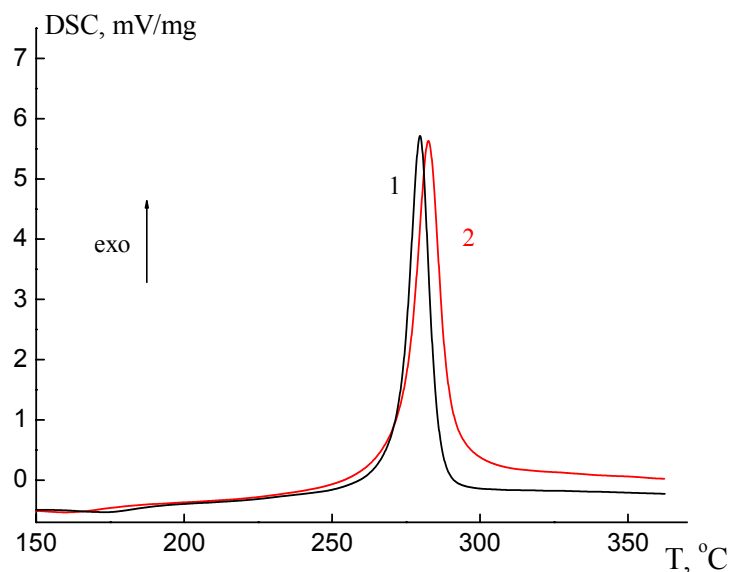


Fig. 13. DSC curves of a sample of the copolymer of MA and AN (M2), synthesized in DMSO, obtained by heating the polymer in an inert atmosphere (1) and in air (2)

To study the characteristics of the formation of polyconjugated structures M1 sample was subjected to IR-pyrolysis. In Fig. 14 shows the IR-spectra of the films M1, formed from DMSO, prior to annealing in the IR-camera and after stepwise annealing up to 200 °C. The structure of PCS is similar to the PCS from homopolymer PAN 2,4 and 5, and differs from the PAN homopolymer synthesized in DMSO (sample 1).

The presence in the IR-spectrum absorption bands of the copolymer nitrile groups (2243 cm^{-1}) and residual CH_2 -groups (1450 cm^{-1}) show that AN and MA copolymer by 200 °C IR pyrolysis does not form a deep of conjugation

4. CONCLUSIONS

As a result of this work can be argued that beginning of formation of MSS depends on the polymer molecular weight, the content of isotactic triads in the chain and the presence of residual solvent, which can communicate with the PAN and contribute more as a structuring of the polymer chain and the formation of defects during carbonization. In the case of the solvent interaction with the macromolecule does not occur, then the similar molecular masses of the low content of isotactic triads results in lowering the onset temperature of education and the rapid formation of short sections of conjugation. The use of RAFT- polymerization mechanism independently of the type of initiation

(substantial or radiolysis) has little effect on the stereoregularity of PAN, but results in a polymer with narrow MWD. In this case thermal effects are observed at lower temperatures, the terminal nitrile and CH₂-groups are fully expended on the formation of deep PCS with a large number of sites rather short conjugation. Copolymerization of AN with MA leads to a deterioration of the structure of the MSS. Thus, it is shown that changing the method of synthesis, you can control the structure of the MSS.

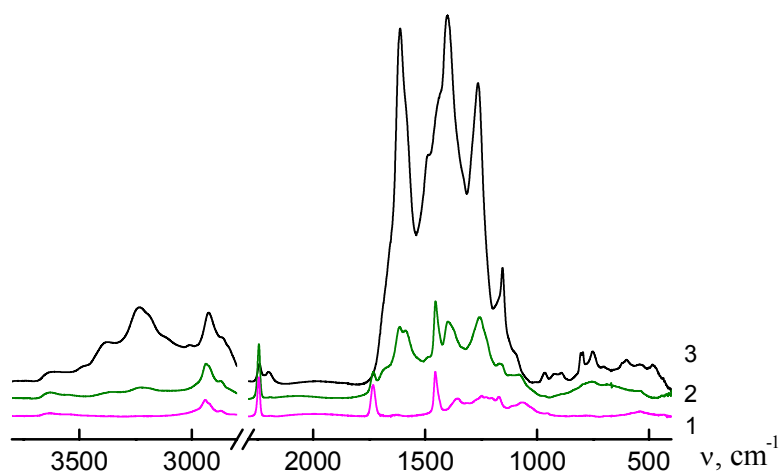


Fig. 14. The IR spectra of the original copolymer PAN-MA, at 20 °C (curve 1) and the same film after annealing in the IR-cell at 150 (curve 3) and 200 °C (curve 5)

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