Facile synthesis of stereoregular carbon fiber precursor polymers by template assisted solid phase polymerization

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Abstract. Predominantly isotactic stereoregular polyacrylonitrile copolymers (PAC) were prepared by solid phase polymerization techniques using hexagonal crystalline metal salts as template compounds. Stereoregular distributions of the prepared polymer were studied using high resolution ¹³C nuclear magnetic resonance spectroscopy (¹³C NMR) spectra. The extent of isotacticity was directly determined from the peak intensity of the methine carbon (CH). The triad tacticity from the intensities of methine carbon peaks were examined by statistical methods. It was found that the PAC was predominantly isotactic in stereoregularity, and its sequence distribution obeys Bernoulli statistics. The optimum polymerization conditions ensuring isotactic content over 50% were disclosed experimentally. The chemical composition of PAC was confirmed with ¹H NMR data. The obtained polyacrylonitrile copolymers were also characterized for molecular parameters such as viscosity average molecular weight (M_v), number average molecular weight (M_n), weight average molecular weight (M_w) and polydispersity index.

Keywords: polymer synthesis, polyacrylonitrile copolymer, NMR, stereoregularity, molecular weight distribution

1. Introduction

Carbon fibers generally have excellent mechanical properties such as high specific strength, specific modulus and are therefore widely used as strength modifiers for various reinforcing materials in aerospace applications, leisure goods, industrial materials and the like. Because of their superior mechanical properties, they have potential application for reducing automobile weight and are receiving increasing attention as an important advancement in solving the urgent problem of reducing carbon dioxide [1]. Acrylonitrile based copolymers (PAC) are an important class of precursors for high value carbon based materials, such as carbon fiber composites with high mechanical, thermal resistance and mesoporous carbon for use in photoelectronic

devices [2–5]. The essential requirements that PAC precursors for high performance carbon materials must possess are high molecular weight and well controlled molecular architecture [6–7].

Commercially high molecular weight PAC is prepared by conventional radical polymerization much of them aqueous slurry process using various water soluble free radical initiators [8]. Various parameters such as comonomers type, temperature, initiator systems, polymerization media etc., influence the properties of the final polymer [9]. It is difficult to control polydispersity index (typically, $M_w/M_n < 3.0$). Similarly, it is difficult to control the chain architecture and microstructure of the polymer, specifically the stereoregularity of the polymer main chain described by its tacticity. The carbon

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fiber microstructure depends on the precursors and processing conditions. The stereoregularity as defined in terms of isotactic triad content of PAC often significantly affects the properties and functions of the polymers. Therefore, stereocontrol during polymerization is very important. More than three decade ago, Lewis acids were found to significantly influence the monomer reactivity during free-radical polymerization [10], and later, its stereochemistry [11]. However, the influence of Lewis acids on the stereochemistry during radical polymerization had not been reported. Isobe *et al.* [12] reported the efficient stereocontrol radical polymerization of acrylamides using Lewis acids as catalyst such as scandium trifluoromethanesulfonate and benzyl α -methoxymethylacrylate. In general, stereospecific polymerization has been attained through an ionic or coordination process with metal based initiator as catalyst, which can provide a countercationic or anionic species at the growing end. Conventional radical polymerization as applied to all vinyl monomers lacks a counter ionic species in the process, thereby resulting in the stereoirregular structures in the obtained polymers. Most commonly employed method for preparing high molecular weight PAC with well controlled stereoregularity is anionic polymerization, however this method yields polymer with branched structures which affects the process efficiency during the solution spinning process and stability of the polymer solution. Therefore, a method for facile synthesis of stereo controlled PAC continues to be subject of study. The stereoregularity of polyacrylonitrile was first determined by Matsuzaki *et al.* [13] from proton NMR spectra of deuterated polymers and established that the radically obtained polymer has an atactic structure.

