Synthesis And Characterization of Polyacrlonitrile Copolymers

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Abstract

Polyacrylonitrile (PAN) and copolymers of PAN with monomers like MMA, BA, VA, AM, AA, and S of varying compositions and molecular weights were prepared by emulsion polymerization in a continuous aqueous phase in the presence of sodium lauryl sulfate as emulsifier and potassium persulfate/ammonium persulfate as initiator. The molecular weights were determined from the dilute solution viscosity using Mark-Houwink equation. The chemical compositions of copolymers were characterized by FT-IR spectroscopy.

Keywords: Polyacrylonitrile (PAN), Polymer, Emulsion polymerization, FT-IR

Introduction

Polyacrylonitrile (PAN) is an important precursor for high value carbon based materials, such as highly chemical and mechanical resistant carbon composites [1] and mesoporous carbons used in photoelectronic devices [2-4]. Two of the important requirements for an ideal PAN precursor are that it must posses' high molecular weight and well controlled chemical structure [5-6]. High performing PAN precursors for carbon composites were successfully synthesized by Atom Transfer Radical Polymerization (ATRP) [7], by γ-irradiation [8], by Miniemulsions Polymerization [9], by metal catalyzed Living Radical Polymerization [10], RAFT Polymerization [11], by Inverted Emulsion Polymerization [12], by Dispersion/Emulsion Polymerization [13], and by Electron Transfer ATRP method [14]. Commercially available high molecular weight PAN ($Mv < 106$) is normally prepared by conventional free radical polymerization method. In classical emulsion polymerization method, the monomer is insoluble, or partially soluble, in the polymerization medium, but is emulsified by the addition of a surfactant (usually an emulsifier) [15]. The initiator is soluble in the medium but not in the monomer. Under these conditions the monomer is present in the mixture partly in the form of droplets and partly dissolved in the surfactant's micelles, while a small portion is molecularly dissolved in the medium [16]. The initiation point for the polymerization process is in the medium, where the initiator is present. The oligoradicals formed in the medium can be absorbed by the monomer' containing micelles and subsequently, by absorbing more oligoradicals and monomer molecules from the medium, the main point of polymerization changes from medium to the micelles interior. In this way, the primary particles grow gradually until the monomer is consumed or the radicals are disappear [17-21].

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In characterization of polymer, the intrinsic viscosity [□□ remains among the most significant molecular hydrodynamic characteristics of polymer. A relatively simple and descriptive viscometric method is widely used for the molecular physics and rheology of polymer and also for the study of polymer solutions in terms of technology of macromolecular compounds [24-25].

Experimental

Materials

N, N-dimethylformamide (DMF) (Fluka) was used as received. Acrylonitrile (AN), Methyl methacrylate (MMA), Acrylamide (AM), Acrylic acid (AA), Butyl Acrylate (BA), Vinyl acetate (VA), Styrene (S), were obtained from local polymer industry which were freed from inhibitors (monomethyl ether hydroquinone) and impurities by passing through an activated alumina column. The purified monomers were refrigerated and stored in a sealed container to avoid monomer's degradation or premature polymerization. The emulsifier Sodium dodecyl sulfate (SDS) or sodium lauryl sulfate (SLS) (Merck) and free radical initiators, Potassium persulfate (KPS) (Merck) and ammonium persulfate (APS) (Merck) were used as received.

Polymer Synthesis

Reaction scheme for the polymerization of acrylonitrile and vinyl monomers is shown as:
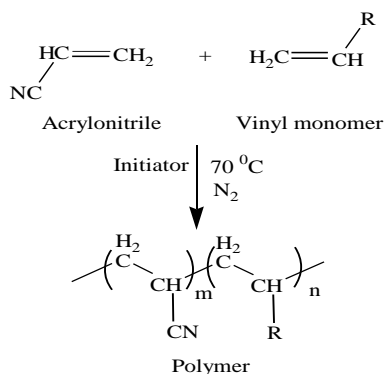
Emulsion polymerization was carried out in a five necked round bottom reaction flask (1000 ml),

fitted with a thermocouple, a condenser, a mechanical stirrer, and a thermometer. A quick fit pressure equalizing funnel was used in the fourth neck for drop wise feeding of initiator's solution.

