A MODIFIED POLYMER FROM POLYACRYLONITRILE

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(*Received* 10 *August* 1968 ; *revised* 26 *September* 1968)

Polyacrylonitrile has been modified by introducing thioamide groups ($—CSNH_2$) in place of nitrile groups ($—CN$) in the polymer chain by passing dry H_2S gas through a 5% solution of the polymer in *N-N* dimethylformamide. The modified polymer is soluble in acetone. X-ray study revealed the complete loss of crystallinity in the modified polymer. Infra-red spectrum of the polymer film shows strong absorption bands at 3390 cm^{-1}, 3280 cm^{-1}, 2273 cm^{-1} and 1667 cm^{-1} indicating the presence of both thioamide and nitrile groups in the polymer chain.

Polyacrylonitrile (PAN), an important polymer for the production of synthetic fibres and elastomers, was for a long time regarded as a 'dark horse' in the polymer race as no suitable solvent could be found for it. As a result of intensive research by duPont chemists a number of highly polar solvents such as dimethylformamide (DMF), dimethyl acetamide, dimethyl sulphoxide (DMSO), dimethyl sulphone etc. were discovered for the polymer.

First report on a modified polyacrylonitrile soluble in a common organic solvent like acetone appeared in a Russian note by Gabrielyan *et al*[1]. In the present communication, we describe a method of preparation of modified-PAN following a process similar to that used for the preparation of thioamides from organic cyanides by Fairfull *et al*[2]

EXPERIMENTAL PROCEDURE

Material used : PAN used for this study was prepared by polymerising monomeric acrylonitrile supplied by BDH, in presence of toluene using benzoyl peroxide (0·1 per cent on weight of monomer) as initiator at 50°C in an atmosphere of nitrogen. The polymer which separated out as white granules from the reaction medium, was filtered and washed several times with rectified spirit till free from the smell of the monomer. It was then dried under vacuum at 60°C for 12 hours.

Preparation of modified polymer : Dry H_2S gas was passed through a 5 per cent solution of PAN in DMF at 50°C for 2 to 4 hours as desired. The colour of the solution slowly changed from yellow to bluish-green. Excess H_2S was removed by passing dry nitrogen gas through the solution at 50°C for one hour. The polymer was then precipitated by adding methyl alcohol to the solution and filtered. The precipitate was redissolved in acetone and precipitated again by methyl alcohol, filtered and dried under vacuum at 60°C for 12 hours.

Five fractions of the modified-PAN differing in molecular weight were prepared using the usual fractionation technique from a 1·5 per cent solution of modified-PAN in acetone using ethyl alcohol as precipitant.

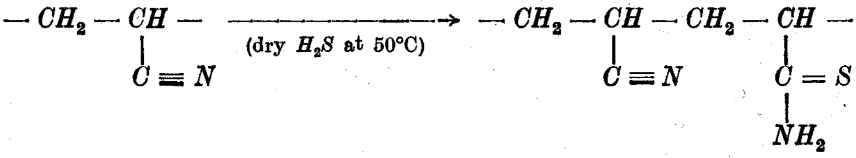
Nitrogen estimation : Nitrogen content of both modified-PAN and PAN was determined by the method described by Steyermark[3] using Pregl semi-micro distillation apparatus.

Molecular weight of PAN : The viscosity average molecular weight of PAN was determined from a knowledge of the intrinsic viscosity of the polymer using the following equation due to Cleland and Stockmayer[4].

$$[\eta] = 2{\cdot}43 \times 10^{-4}\ [M_v]^{0{\cdot}75}$$

RESULTS AND DISCUSSIONS

Solubility : Results of the solubility study of the modified-PAN in thirteen different solvents are shown in Table 1. Modified-PAN readily goes into solution in acetone as also in DMF and DMSO. PAN reacts with H_2S to produce the modified-PAN having both the $-CN$ and $CSNH_2$ groups attached to the polymeric backbone.



