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Effect of Furfuraldehyde on the Polymerization of Acrylonitrile Initiated by Benzoyl Peroxide

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Abstract: PAN (polyacrylonitrile) is a synthetic, semicrystalline organic polymer resin, with the linear formula $(C_3H_3N)_n$. PAN is one of the versatile polymers that is widely used for making membranes due to its good solvent resistance property. It has been used as a substrate for NF (nanofiltration) and RO (reverse osmosis). The thermosetting characteristic offered by PAN makes it suitable as a carbon membrane precursor. It usually does not liquefy or soften during any stage of pyrolysis and preserves its morphology upon the pyrolysis. In the present study, effect of Furfuraldehyde on the polymerization of acrylonitrile initiated by benzoyl peroxide has been studied. The different techniques like, FT-IR and UV-VIS were used for characterization. The UV-VIS study showed that the rate of polymerization of acrylonitrile decreases with increase in the concentration of furfuraldehyde. The FT-IR study proves the successful interaction of polyacrylonitrile with Furfuraldehyde.

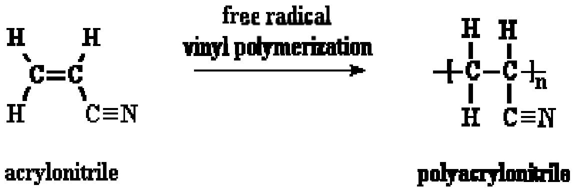
Key words: Polyacrylonitrile**,** furfuraldehyde**,** FT-IR, UV-VIS**.**

1. Introduction

1.1 Polyacrylonitrile

PAN (polyacrylonitrile), is a synthetic, semi crystalline organic polymer resin, with the linear formula $(C_3H_3N)_n$. Though it is thermoplastic, it does not melt under normal conditions. It degrades before melting. It melts above 300 °C if the heating rates are 50 degrees per minute or above [1].

Polyacrylonitrile is a vinyl polymer, and a derivative of the acrylate family of polymers. It is made from the monomer acrylonitrile by free radical vinyl polymerization

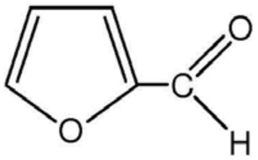


Polyacrylonitrile is the precursor for carbon fiber for high strength applications ranging from aircraft parts to sporting equipments. PAN based carbon fiber is still a low volume specialty material due to its relatively high cost of produce [2].

1.2 Furfuraldehyde

Furfuraldhye is an organic compound derived from a variety of agricultural byproducts, including corncobs, oat, wheat bran, and sawdust. The name furfural comes from the Latin word furfur, meaning bran, referring to its usual source.

Furfural is a heterocycles aldehyde, with the ring structure [3-4].



2. Material and Methods

2.1 Chemicals

Acrylonitrite, benzoyl peroxide and furfuraldehyde were procured from Sisco Chemicals Pvt. Limited Mumbai. Common organic solvents of AR Grade were of Qualigens or E-Merk make, solvents such as benzne,

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toluene, butanol, carbon tetrachloride, acetone, DMF, DMSO, calcium chloride etc. were used as such and were kept in cool and dry place [5].

2.2 Purification of Monomer

Purification of acylonitrile—Acrylonitrile was purified by shaken with 10% NaOH to extract inhibitor and then washed in turn with 10% H_2SO_4, 20% Na_2CO_3 and distilled water, dried for 24 h over $CaCl_2$. Acrylonitirile is distilled off as required [6].

2.3 Synthesis

(a) Synthesis of PAN

The synthesis involves the placing of 5 mL of AN into 0.047 g (0.7%) of benzoyl peroxide (BPO), used as a initiator. The product was then heated in a closed flask (to avoid liquid evaporation) at 60 °C for 2 h to polymerize the AN, followed by a drying treatment at 110 °C. The final products were finely grinded using a knife of stainless steel [7].

(b) Synthesis of PAN in presence of furfuraldehyde

The synthesis of PAN (polyacrylonitrile) in presence of furfuraldehyde was undertaken, which involve the placing of 5 mL of PAN into 0.047 g (0.7%) of BPO (benzoyl peroxide), used as an initiator. The product was then heated in a closed flask (to avoid liquid evaporation) by adding different ratios of furfuraldehyde (0.5%, 1.0%, 1.5%) at 60 °C for 5.30 h to polymerize the AN, followed by drying treatment at 110 °C. The final product was finely grinded using a knife of stainless steel.