The homo and copolymerization of acrylonitrile (AN) was carried-out using SLS as an emulsifier and KPS or APS as initiators as described in Table-1. In a typical emulsion polymerization, the reaction started with initial heating of distilled, deionized water in the reaction flask to 40 °C with stirring rate of 150 rpm, while purging with N2 for 20 min. After acquiring the temperature of 40 oC, the emulsifier was added. After 30 min. by rising temperature up to 50 oC, the purified monomers were added to the reaction flask. The solution was then heated to 70 °C in the vessel. The initiator was dissolved in 10 ml of water. The initiator solution was then added drop wise by using quick fit pressure equalizing funnel to reaction flask containing micelles to begin the polymerization. Various amounts of acrylonitrile and vinyl monomers were used to vary the charging ratios in a systematic manner as shown in Table-1.

The polymer was precipitated by using an excess of brine solution (non solvent) in a beaker. After 1h the mixture of polymer in brine solution was filtered, the resulting polymer cake was subjected to excessive washing with brine solution, twice at 40 oC by vigorous stirring for 2h in order to remove water soluble emulsifier and initiator from polymer cake followed by strong washing with distilled water. The polymer cake was further washed twice with methanol to remove organic traces like unreacted monomers and organic initiators. At this stage the polymer became odorless. The drying of the polymer cake was performed in a vacuum oven at an elevated temperature (up to 100 °C) for 8h. The polymer was removed from the oven and placed in a dessicator for characterization.

Characterization

The viscosity is proportional to the ratio of the time for the polymer solution to the time for the pure solvent, so extreme care was done in

measuring the flow time. The viscometer was scrupulously cleaned firstly with cleaning solution (dichromate acid, according to ASTM D445) followed by a thorough rinsing with distilled water and acetone, than dried by aspirating air through it. Ubbelohde viscometer was suspended in the thermo stated bath at 35 oC so that the upper ficidual mark was below the bath surface. An appropriate amount of the solution was pipetted into the viscometer (the amounts pipetted were the same in all experiments). The solution was drawn above the upper ficidual mark using pipette pump and the flow time of the solution meniscus between the upper and lower ficidual mark was determined (within +/- 0.01 sec. accuracy). This procedure was repeated three times for each solution concentration (0.2 g/dl, 0.4 g/dl, 0.6 g/dl, 0.8 g/dl, and 1 g/dl).

Sr #	Monomers	Comonomer	Emulsifier	Initiator	Temp. °C	Reaction time	Percentage
1	AN (23ml)	None	SDS (6g)	KPS (1g)	70	5h	AN (100)
2	AN (23ml)	MMA (1.15ml)	SDS (6g)	KPS (1g)	70	10h	AN/MMA (95:5)
3	AN (23ml)	AA (1.15ml)	SDS (6g)	KPS (1g)	70	10h	AN/AA (95:5)
4	AN (23ml)	BA (1.15ml)	SDS (6g)	KPS (1g)	70	10h	AN/BA (95:5)
5	AN (23ml)	S (1.15ml)	SDS (6g)	KPS (1g)	70	10h	AN/St (95:5)
6	AN(23ml)	VA (1.15ml)	SDS (6g)	KPS (1g)	70	10h	AN/VA (95:5)
7	AN(23ml)	AM (1.15ml)	SDS (6g)	KPS (1g)	70	10h	AN/Am (95:5)
8	AN(23ml)	MMA (0.92ml)	SDS (1g)	APS (0.1g)	50	04h	AN/MMA(96:4)
9	AN(96.1ml)	MAA (3.2g) – AM (0.7g).	SDS (1g)	APS (0.1g)	50	03h	AN/MAA/AM (96.1:3.2:0.7)

Table 1: PAN and PAN comonomer composition and experimental conditions.