Kamide and coworkers [14, 15] have synthesized highly isotactic PAN by gamma-ray irradiation assisted solid state polymerization on acrylonitrile-urea canal complex. Matsuzaki and coworkers [13, 16] and later Minagawa *et al.* [17] established that polyacrylonitrile obtained through X-ray or gamma-ray irradiation by solid phase polymerization of urea-canal complex has isotactic rich structure. Kamide *et al.* [18] have reported a polymer synthesis procedure for preparing high molecular weight, linear and high stereoregular polyacrylonitrile using anionic initiators including dialkylmagnesium. Considering the large scale requirements of PAC in

the manufacture of carbon fiber precursor polymers, these processes seem to be extravagant. The synthesis of a carbon fiber polymer precursor with high linearity, molecular weight and isotactic stereoregularity include the solid phase polymerization at low temperature (-75°C) using a urea/monomer clathrate complex reported by White [19]. However the unsaturated comonomers are absorbed on to crystalline materials, reducing the comonomer content in PAC. Therefore a robust synthesis procedure is a huge step toward development of a process for industrial scale production of high molecular weight PAC with isotacticity content more than 30 wt%.

PAC with high isotactic stereoregularity is preferred over atactic and syndiotactic contents in the manufacture of high tensile grade carbon fibers. One of the critical stages in the carbon fiber production is thermal oxidative stabilization reaction which involves intramolecular cyclization of adjacent nitrile groups in the structural chain. PAC with high isotactic content, wherein the nitrile groups are in a meso configuration is advantageous from a positional point of view for cyclization of the adjacent nitrile groups as compared to the other stereo structures [12]. Moreover, the dimensions of the hexagonal plane layer which forms during the subsequent carbonization or graphitization is larger than one achieved using conventional PAC with an atactic structure and thereby the strength of the resulting carbon fibers is increased.

Controlled radical polymerization (CRP), which has undergone significant progress in the past decade, enables the facile synthesis of polymers with controlled molar mass, narrow distribution of molecular weights, well defined architecture and site specific functionalities [20–26]. Among these CRP methods, atom transfer radical polymerization is perhaps the most desirable mechanism in terms of controllability. However, it is difficult to scale-up these processes due to the complex synthesis procedures involved. Moreover the physical properties of polymer depend on the primary structure of the polymer chain; therefore the polymer synthesis is designed to control the primary structure such as molecular mass of polymer, molecular mass distribution, branch structure and terminal structure or stereo structure [27–30]. The main objective of this study was the synthesis of well defined, linear, high stereo

regular PAC by applying a new polymerization technique.

In this research work, the PAC polymers such as poly(acrylonitrile-co-itaconic acid) and poly(acrylonitrile-co-acrylamide) were synthesized using template assisted solid phase polymerization technique and characterized for their molecular characteristics such as viscosity average molecular weight (M_v), weight average molecular weight (M_w), number average molecular weight (M_n), molecular weight distribution and stereo regularity in terms of isotactic triad content [mm wt%]. This research has revealed that carbon fiber precursor polymer with high linearity, average molecular weight and isotacticity triad content greater than 50% could be successfully obtained through the solid phase polymerization assisted by template compounds.

2. Experimental

2.1. Materials

Synthesis grade acrylonitrile (AN) (110213), acrylamide (ACM) (79-06-1) and itaconic acid (ITA) (129204) [Sigma Aldrich Co. Ltd., Germany] were used in the polymer synthesis. Acrylonitrile was washed with sodium hydroxide solution of lower concentration 0.5 wt% and distilled at its boiling range just before polymerization to remove the inhibitor content. The hexagonal crystalline metal salts (anhydrous nickel chloride or magnesium chloride) (449172) [Sigma Aldrich Co. Ltd., Germany] was used as a template compound. Acrylamide and Itaconic acid were used as comonomers without further purification. Commercially available α , α azoisobutyronitrile (AIBN) (78-67-1) [Sigma Aldrich Co. Ltd., Germany] was used as initiator after crystallization in methanol. Analytical grade dimethylsulphoxide (DMSO) (276855) [Sigma Aldrich Co. Ltd., Germany] was used for the measurements of polymer solution properties.