2.4 Experimental Techniques

Physical measurements

2.4.1 Solubility and chemical resistance

The polyacrylonitrile were immersed in various organic and inorganic solvents for 24 h for checking solubility and chemical resistance. Results were noted and presented in chapter four (Table 5).

2.4.2 Softening range

The synthesized polymers have softening range 110-140.

2.5 Characterization

The polyacrylonitrile with furfuraldehyde samples were characterized using UV, FTIR Spectroscopy.

2. 5.1 Ultra-violet spectra

The UV spectra of PAN with furfuraldehyde were recorded on a Shimadzu-1800, Double Beam UV-visible spectrophotometer in Department of Chemistry, Institute of Basic Science, Dr. B. R. Ambedkar University, Agra.

2.5.2 FTIR (fourier transforme infrared) spectra

The FTIR spectra of the newly synthesized compounds were recorded on a PerkinElmer RXI Spectrophotometer in Department of Chemistry, Institute of Basic Science, Dr. B. R. Ambedkar University, Agra, within the range of 500-4,000 (m^{-1}) using resolution of 4 cm^{-1}, an average of 16 Scan has been reported for each sample.

3. Observation

3.1 Experimental Conditions

(A) Polymer formation condition—I

(a) Time: 2 h

(b) Temperature: 60 °C

At constant temperature of 60 °C, 5 mL of acrylonitrile was added with increasing concentration for furfuraldehyde, the maximum yield of product was found when concentration of furfuraldehyde was 1.00 mL.

(B) Polymer formation condition—II

(a) Time: 2 h

(b) Variable Temperature: 50-60 °C

At different temperatures, a fix amount of acrylonitrile was added to a fix amount of furfuraldehyde, the maximum yield of the product was found at 60 °C.

(C) Polymer formation condition:—III

(a) Variable time: 5.00-6.00 hour

(b) Temperature: 60 °C

At different time of fix amount of acrylonitrile was added to a fix amount of furfurdldehyde, the maximum yield of the product was found at 5.30 hour.

(D) Polymer condition:—IV

(a) Time: 2 h

(b) Temperature: 60 °C

(c) Different amount of initiator

At different amount of initiator fix amount of acrylonitrile was added to a fix amount of furfurdldehyde, the maximum yield of the product was found at 57 mg.

3.2 Characterization

(i) Physical Characterization

(ii) Chemical Characterization

4. Results and Discussion

Physical Measurements

Appearance—The physical appearance of newly synthesized polymers is different, and the appearance of the polymers depends upon the constituents of monomers and also on initiator.

Solubility—The solubility of the prepared compound was checked at two temperatures i.e. 25 °C and 60 °C in various solvents, like water, carbon tetra chloride, DMSO, DMF, acetone, butanol and toluene, of which the prepared compound was soluble in DMSO

Table 1 Effect of furfuraldehyde concentration in the preparation of polyacrylonitrile initiated by BPO.

yield (gram)	Temperature °C	initiator BPO (mg)	Furfuraldehyde (mL)	Monomer Acrylonitrile (mL)	Sr. No.
0.054	60	47	0.50	5	1
0.67	60	47	1.00	5	2
0.055	60	47	1.50	5	3

Table 2 Effect of temperature in the preparation of polyacrylonitrile initiated by BPO.

yield (gram)	Temperature °C	initiator BPO (mg)	Furfuraldehyde (mL)	Monomer Acrylonitrile (mL)	Sr. No.
0.013	50	47	0.50	5	1
0.022	55	47	0.50	5	2
0.054	60	47	0.50	5	3

Table 3 Effect of time in the preparation of polyacrylonitirle initiated by BPO.

yield (gram)	time	Temperature °C	initiator BPO (mg)	Furfuraldehyde (mL)	Monomer Acrylonitrile (mL)	Sr. No.
0.029	5.00	60	47	0.50	5	1
0.041	5.30	60	47	0.50	5	2
0.014	6.00	60	47	0.50	5	3

Table 4 Effect of initiator in the preparation of polyacrylonitrile initiated by BPO.

yield (gram)	Temperature °C	initiator BPO (mg)	Furfuraldehyde (mL)	Monomer Acrylonitrile (mL)	Sr. No.
0.049	60	37	0.50	5	1
0.054	60	47	0.50	5	2
0.055	60	57	0.50	5	3

Table 5 Solubility of polyacrylonitrile with furfuraldehyde initiated by BPO.

