



Study of Intermolecular Interaction Between Polyacrylonitrile and Amphoteric Surfactant (Betaine) in Dimethylformamide Medium

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Monomers of polyacrylonitrile were determined by the use of infrared spectroscopy. Viscosity and specific electrical conductivity of polyacrylonitrile were studied in *N,N*-dimethylformamide medium at different concentrations and temperatures. The critical micelle concentration of amphoteric surfactant (betaine) was determined in *N,N*-dimethylformamide medium. It was proved that viscosity and conductivity of polyacrylonitrile solutions containing betaine decrease at the field of critical micelle concentration. Crystalline structure of polyacrylonitrile in the solid phase in the presence of betaine was performed by X-ray diffraction and scanning electron microscope, found that betaine contributes in the development of polymer structure.

Keywords: Polyacrylonitrile, Interaction, Fiber, Spinning, Mechanical and structural properties, Surfactants.

INTRODUCTION

Polyacrylonitrile is an important polymer, mainly due to its excellent properties of rigidity and resistance against oil. It can be spun into acrylic, which is one of the most widely used synthetic fibers. Polyacrylonitrile is also the precursor of carbon fiber¹⁻³. Nanofibers structure of polyacrylonitrile in the solid phase can be controlled by changing the properties of its solutions, such as viscosity and electrical conductivity and surface tension⁴.

The mechanical and structural properties of polymeric solutions are strongly affected in the presence of surfactants; because the effectiveness of interactions between macromolecules themselves is significantly affected by these substances. These surfactants also affect the shape and dimensions of crystals being formed and the conditions under which they grow⁵⁻¹⁰.

Unfortunately, studies about the effect of surfactants on the intermolecular interactions in polyacrylonitrile are still few and rare. However, the surfactants may be essential when developing fiber spinning procedures that would allow the control of mechanical and structural properties¹¹.

The effects of surfactant properties, such as concentration, chain length and ionic character, on the structure of the resulting polymer nanofibers were investigated. It was found that the average diameter of polyacrylonitrile nanofibers increased with increasing surfactant chain length. In contrast, it decreased with increasing surfactant concentration¹².

It was demonstrated that small variations in the structure of surfactants can lead to significant differences in their intermolecular interactions and association with polymers¹³.

The purpose of this study is to show the effect of betaine surfactant on the hydrodynamic and structural properties of polyacrylonitrile.

EXPERIMENTAL

Industrial fiber of polyacrylonitrile with a molecular weight 100000 g mol⁻¹, containing an acrylonitrile monomer (85 wt. %) which contains a nitrile group with a large dipole moment (3.4D)¹⁴ (Adnan Shabarec Co.). DMF solvent, pH value 7, purity (GC) ≥ 99.5 % (MERCK Co.). 2-[(3-Dodecanamidopropyl)dimethylamino]acetate (betaine C₁₉H₃₈N₂O₃) as amphoteric surfactant (Shanghai Oli Enterprised Co.). The XRD patterns of polyacrylonitrile were obtained using a STOE transmission STADI diffractometer, with copper as target and nickel as filter ($\lambda = 1.5408 \text{ \AA}$) at 30 kV and 30 mA. The scanning speed was 3.7 min⁻¹ in the range $2\theta = 10-90^\circ$ at 298 K.

The scanning electron microscope (TESKAN VECA II) was used to investigate the morphology of polyacrylonitrile. The falling ball viscometer (HAAKE Co.) corresponds to the requirements of many international standards (ISO 12058 and the German standard DIN 53015). The measuring tube is jacketed by means of an outer glass tube, to control the solution temperature ($\pm 0.03 \text{ }^\circ\text{C}$ for test temperatures between 10 up to 80 °C). This device can measure the viscosity ranging between

(0.3 -75000) mPas. Every value was measured three times and then averaged. Specific electrical conductivity was measured by SANXIN-MP 513 Lab Conductivity Meter. Polyacrylonitrile solutions were prepared in range (0.5-10) wt. %, where polyacrylonitrile fibers were dissolved in DMF, by continuous stirring at laboratory temperature and then transparent polymeric solutions were obtained. Also, polyacrylonitrile solutions were prepared in the presence of different concentrations of surfactant. Then viscosity and specific electrical conductivity of prepared solutions were studied. The solid samples of polyacrylonitrile were prepared to study their crystalline structure in the following way: polyacrylonitrile solutions were prepared in the presence or absence of surfactant, then poured in petri dishes and put in dryer at 50 °C until the complete vaporization of DMF, where solid samples were obtained; these samples were examined by XRD and SEM.