Sample (%)	$[\eta]$	M_v	%yield
PAN (100)	1.3	75403.69	94.5
P(AN-co-MMA; 95:5)	1.1	60179.67	62.1
P(AN-co-BA; 95:5)	0.7	32692.77	62.1
P(AN-co-VA; 95:5)	0.7	32692.77	59.4
P(AN-co-AM; 95:5)	0.8	39150.87	52.1
P(AN-co-AM-co-MAA; 96.1:3.2:0.7)	2.1	144067.50	90.2
P(AN-co-AA; 95:5)	0.2	6025.04	81.98
P(AN-co-S; 95:5)	1.3	10415.58	37.2
P(AN-co-MMA; 96:4)	1.3	75403.85	72.4

Table 2: PAN Comonomer composition, intrinsic viscosity, molecular weight and percentage yield. Intrinsic viscosity was determined in DMF at 35 ^{O}C using K =31.7×10^5 and a=0.74.

Intrinsic viscosity [η] was measured by plotting ηsp/C versus C and extrapolating to C = 0, where C is concentration. Specific viscosity (ηsp) is determined from equation (1)

$$\eta_{sp} = (t - t_o)/t_o = (\eta - \eta_o)/\eta_o \qquad (1)$$

where t and t_o are the efflux time of solution and solvent respectively whereas η and ηo are the viscosity of the solution and solvent respectively.

Intrinsic viscosity [η] is also determined from plotting ηinh versus C and extrapolating to C = 0.

Inherent viscosity (ηinh) is determined by equation (2). The graphs of ηred versus C and ηinh versus C are shown in Figure 1.

$$\eta_{inh} = (1/C)\ln(\eta/\eta_o) \qquad (2)$$

Intrinsic viscosity [□] of PAN in DMF solutions was determined from the intercept of both □inh and □red versus concentration (C) [26]. An Ubbelohde viscometer (Cannon, C450) was used for the viscosity study. Kuhn-Mark-Houwink-Sakurada relationship (equation 3) was used for the determination of molecular weight of the polymer [23, 27-29].

$$\eta_{inh} = K M^{\alpha} \qquad (3)$$

where a and K are the parameters tabulated for a variety of systems polymer-solvent (Table 2) [27]. There were a number of extrapolation procedures allowing estimation of [η] for neutral macromolecules [22, 25, 28]. The molecular weight was calculated using equation 4.

$$M_v = (\eta inh/K)^{1/\alpha} \qquad (4)$$

The chemical structures of homo and copolymers of AN were characterized by FTIR spectroscopy. Infrared spectra of samples were recorded in KBr pellete using Perkin Elmer, A-100 FTIR spectrophotometer. The spectrometer range was 500 – 4000 cm-1 and 16 scans were used for recording each spectrum. Each sample was prepared thrice at the same conditions.

Results and Discussion

Table 2 shows the viscosity average molecular weight and percentage yield of various copolymers synthesized in this emulsion polymerization study. We have achieved a maximum yield of 94.5 % for P(AN; 100) and 90.2 % for the P(AN-co-AM-co-MAA; 96.1:3.2:0.7) copolymers. Table-2 also shows that In copolymerization 95% concentration of AN was used with different monomers (MMA, BA, VA, AM, AA, S) and best monomer was found to be MMA, than concentration of AN was increased to 96% with MMA and found that molecular weight of copolymer of AN with MMA is proportional to the concentration of AN, while the highest molecular weight, Mv = 144068 was found for the P(AN-co-AM-co-MAA; 96.1:3.2:0.7) copolymer and Mv = 75403.85 for the P(AN-co-MMA; 96:4) copolymer followed by Mv = 75403.69, for the P(AN; 100) homo-polymer. As commercially available PAN precursor for carbon fiber have molecular weight about 150000 [33], we have achieved Mv = 144068 for the P(AN-co-AM-co-MAA; 96.1:3.2:0.7) copolymer.