At 60°C	At 25 °C	Solvents	Sr. No.
IS	IS	H_2O	1
IS	IS	Acetone	2
PS	PS	Butanol	3
S	PS	DMF	4
S	S	DMSO	5
IS	IS	Toluene	6
IS	IS	CCl_4	7

Table 6 Important IR intensity peak of polyacrylonitrile.

Peak (cm^{-1})	Mode of vibration	Group	Sr. No.
2,924.74	Stretching	= C – H	1
2,243.41	Stretching	C ≡ N	2
1,633.76	Bending	C = C (Conjunction)	3
1,226.69	Bending	C – C	4

Table 7 Reported IR intensity peaks of polyacrylonitrile.

Peak (cm^{-1})	Mode of vibration	Group	Sr. No.
2,950	Stretching	= C – H	1
2,237	Stretching	C ≡ N	2
1,650	Bending	C = C (Conjunction)	3
1,247	Bending	C – C	4

Table 8 Important IR intensity peaks of polyacrylonitrile with furfuraldehyde.

Peak (cm^{-1})	Mode of vibration	Group	Sr. No.
2,925.21	Stretching	= C – H	1
2,249.20	Stretching	C ≡ N	2
1,637.23	Bending	C = C (Conjunction)	3
1,256.42	Bending	C – C	4
1,599.52	Breathing vibrations	Furan ring	5

Table 9 Important U. V. wave length of polyacrylonitrile in DMSO.

Abs (ε)	A max	S. No.
0.050	367.00	1
0.240	302.00	2
0.567	269.00	3

Table 10 Reported U. V. wave lengths of polyacrylonitrile in DMSO.

Abs (ε)	A max	S. No.
1.065	367.00	1
1.092	362.00	2
1.154	353.00	3

and partially soluble in butanol and insoluble in rest (Table 5).

Softening range—The temperature in which material without a melting point goes from rigid to soft. The temperature of softening ranges varies for the prepared compound. It does not melt but decomposes directly above 300 °C.

Structural elucidation—For confirming the structure of prepared polymers, two spectroscopic techniques have been used:

(A) UV-spectra

(B) IR-spectra

(A) UV (Ultra-violet) spectral studies:

UV absorption spectra are attributed to a process in which the outer electrons of atom absorb radient energy and under transition to higher energy level [8]. The electronic transitions are quantized and depend on the electronic structure of the molecules [9].

The wave length, at which an UV absorbance maximum is found, depends upon the magnitude of energy involved for a specific electronic transition [10].

The transition of closely spaced vibrational and rotational level is also superimposed on electronic transition. Solid and liquid transition are even influenced by the presence of neighboring molecule and therefore the UV spectra consists of one or more broad peaks, the wavelength region between 200-400 nm [11].

(a) Effect of furfuraldehyde concentration in the preparation of poly acrylonitrile initiated by BPO.

(b) Effect of temperature in the preparation of poly acrylonitrile initiated by BPO.

(c) Effect of time in the preparation of poly acrylonitrile initiated by BPO.

(d) Effect of initiator in the preparation of poly acrylonitrile initiated by BPO.

(1) Effect of furfuraldehyde concentration in the preparation of poly acrylonitrile initiated by BPO

The effect of furfuraldehyde on the polymerization of acrylonitrile with benzoyl peroxide as a initiator was studied. We get the best yield of poly acrylonitrile with 1 mL of furfuraldehyde. It indicates that 1 mL of furfuraldehyde is sufficient amount for preparing the polymer (Table 1). With further addition of furfuraldehyde, the yield of polymer decreases due to the formation of a weak complex between the monomer and furfuraldehyde. UV spectra studies showed that when 1 mL of acrylonitrile was added to the 1 mL of furfuraldehyde then wave length increases because the rate of polymerization increases, with more addition of furfuraldehyde wave length was decreased because the rate of polymerization decreases but on further increasing furfuraldehyde concentration, the polymer was decomposed for which wave length is decreased so it proves that furfuraldehyde is working as a retarder for acrylic monomers (Table 10).