RESULTS AND DISCUSSION

Monomers of polyacrylonitrile were determined by FT/IR. Fig. 1 showed the spectrum of polyacrylonitrile.

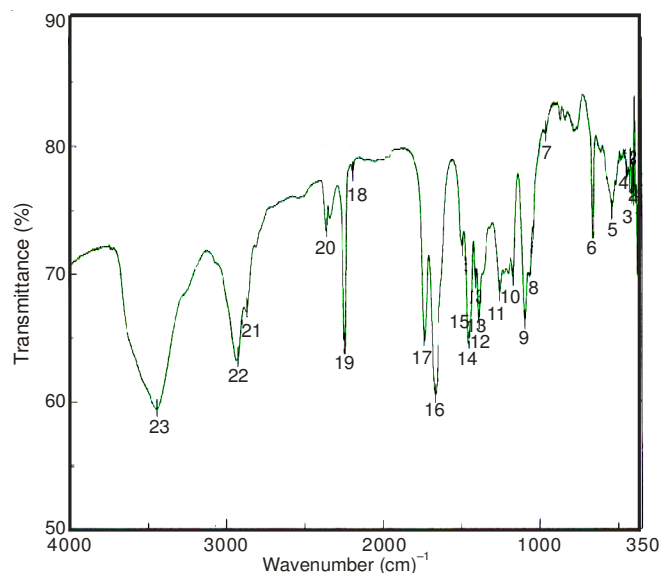


Fig. 1. IR spectrum of polyacrylonitrile

The IR spectrum showed the following groups: Nitrile group which shows a band around 2247 cm^{-1} (19) belongs to acrylonitrile monomer $\text{CH}_2=\text{CH}-\text{C}=\text{N}$. Acetate group which shows a band around 1168 cm^{-1} (10) belongs to C-O group and a band around 1736 cm^{-1} (17) belongs to C=O, this proof that the existence of vinylacetate monomer $\text{CH}_2=\text{CH}-\text{O}-\text{CO}-\text{CH}_3$ in the polyacrylonitrile composition. Amide group which shows a band around 1640 cm^{-1} (shoulder 16) belongs to N-H group and a band around 1669 cm^{-1} (16) belongs to C=O, this proof that the existence of acrylamide monomer $\text{CH}_2=\text{CH}-\text{CO}-\text{NH}_2$ in the polyacrylonitrile composition.

Viscosity (η) of polyacrylonitrile solutions was measured at (298, 308, 318, 328) K and specific electrical conductivity (SEC) was measured at (298,308) K. Viscosity of polyacrylonitrile solutions was estimated through the following equation:

$$\eta = \kappa(d_1-d_2)t$$

where: κ -ball constant

d_1 -ball density

d_2 -solution density

t -falling time of the ball

Table-1 showed the results of measuring the density of polyacrylonitrile solutions at 298 K, whereas DMF density is equal 0.923 g cm^{-3} at the same temperature. The results of measuring the viscosity and the SEC are listed in Tables 2-5, respectively.

TABLE-1
DENSITY OF POLYACRYLONITRILE SOLUTIONS

[PAN] (wt. %)	1	2	3	4	6	8	10
Density (g cm^{-3})	0.936	0.940	0.942	0.945	0.949	0.954	0.958

TABLE-2
VISCOSITY OF DMF

T (K)	298	308	318	328
η (mPa s)	0.473	0.420	0.375	0.339

TABLE-4
SEC (χ) OF DMF

T (K)	298	308
χ ($\mu\text{S cm}^{-1}$)	0.7	0.8

TABLE-3
VISCOSITY OF POLYACRYLONITRILE SOLUTIONS

T (K)	Polyacrylonitrile concentration (wt. %)						
	1	2	3	4	6	8	10
	Polyacrylonitrile viscosity (mPa s)						
298	1.495	3.210	8.831	15.813	46.338	109.333	264.968
308	1.221	2.751	7.359	12.876	37.971	90.210	224.973
318	1.097	2.293	6.227	10.843	30.892	70.102	164.980
328	0.955	2.030	5.321	9.261	25.743	56.234	129.980