$$-CH_2-\underset{\underset{C\equiv N}{|}}{CH}- \xrightarrow[\text{(dry } H_2S \text{ at } 50°\text{C)}]{} -CH_2-\underset{\underset{C\equiv N}{|}}{CH}-CH_2-\underset{\underset{\underset{\underset{NH_2}{|}}{C=S}}{|}}{CH}-$$

By passing H_2S for two hours approximately 50 per cent of the $-CN$ groups are converted into $-CSNH_2$ groups as will be evident from the nitrogen content of the fractionated and unfractionated modified-PAN (Table 2). It will be seen from Table 2 that the conversion of reactive nitrile groups into thioamide groups is almost independent of the chain length of the polymer molecules. The nitrogen content of the polymers in almost

Table 1

Solubility of modified-PAN in different solvents

Solvent	Solubility
Acetone	Soluble
Methyl ethyl ketone	Insoluble
Dioxane	,,
Cyclohexanone	,,
Acetonyl acetone	,,
Acetic acid	,,
Chloroform	Slight swelling
Carbon tetrachloride	Insoluble
Benzene	,,
Toluene	,,
Petroleum ether	,,
Dimethylformamide	Soluble
Dimethylsulphoxide	,,

TABLE 2

NITROGEN CONTENT OF UNFRACTIONATED AND FRACTIONATED MODIFIED-PAN AND PAN

Polymer	Nitrogen %
Modified-PAN (unfractionated)	20·45
Modified fraction-1	20·68
Modified fraction-2	19·70
Modified fraction-3	20·03
Modified fraction-4	18·91
Modified fraction-5	19·88
PAN (unmodified)	26·38

(Molecular weight of PAN used in this study was 1,33,700).

TABLE 3

INTRINSIC VISCOSITY AND HUGGINS' CONSTANT OF MODIFIED-PAN AND PAN POLYMERS IN DMF

Polymer	Concentration gm/100 ml	η_{sp}/C	$[\eta]$	Huggins' constant k
PAN	0·50	2·28	1·70	0·40
	0·25	2·01		
	0·125	1·87		
Modified-PAN	0·50	2·46	2·05	0·19
	0·25	2·20		
	0·125	2·15		

all the cases is near 20 per cent which is the theoretical value for a polymer in which 50 per cent of the nitrile groups have been converted into thioamide groups. If the reaction is allowed to continue for four hours, the resulting polymer becomes rubbery and does not easily dissolve in acetone or DMF. Solubility of the modified-PAN is also greatly affected by the molecular weight of the starting polymer. Reaction conducted with a polymer having very high molecular weight ($[\eta] > 9$) resulted in a modified polymer with very poor solubility in acetone and DMF. An experiment conducted under identical conditions but taking dimethyl-sulphoxide (DMSO) as solvent for the polymer, resulted in partial introduction of thioamide groups and formation of sulphur.

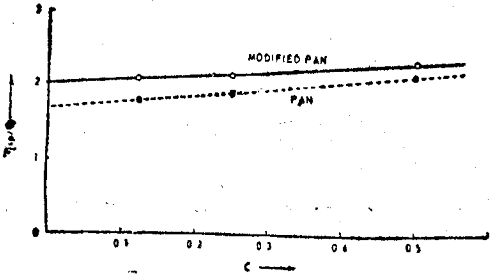


Fig. 1—$\eta sp/C$ *vs* C for PAN and modified-PAN in DMF.

Viscosity study : Intrinsic viscosity, $[\eta]$, of PAN and modified-PAN were measured in DMF in an Ostwald capillary viscometer at 35°C. Intrinsic viscosity, $[\eta]$ and Huggins' constant, k, were determined by plotting η_{sp}/C against C following the relation,

$$\eta_{sp}/C = [\eta] + k\,[\eta]^2\,C.$$

The results of viscosity study are shown in Fig. 1. The modified-PAN shows higher intrinsic viscosity in DMF than the parent polymer (Table 3). This is due to the replacement of the highly polar and small sized nitrile groups by the thioamide groups having comparatively bigger size and less polarity, from the polymer chain, resulting in the decrease in hydrogen bonding and hence increased solubility and expanded structure of the polymer molecules in the solvent. This is also confirmed by the small value of the Huggins' constant ($k = 0 \cdot 19$) of the modified polymer in DMF.

