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X–RAY DIFFRACTION AND CONDUCTIVITY MEASUREMENTS OF ACRYLONITRILE–ITACONIC ACID COPOLYMER

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ABSTRACT

Acrylic fibre manufacture requires a polymer with specific composition, controlled molecular weight and some dye sites. Thus, the polymerization process is an important step in the overall fibre manufacturing process. All acrylic fibres are made from acrylonitrile (90–95 %) combined with atleast one or two comonomers. Copolymerization of acrylonitrile with itaconic acid by aqueous suspension polymerization has been carried out. This produces dry polymer – free of solvent. Ammonium persulphate and sodium metabisulphite has been used as redox initiators. X–ray studies and conductance measurement of the product was also carried out.

Key Words: *Acrylonitrile, Itaconic acid, Copolymerization, Redox initiators*

INTRODUCTION

Among the comonomers used for the synthesis of acrylonitrile based copolymers vinyl acids such as acrylic acid[1], methacrylic acid[2], itaconic acid[2] and cinnamic acid[3] occupy an important position although copolymer solutions containing cinnamic acid are unstable. These comonomers not only improve the hygroscopic property of AN copolymer fibres but also aid in the cyclization of the –C=N groups during the manufacture of carbon fibres[4]. Polyacrylonitrile (PAN) fibres prepared by the copolymerization of AN with α–chloroacrylic acid display polyelectrolyte properties and good dyeability with basic dyes[5]. Similarly, modified PAN fibres (AN/MA/IA) containing 10 per cent natural silk surpass ordinary PAN fibres in dyeability and hygroscopicity[2].

Copolymerization of AN with various comonomers can be accomplished by different routes[6] including radical, solution, suspension and emulsion. Many groups[7] have employed suspension polymerization for the synthesis of AN copolymers. Effect of mixed solvent (DMF/H_2O) on the kinetics of copolymerization of acrylic acid and AN has also been studied[1]. Bajaj *et al.* have synthesized AN–vinyl acid copolymers by both solution[6,8] and suspension[7] polymerizations. Monomers such as acrylic acid, itaconic acid, methacrylic acid and

2–hydroxyalkyl methacrylates have been used by them. For aqueous suspension polymerization, three loci polymerization, has been reported by Peebles[9].

Since vinyl acids, when used as comonomers, influence important properties of acrylic fibres such as hygroscopicity, dye–uptake and thermal behaviour, hence, it was felt of interest to study the acrylonitrile/itaconic acid system. The present study describes copolymerization of acrylonitrile with itaconic acid by aqueous suspension polymerization. Ammonium persulphate and sodium metabisulphite have been used as redox initiators.

EXPERIMENTAL

Materials

Acrylonitrile (AN) Merck was freed from inhibitor by washing with 0.1 N sodium hydroxide solution and then with water until completely free from sodium hydroxide. The washed acrylonitrile was kept over fused calcium chloride overnight and then distilled under nitrogen atmosphere at 77°C before use. Itaconic acid (IA) Loba (m.p. 166–167°C) and the initiators i.e. ammonium persulphate (BDH) and sodium metabisulphite (BDH) were used as received.

Polymerization

Copolymerization of acrylonitrile with itaconic acid was carried out in a four neck reactor glass vessel using deionized water as reaction medium at 45°C under nitrogen atmosphere. The mole fraction of the comonomer in the reaction feed was varied from 1.0 to 3.6 % and the water to monomer ratio was kept as 10. Ammonium persulphate and sodium metabisulphite (0.0576 and 0.0557 mole % with respect to monomer feed) were used as redox initiators. The pH of the reaction medium was adjusted to 3.5 by adding dilute acetic acid. The monomer mixture was added slowly to the reaction mixture in 25–30 min and the polymerization was continued for 90 minutes (including the time required for the addition of the monomer mixture) with constant stirring. Reaction was quenched by the addition of ice–cold water. The polymer was isolated by filtration, washed successively with water and methanol and dried under vacuum at 75–80°C.