TABLE-5
SEC OF POLYACRYLONITRILE SOLUTIONS

T (K)	Polyacrylonitrile concentration (wt. %)							
	0.5	1	2	3	4	6	8	10
	Polyacrylonitrile conductivity ($\mu\text{S cm}^{-1}$)							
298	12.3	23.0	39.1	52.8	64.0	82.6	92.1	97.5
308	14.5	27.8	44.0	59.8	70.9	88.9	102.0	111.4

Fig. 2 showed the dependence of viscosity and conductivity on polyacrylonitrile concentration. It showed that the viscosity changes of polyacrylonitrile solutions are accompanied by conductivity changes. Viscosity increases in an almost straight line at low concentrations and then markedly increases starting with concentration of 5 wt. % approximately, this refers to the crystalline structure formation. At this concentration strong association of macromolecules begins, this is because of intermolecular interactions between dipoles and the formation of hydrogen bonds, which in turn leads to a significant increase in viscosity. While SEC increases with increasing of polyacrylonitrile concentration, then after a concentration of 5 wt. %, conductivity becomes practically independent of concentration; this is because of the completion of crystal structure⁵⁻⁷.

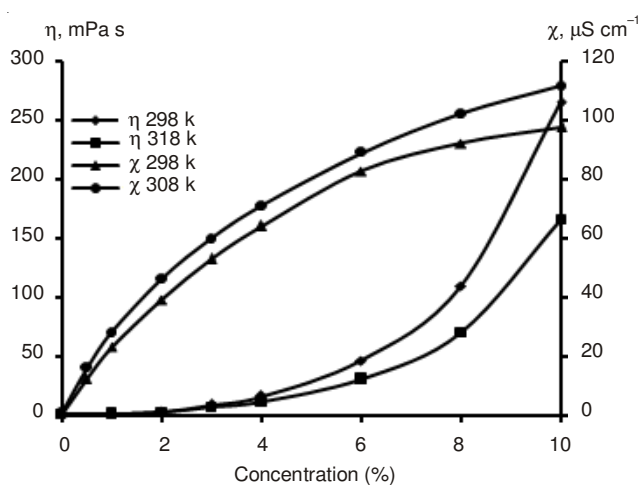


Fig. 2. Viscosity dependence at (298,318) K and conductivity at (298, 308) K on concentration of polyacrylonitrile

The effect of surfactants is related to their conditions in the liquid phase and distinguish them are their colloid chemical properties such as micelles formation. But unfortunately, the information on the micelles formation in the organic mediums is very scarce and fragmentary. It is necessary to note here, that there is a difference between micelles formation in organic mediums and water⁹⁻¹¹.

The critical micelle concentration of the betaine solutions was determined by SEC at 298 K. The results are shown in the Table-6.

Betaine concentration ($C \times 10^2 \text{ mol L}^{-1}$)	χ ($\mu\text{S cm}^{-1}$)	$\log \mu$
0.312	5.24	0.719
0.625	7.07	0.849
1.250	13.18	1.119
1.700	20.42	1.310
2.000	26.30	1.419
2.500	28.18	1.449
3.500	31.62	1.499
5.000	37.15	1.569
7.500	46.77	1.669
10.000	61.5	1.788

The critical micelle concentration of betaine solutions was determined by using the following equation $\log \chi = f(c)$, as it is shown in Fig. 3.

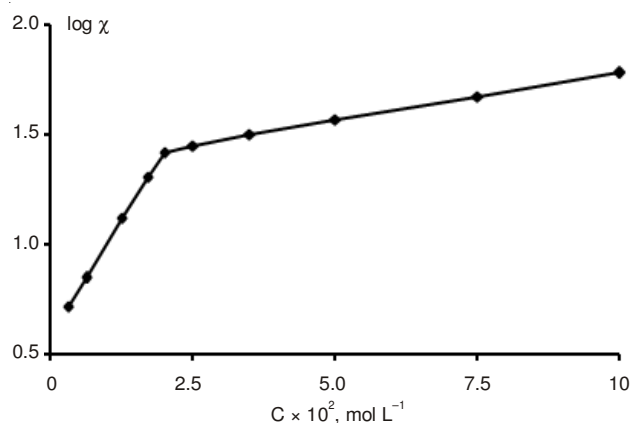


Fig. 3. $\log \chi$ dependence on the concentration of betaine

Fig. 3. showed that the conductivity vs. concentration plot shows an inflection, which was assigned to the critical micelle concentration (0.019 mol L^{-1})^{10,15}.