(2) Effect of temperature in the preparation of poly acrylonitrile initiated by BPO

The effect of temperature on the polymerization of acrylonitrile with benzoyl peroxide as an initiator was studied. At 50 °C, the collisions between the acrylonitrile and furfuraldehyde were less so we got the lesser yield but on increasing the temperature to 55 °C polymerization increase and on further increasing the temperature, increasing the yield of the polymer is highest (Table 2). It is clear from the UV spectra studies that 60 °C is the optimum temperature for the polymerization (Table 9-10).

(3) Effect of time in the preparation of poly acrylonitrile initiated by BPO

The effect of time on the polymerization of acrylonitrile with benzoyl peroxide as an initiator was studied. At different time, a fixed amount of AN was added to a fixed amount of furfuraldehyde, the maximum yield of the product was found at 5:30 on increasing the time rate of reaction increasing and absorbance increases. UV spectra studies showed that on increasing the time, polymerization between the acrylonitrile and furfuraldehyde increases (Table 3, Table 9-10).

(4) Effect of initiator in the preparation of poly acrylonitrile initiated by BPO

The effect of initiator on the polymerization of acrylonitrile with benzoyl peroxide as a initiator was studied. At different amount of initiator, a fixed amount of AN was added to a fixed amount of furfuraldehyde, the maximum yield of the product was found with 57 mg (Table 4). UV spectra studies showed that on increasing the amount of initiator the rate of reaction increases may be the complex formation between the reactant molecules due to which absorbance increases (Table 9).

(B) FT-IR (fourier transform infrared) spectral studies:

Infrared spectroscopy provides the ability to study the interactions of the vibrational and rotational energies of atoms or groups of atoms within molecules. Infrared spectra reflect vibrational motions that provide a change in the permanent dipole moment of the molecule. It is a powerful quantitative tool. Utilization of lasers as light sources has decreased experimental difficulty in this techniques and the method has now become one of the standard tools for the polymer analysis [12-15].

IR—spectral studies of polymers at different conditions:

(1) Polymer of polyacrylonitrile initiated by BPO:

acrylonitrile which was initiated by benzoyl peroxide. It is more particularly concern with the polymerization of acrylonitrile by the effect of furfuraldehyde concentration. It is an object of the study to prove that furfuraldehyde works as retarder.

The FT-IR spectra of acrylonitrile monomer shows that the characteristic absorption bands of polyacrylonitrile are similar to those prepared by traditional methods [16-19]. The IR spectra of polymer film exhibited a peak at 2,924.74 cm^{-1} (2,950 cm^{-1}) may be due to = C-H polyacrylonitrile, peak at 2,243.41 cm^{-1} (2,237 cm^{-1}) may be due to C = N group of polyacrylonitrile, peak at 1633.76 cm^{-1} (1,650 cm^{-1}) may be due to conjugation of C = C group of polyacrylonitrile. The stretching vibration at 1,226.69 cm^{-1} (1,247 cm^{-1}) may be due to C-C of polyacrylonitrile (Table 6-7).

(2) Polymer of polyacrylonitrile with furfuraldehyde initiated by BPO:

FT-IR spectra of acrylonitrile monomer with furfuraldehyde shows that the characteristics absorption bands of polyacrylonitrile are similar to those prepared by traditional method [20-21]. The IR spectra of polymer exhibited a peak at 2925.27 cm^{-1} may be due to = CH-H polyacrylonitrile, peak at 2243.50 cm^{-1} present may be due to C = N of polyacrylonitrile, appearance of peak at 1226.83 cm^{-1} may be due to C-C group of furfuraldehyde, appearance of peak at 1,599 cm^{-1} may be due to furan ring (Table 8).

5. Conclusions

In this study, the effect of furfuraldehyde on the polymerization of acrylonitrile initiated by benzoyl peroxide showed that the rate of polymerization of acrylonotrile decrease with increase in the concentation of furfuraldehyde, so furfuraldehyde acts as a possible retarder.

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