The representative FTIR spectra of homo PAN and copolymer have many similar characteristics. The FTIR spectrum of PAN shows a broad band in the region 3505 cm-1, due to –NH (amide) formed by partial hydrolysis of PAN. A peak around 2931 cm-1 is due to CH2 group and a peak at 2272 cm-1 is due to $-C\equiv N$ group of acrylonitrile. The peak in the region 1439 cm-1 can be attributed to aliphatic –CH bending [30-31]. The FT-IR spectra of the PAN copolymers with different compositions have been analyzed by monitoring the relative intensities of the peaks in the range of 4000-500 cm-1. The spectra of copolymers are similar to the spectrum of homopolymer except with small intensity peaks of comonomer's functionalities. Almost all the main vibration bands of PAN are overlapped with the
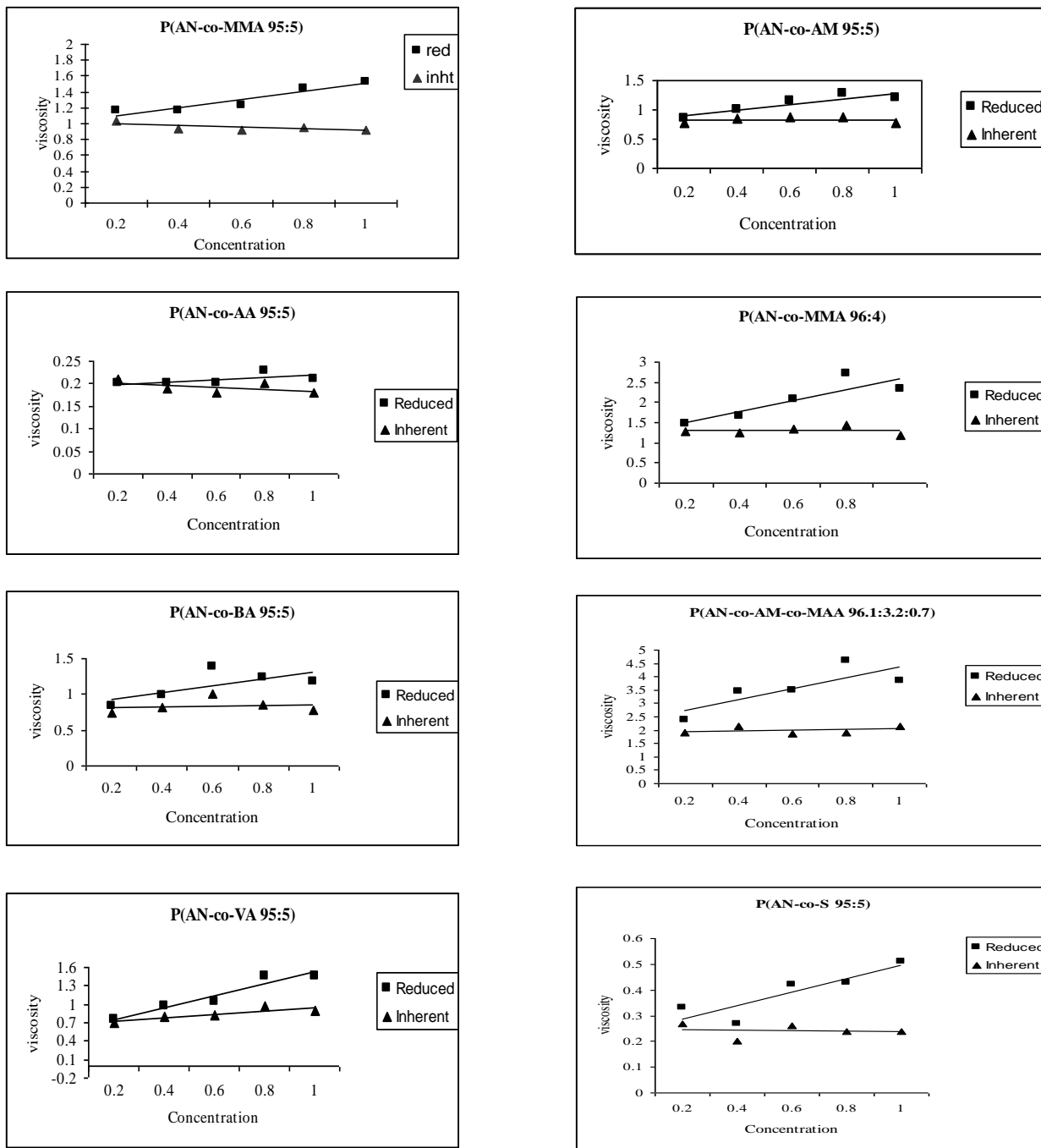
Figure 1:   Plot of viscosity (reduced ■, inherent ▲) versus concentrations of homo and copolymers of PAN.
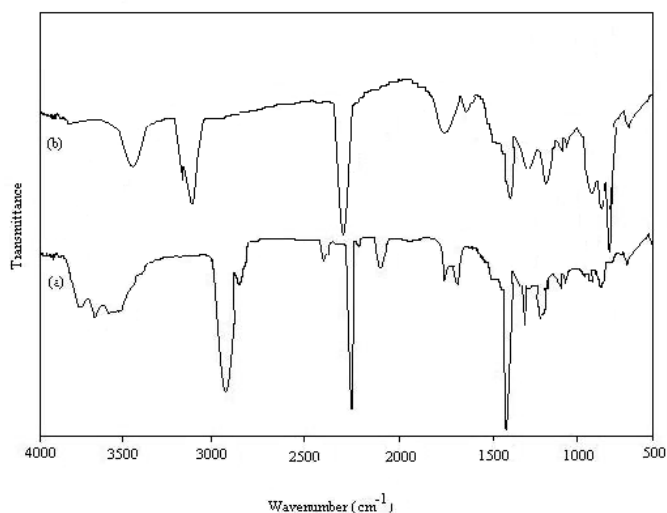
Figure 2: FTIR spectra of PAN (a) and PAN
copolymer P(AN-co-MMA, 96:4) (b)