It should be note here that amphoteric surfactants act as a nonionic surfactant in the field of $\text{pH} = 4-9$ ^{11,16}.

The results of measuring the viscosity and the SEC of polyacrylonitrile solutions (2, 6 and 10) wt. % containing different concentrations of betaine at 298 K are shown in Tables 7 and 8.

Betaine concentration ($C \times 10^2 \text{ mol L}^{-1}$)	Polyacrylonitrile viscosity (mPa s)		
	2 wt. (%)	6 wt. (%)	10 wt. (%)
0.312	3.225	47.533	277.212
0.625	3.227	47.754	279.700
1.250	3.222	45.310	268.934
1.700	3.216	42.559	239.767
2.000	3.213	40.337	214.342
2.500	3.211	37.454	187.501
3.500	3.200	36.353	150.002
5.000	3.198	35.651	135.110
7.500	3.199	35.542	136.334
10.000	3.197	35.610	135.025

Betaine concentration ($C \times 10^2 \text{ mol L}^{-1}$)	Polyacrylonitrile conductivity ($\mu\text{S cm}^{-1}$)		
	2 wt. (%)	6 wt. (%)	10 wt. (%)
0.312	39.8	83.6	98.5
0.625	39.9	83.7	99.1
1.250	39.5	83.2	96.5
1.700	37.5	80.0	93.2
2.000	37.0	78.1	91.2
2.500	36.3	77.5	89.0
3.500	36.1	76.5	88.5
5.000	36.2	76.8	88.7
7.500	36.3	77.1	88.6
10.000	36.2	77.2	88.7

Fig. 4 showed the viscosity dependence of polyacrylonitrile solutions (2, 6 and 10) wt. % on betaine concentration. It showed that the viscosity of polyacrylonitrile solutions (2, 6 and 10) wt. % in the presence of betaine, starts decreasing at the field of critical micelle concentration for each of them, but this decline will be sharp for the solution 10 wt. %, less marked for 6 wt. % and for 2 wt. % it almost disappears. This is due to the influence of betaine and micelles formation on conformation of polyacrylonitrile molecules, which led to a weakening of the intermolecular interaction between polyacrylonitrile molecules. But at concentrations greater than critical micelle concentration, the viscosity takes a constant value in practice and we must not forget here that the small decrease in viscosity is related to the compression threshold of the coil polymer chains. Fig. 4 also showed that the proportion of decrease in the viscosity of both solutions 6 and 10 wt. % is 23 and 49 %, respectively, this is because the crystalline structure in 10 wt. % solution is more developed than in 6wt. %. While viscosity of 2 wt. % solution is not related to concentration in practice, this is because of the non-crystalline structure formation. Thus, effectiveness of the effect of betaine on the viscosity is determined by the concentration of polymer significantly^{5,17}.

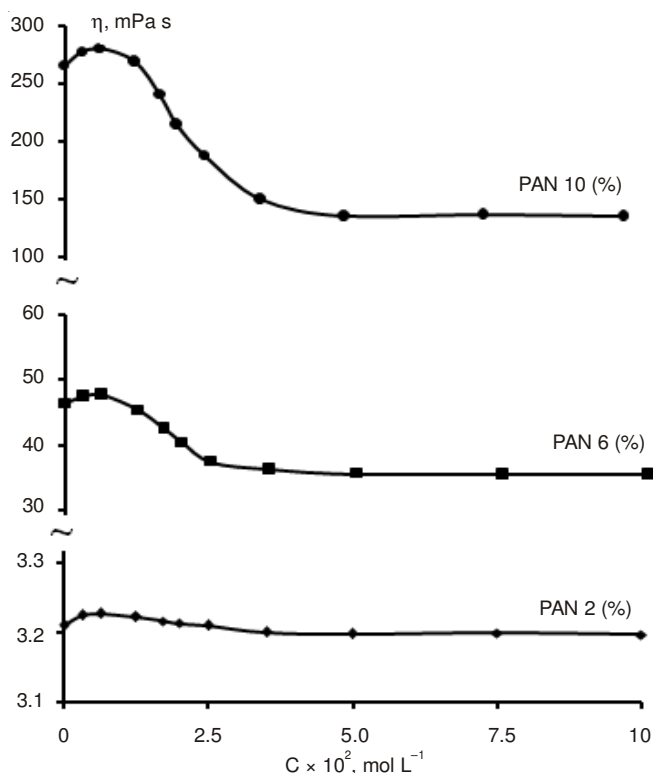


Fig. 4. Viscosity dependence of polyacrylonitrile (PAN) solutions (2, 6 and 10) wt. % on concentration of betaine