X-ray study : X-ray diffraction patterns of the unoriented powders of modified-PAN and PAN are shown in Fig. 2. The pictures were taken in a Debye Scherrer Powder camera 57·3 mm diameter. CuK_α radiation ($\lambda = 1 \cdot 54$ Å) was employed at 40 kV and 15 mA. The exposure time in both the cases was four hours.

PAN prepared by free radical polymerization normally show little evidence of crystallinity. The most prominent feature of the X-ray diagram of unoriented PAN is a fairly narrow ring ($d = 5 \cdot 2$ Å) as shown in Fig. 2a. The poor quality of the X-ray diffraction pattern is due to the atactic nature of the polymer and the irregular arrangement of the $-CN$ groups on the polymer chain. The diffraction picture for modified-PAN (Fig. 2b) showed the complete absence of the ring which clearly indicates that whatever order or crystallinity was there in the original PAN had been completely destroyed by the introduction of the bulky thioamide groups.

Infra-red study : The infra-red spectrum of the modified-PAN film is shown in Fig. 3. This spectrum was taken with a Perkin-Elmer Model 221 Spectrophotometer ($N_\alpha Cl$ prism) from a film cast from acetone solution of the polymer. The absorption bands in the spectra and their possible assignments are shown in Table 4. The assignments of the bands have been discussed in a separate note[5] on the subject. The sharp bands at 3390 cm^{-1} and 3280 cm^{-1} are due to the asymmetric and symmetric stretching of NH_2. The band at 2994 cm^{-1} is due to the asymmetric stretching of CH_2.

The band at 2273 cm^{-1} is due to the stretching of $C \equiv N$ group. In the spectrum of PAN[6], the band due to $C \equiv N$ stretching appears at 2237 cm^{-1}. The shift of the band towards higher frequency indicates the decrease in hydrogen bonding in the modified-PAN.

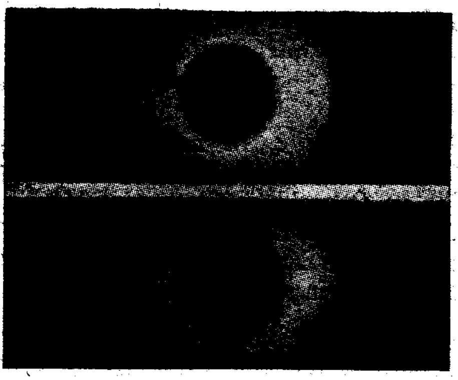


Fig. 2—X-ray diffraction pattern of PAN(a) and modified-PAN(b).

The most prominent band at 1667 cm^{-1} has been assigned as due to the bending of $-NH_2$ of the thioamide. The high intensity of this band as well as the bands at 3390 and 3380 cm^{-1} is probably associated with changes in dipole moment resulting from displacement of lone pair of electrons.

The sharp band at 1450 cm^{-1} is due to the bending of $-CH_2$ and is common in spectrum of PAN and modified-PAN. The sharp band of medium intensity at 1398 cm^{-1} may be due to the coupled modes[7] involving stretching of $C=S$ and $C-C-N$ groups and rocking of NH_2 groups. The band at 1100 cm^{-1} is probably due to $C=S$ stretching. It may have