RESULTS AND DISCUSSION

X–Ray diffraction pattern of mixtures

All the X–ray diffractograms were recorded on a Rigaku Miniflex X–ray difractometer at 30 kV and 15 mA power. The wavelength used was 1.54 Å, corresponding to the Cu Ka line. The powder samples for X–ray studies were prepared by mounting about 500 mg of the powder on glass slides, gently pressing and then covering with transparent tape. Samples in the form of pellets were also positioned on glass slides and kept in position using transparent tape. The scan for all samples was made from 5° to 60° at room temperature. A scan speed of 2 degree/minute and a step size of 0.2^{0} was used. Instrument calibration was done using a standard silicon spectrum.

X–ray studies of pelletized samples of pure PAN and those of $(PAN)_{100-x}$ (Itaconic acid), were made. X–ray study of a powdered sample of pure PAN was also made. Table 1 give the d values obtained for the powder and pellet samples of PAN. This table also gives the d values for PAN as reported in JCPDS card (No. 48–2119). It can be seen that the d–values for our sample and that given in the JCPDS are very different. There is a strong reflection of 25 % relative intensity at d around 6 Å in both the powder sample as well as the pelletized one. Additional reflections are also observed for the powder sample at approximately 4.9 Å, 4.3 Å and 3.6 Å in our powder sample but are not observed for the pellet sample. These reflections have not been reported in the JCPDS card too.

On comparing the reflections of the powder and pellet samples, one can see that there is a shift in the most intense (100 %) relative intensity and other lines to lower d–values for the pellet sample as compared to the powder samples. This can be due to a decrease in the cell size due to application of pressure in the case of the pellet samples.

Table 1 : X–Ray diffraction 'd' values for pure PAN

Standard PAN	Powder	Pellet
	6.3656 (27)	
		5.9405 (25)
	5.4333 (100)	
	5.3041 (100)	
5.2727 (100)		
		5.0348 (100)
	4.9511 (13)	
	4.8438 (13)	
4.5483 (36)		4.5950 (28)
	4.2873 (7)	
3.8969 (43)		3.8969 (23)
3.7828 (48)		
	3.5588 (16)	
3.5036 (59)	3.5036 (16)	3.5036 (25)

Table 2 gives the d values for $(PAN)_{100-x}$ $(\text{Itaconic acid})_x$ series. New reflections ranging between d = 5.90 Å to 5.60 Å are seen for the samples containing itaconic acid, which are not present in either the pure powder or pellet samples. Other new reflections observed in the itaconic acid added samples are in the range : 4.81 Å to 4.59 Å. As X–ray is not very sensitive

Table 2. X–Ray diffraction 'd' values for PAN and itaconic acid mixture

Powder	Pellet	99.0+1.0	98.7+1.3	98.0+2.0	97.6+2.4	97.3+2.7	97.0+3.0	96.4+3.6
			6.4581 (24)	6.5053 (25)				6.4581 (25)
6.3656 (27)					6.3656 (24)	6.3656 (27)		
		6.3203 (25)				6.3203 (24)		
	5.9405 (25)							
				5.9012 (16)				5.9012 (15)
					5.8240 (15)	5.8623 (26)		
				5.7119 (25)		5.7119 (19)		
		5.6755 (22)		5.6755 (27)			5.6755 (22)	5.6735 (23)
		5.6041 (25)			5.6041 (22)			5.6041 (28)
		5.4333 (26)			5.4004 (25)			
5.3041 (100)		5.2727 (100)	5.3679 (100)	5.3679 (100)	5.3041 (100)	5.3041 (100)	5.3041 (100)	5.3679 (100)
	5.0348 (100)							
4.9511 (13)		4.8968 (19)	4.8968 (15)	4.9868 (17)	4.8702 (17)	4.9869 (17)		4.9511 (17)
						4.8438 (17)	4.8438 (16)	4.8438 (16)
			4.8177 (19)		4.7919 (16)	4.7919 (16)		
	4.5950 (28)							
	3.8969 (23)							
3.5588 (16)								
3.5036 (16)	3.5036 (25)			3.5036 (24)		3.5036 (25)		

to the sort of concentrations considered in this study, a systematic trend with respect to the concentration of itaconic acid could not be obtained. Also, as all the main reflections of the pure PAN sample are also present in all the samples containing itaconic acid with small variations in the actual d values. It can be concluded that introduction of itaconic acid to PAN in the concentrations considered does not change the basic structure, which is that of pure PAN. However, as the standard JCPDS card (No. 38–1509) for itaconic acid shows too many lines, no attempt has been made to look for any correlation with this standard card and the peaks obtained in the samples containing itaconic acid.