Fig. 5 showed the SEC dependence of polyacrylonitrile solutions (2, 6 and 10) wt. % on betaine concentration. It showed that the SEC of polyacrylonitrile solutions (2, 6, 10) wt. % begins to decline slowly at the field of critical micelle concentration for each of them, this decline is due to micelles formation and intermolecular interaction between betaine and polyacrylonitrile^{11,17}.

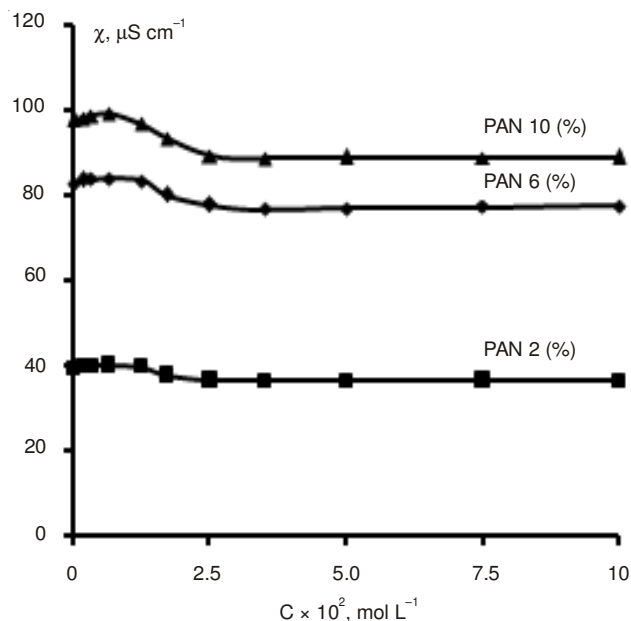


Fig. 5. SEC dependence of polyacrylonitrile (PAN) solutions (2, 6 and 10) wt. % on concentration of betaine

Crystalline structure of polyacrylonitrile in solid phase in the presence or absence of betaine was studied by XRD and SEM. Two solid samples were prepared, the first one is polyacrylonitrile 10 wt. % and the second one is polyacrylonitrile 10 wt. % containing 0.075 mol L⁻¹ of betaine. Then these samples were tested by XRD. The X-ray diffractometer has software to evaluate the crystalline structure. Fig. 6 showed the X-ray diffraction patterns.

Fig. 6 showed that X-ray diffraction patterns have two peaks; the first one has a strong intensity, while the second is weak and broad, the first peak indicates to a crystalline structure, while the second peak indicates that there is still some kind of amorphous structure¹⁸. Fig. 6a also showed that the intensity of the first peak increases slightly, in comparison with the first peak in Fig. 6b, proves that the crystalline structure has developed in the presence of betaine.

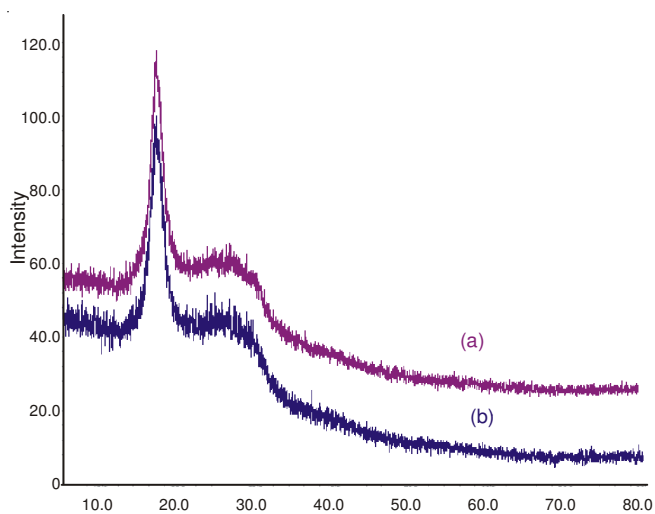


Fig. 6. X-ray diffraction patterns (a) polyacrylonitrile 10 wt. % containing 0.075 mol L⁻¹ of betaine (b) polyacrylonitrile 10 wt. %