bands of comonomers, except for $-C\equiv N$ group (2272). As the acrylonitrile content in copolymer is very high, the intensity of band at 2272 cm-1 due to $-C\equiv N$ group of acrylonitrile remains highest. The bands in the regions of 2865-2930 cm-1 were assigned to C-H stretching in CH, CH2, and CH3. The band at 1439-1497 cm-1, 1389 cm-1 and 1255 cm-1 are due to the C-H vibrations of different modes. The band in the region 1677 cm-1 may be attributed to the hydrolysis of acrylonitrile unit during the polymerization process. The prominent band in the region of 1631 cm-1 in the spectra of P(AN-co-MMA; 96:4), P(AN-co-MMA; 95:5), P(AN-co-BA; 95:5), P(AN-co-AA; 95:5) and P(AN-co-AM-co-MAA; 96.1:3.2:0.7) was due to C=O stretching. The relative intensity of other bands of copolymers is too small to be interpreted. The FTIR spectra also reveal that most of the nitrile unit of acrylonitrile is hydrolyzed during polymerization reaction in these experimental conditions [32].

Conclusion

The synthesis of homo and copolymers of PAN via emulsion polymerization was successfully achieved with a maximum yield of 94.5 %, 90.2 % for polyacrylonitrile (100) and P(AN-co-AM-co-MAA, 96.1:3.2:0.7) respectively. The highest molecular weight, Mv = 144068, was found for the copolymer P(AN-co-AM-co-MAA, 96.1:3.2:0.7) followed by Mv = 75403.85 for P(AN-MMA, 96:4) and Mv = 75403.69 for PAN (100). MMA was found to be the best monomer for copolymerization of AN. As commercially available PAN precursor for carbon fiber have molecular weight about 150000 and we have achieved 144068 MW for P(AN-co-AM-co-MAA, 96.1:3.2:0.7), this sample of PAN can be a very suitable precursor for carbon fiber. The optimum conditions for this reaction were 3h reaction time with 4.18 % emulsifier and 0.41 % initiator at 50 oC for this sample.

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