On comparing the X–ray diffractogram obtained for the pure PAN samples, both in the powder as well as pellet form, to the standard PAN reflections quoted in the JCPDS card (No. 48–2119) a good difference in the values was observed. The X–ray diffractograms obtained for the samples doped with itaconic acid show new reflections of fairly good intensity. All the diffractograms have also retained the reflections for pure PAN showing that incorporation of itaconic acid for the concentrations studied in this work have been accommodated within the basic pure PAN structure.

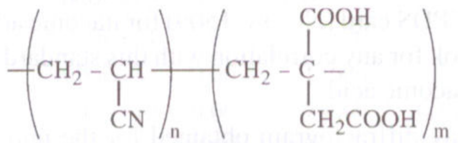
Conductance Measurements

The thermal conductivity of the pure sample of PAN and its mixture with itaconic acid was determined at different temperatures (30°C to 210°C) using conductivity set (Pashpa Scientific Instruments). Itaconic acid was mixed with PAN in the 1.3 %, 2.0 %, 2.4 % and 3.6 % proportion and pellets were prepared. The results are reported in the Table 3.

Table 3 : Conductivity of PAN and itaconic acid mixture

	Conductance (10^{-5} ohm^{-1}m^{-1})				
Samples	I	II	III	IV	V
PAN	100 %	98.7 %	98.0 %	97.6 %	96.4 %
Itaconic acid	0.0 %	1.3 %	2.0 %	2.4 %	3.6 %
Temperature (°C)					
30	0.087	0.118	0.119	0.120	0.265
50	0.109	0.137	0.178	0.219	0.309
70	0.131	0.148	0.209	0.239	0.331
90	0.152	0.158	0.238	0.259	0.353
110	0.174	0.179	0.230	0.280	0.376
130	0.189	0.199	0.268	0.319	0.398
150	0.199	0.199	0.268	0.400	0.487
170	0.205	0.219	0.273	0.410	0.578
190	0.272	0.253	0.350	0.629	0.729
210	0.302	0.313	0.468	0.753	0.995

It was observed that conductivity of pure PAN sample was quite low because of the absence of a suitable polar group, while it increases an addition of itaconic acid in different proportion and depends on the proportion of itaconic acid. This may be due to presence of polar –COOH group in itaconic acid. The probable structure of copolymer will be



$$\left(-CH_2-\underset{\displaystyle CN}{\underset{|}{CH}}- \right)_n \left(-CH_2-\overset{\displaystyle COOH}{\overset{|}{\underset{\displaystyle CH_2COOH}{\underset{|}{C}}}}- \right)_m$$

where n is much higher than m.

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REFERENCES

1. D. Cicenaite, O. Japubavskaite and G. Bajoras. Fiz. Khim. Osnovy Sinteza, **2**, 14 (1977).
2. R. Kh. Kaibusheva, Mater. Resp. Konf. Tekst. Khim., **3**, 64 (1974).
3. N. Asandei, M. Nicu, M. Rusu and M. Lungu, Chem. Abstr., **94**, 16142 (1981).
4. P. Bajaj, A. K. Gupta and D. K. Paliwal. J. Macromol. Sci. Rev., **C31(1)**, 1 (1991).
5. M. A. Askarov, A. J. Dzhalilov, A. Mamov, K. M. Muminov and M. K. Magropova. Chem. Abstr., **87(12)**, 862397 (1977).
6. P. Bajaj and M. Padmanaban. J. Polym. Sci. Polym. Chem. Ed., **26**, 2261 (1983).
7. P. Bajaj, D. K. Paliwal and A. K. Gupta. J. Appl. Polym. Sci., **49**, 823 (1993).
8. P. Bajaj, P. C. Jain and D. Gangopadhyay. J. Polym. Sci. Polym. Chem. Ed., **17**, 595 (1979).
9. L. H. Peebles, in Copolymerization, G.E. Ham, Ed., Wiley, New York, (1964). pp. 564-573.

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