Also, the two preceding solid samples were examined by SEM as shown in Fig. 7. It reveals that the crystalline structure of the first sample (Fig. 7a) is more developed than the second sample (Fig. 7b), this is because of the existence of betaine which worked to decrease the interfacial surface tension and this corresponds with what was mentioned before in the study of structure through XRD.

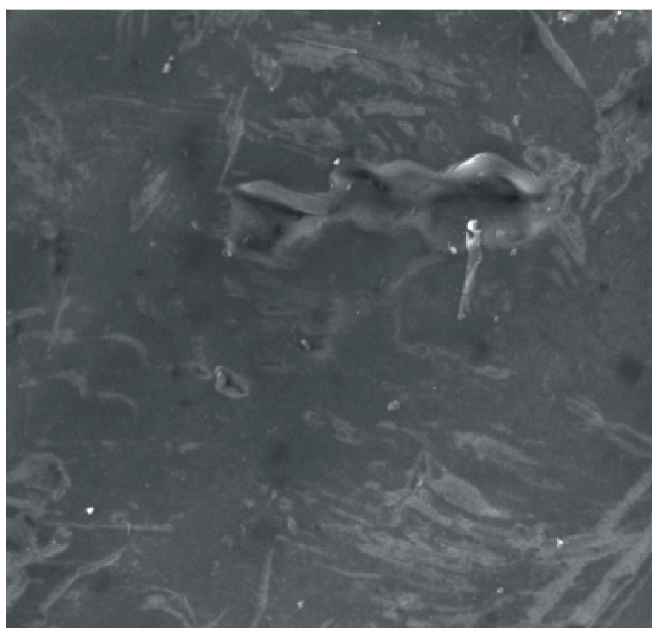
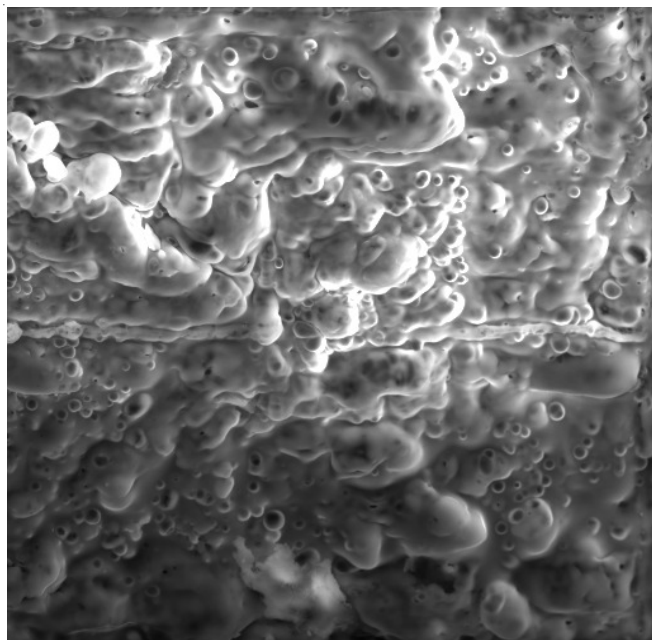


Fig. 7. Morphology of polyacrylonitrile (a) polyacrylonitrile 100 g/L containing 0.075 mol/L of betaine (b) polyacrylonitrile 100 g/L

Conclusions

- Copolyacrylonitrile components were identified by infrared spectroscopy.
- The foundations of changes of hydrodynamic and structural properties of polyacrylonitrile in the presence of betaine or without it have been laid.
- The critical micelle concentration of betaine in DMF medium has been determined.
- Viscosity and conductivity of polyacrylonitrile solutions containing betaine decrease at critical micelle concentration.
- Effectiveness of the effect of betaine on viscosity and conductivity is determined by the concentration of polymer significantly.
- Demonstrated through XRD and SEM that crystalline structure of polyacrylonitrile has developed in the presence of betaine.

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