TABLE 4

INFRA-RED SPECTRUM OF MODIFIED-PAN FILM CAST FROM ACETONE SOLUTION

Position of band cm⁻¹	Intensity	Assignments
3390	vs	(NH_2)-asymmetric stretching of NH_2
3280	vs	(NH_2)-symmetric stretching of NH_2
2994	s	(CH_2)-asymmetric stretching of CH_2
2273	vs	($C\equiv N$)-stretching of $C\equiv N$
1667	vs	(NH_2)-scissoring of NH_2
1450	vs	(CH_2)-bending of CH_2
1398	s	NH_2 rocking, $C=S$ stretching and $N—C—C$ stretching
1100	s	Stretching of $C=S$, NH_2 rocking and $N—C—C$ stretching
1060	m	Skeletal vibration ($C—C$) stretching

vs = very sharp ; s = sharp and m = medium

contributions from the stretching of $—C—C—N$ bonds. The position of this band agrees with the calculation of Spinner[8]. There has, however, been great indefiniteness regarding the assignment of $C=S$ stretching frequency in nitrogen containing compounds. Randall *et al*[9] observed a strong band in the region 1471-1613 cm⁻¹ in compounds where $N—C=S$ unit is present. Elmore[10] showed that this 'thiouride' band is due to the coupling of $C—N$ stretching vibration and NH deformation vibration. In thioamide system, coupling can take place among $C—N$ stretching, $C=S$ stretching and NH deformation vibration.

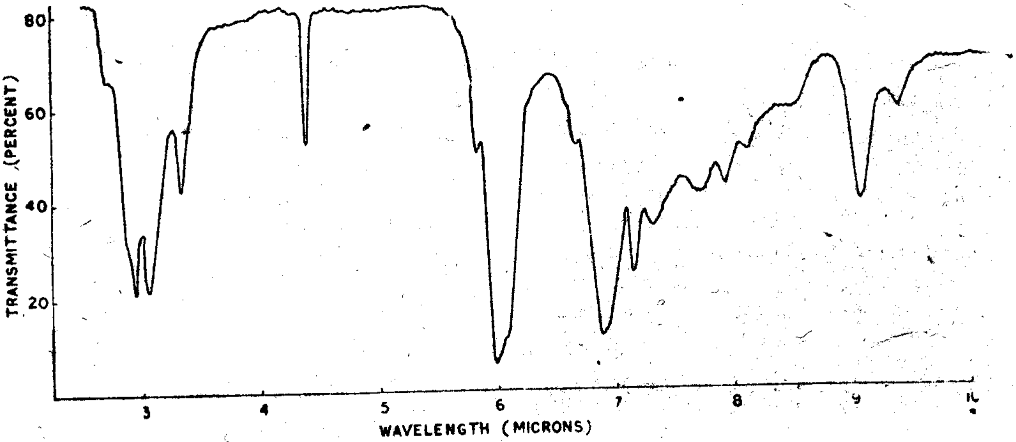
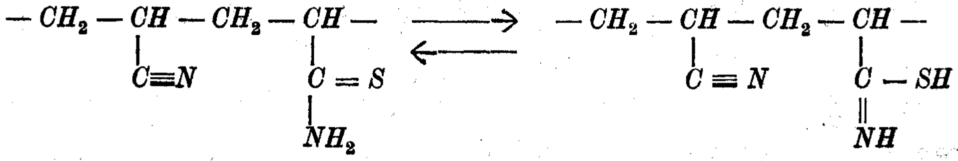


Fig. 3—I.R. spectra of modified-PAN

No band was found in the region 2600-2500 cm^{-1}, the range in which the $S—H$ stretching vibrations are most likely to appear. This clearly indicates the absence of thiol and thione tautomerism in the polymer in the solid state.



$$-CH_2-\underset{\substack{|\\ C\equiv N}}{CH}-CH_2-\underset{\substack{|\\ C=S\\ |\\ NH_2}}{CH}- \;\underset{\longleftarrow}{\longrightarrow}\; -CH_2-\underset{\substack{|\\ C\equiv N}}{CH}-CH_2-\underset{\substack{|\\ C-SH\\ \|\\ NH}}{CH}-$$

ACKNOWLEDGEMENT

The authors express their sincere thanks to Dr. Kartar Singh, Director, Defence Science Laboratory, for his interest in this work and valuable discussions.

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