2.2. Synthesis of isotactic rich stereoregular poly(acrylonitrile-co-itaconic acid), poly(acrylonitrile-co-acrylamide)

The polymerization was carried out in a 500 mL three-necked round bottom flask, equipped with mechanical stirrer and a reflux condenser. The flask was bubbled with ultra pure N_2 gas for 240 min. to ensure an oxygen-free atmosphere. The template compounds used in this polymer synthesis is a

hexagonal crystalline metal salt ($NiCl_2$ or $MgCl_2$). The size of the template metal crystalline particles was in the range of 25–50 μm . The molar ratio of monomer and crystalline template compound was kept between 0.3 and 0.6, to give an optimal amount of monomer to coordinate with template compound. Then, a mixture of acrylonitrile (AN), acrylamide/itaconic acid, and (2–2.5 wt%) AIBN was added to the three-necked flask containing nickel chloride (N) at room temperature, and allowed to thoroughly absorb to prepare an AN/N complex. In order to enhance the interconnectivity between template compound and monomer mixture, the mixture was kept under a constant stirring. A solid-phase polymerization was carried out by keeping the above AN/N complex in a hot air circulating drier for 6 h at 70°C, and the final reaction mixture was poured into a pure methanol and precipitated. The white precipitate was filtered and washed several times with deionized water to remove the traces of metal salts and then dried under vacuum at 40°C for 24 h.

2.3. Characterization

FTIR

FTIR spectra (National Aerospace Laboratories, Bangalore, India) were recorded on a Shimadzu IR Affinity 1 model (Shimadzu Corp. Tokyo, Japan), the resolution being 2 cm^{-1} , using KBr pellets (1 mg samples as 400 mg KBr). Typical conditions were as follows: wavenumber, 400–4000 cm^{-1} , scanning, 32 counts; and purging gas, N_2 (flow rate, 10 L/min). FTIR spectra were recorded using the KBr disk method.

NMR

The 1H NMR and ^{13}C NMR (Bruker AMX-400, at Indian Institute of Science, Bangalore, India) spectra of the copolymers were recorded in DMSO using tetramethylsilane (TMS) as an internal standard [31]. Samples were concentrated in dimethyl sulphoxide about 5% (w/w) for 1H NMR and 5% (w/w) for ^{13}C NMR and 2D NMR by using a 5 mm NMR tube at room temperature. 1H NMR spectra were acquired using 21738 data points, spectral width 6 kHz, broadening 0.3 Hz, pulse delay 1 s, pulse width 90°, and 32 scans. ^{13}C NMR spectra were acquired using 24996 data points, spectral width 22 kHz, broadening 3 Hz, pulse delay 2 s, pulse width 90°, and 1024 scans. Nuclear

overhauser effect (NOE) was suppressed by gating the decouple sequence. Heteronuclear multiple quantum coherence (HMQC) was performed by using the standard Bruker pulse sequence with a pulse program. The spectrum was obtained with 256 increments in the F1 dimension and 1024 data points in the F2 dimension, with 200 scans and relaxation delay 1.5 s.

Solution viscometry

One hundred and fifty milligrams of a PAC sample dried by heat treatment at a temperature of 120°C for 2 hours and is dissolved at a temperature of 60°C into DMSO. The dropping time of the obtained solution between gauge marks is measured at an accuracy of 1/100 seconds using Ubbelohde viscometer at a temperature of 25°C. The measured dropping time is expressed as t [sec]. Similarly the dropping time of DMSO is expressed as t_0 . Intrinsic viscosity (η) was obtained according to the following Equation (1) [32]:

$$[\eta] = \{(1.44 \cdot \eta_{sp} + 1)\}^{1/2} - \frac{1}{0.36} \quad (1)$$

where $\eta_{sp} = t/t_0 - 1$. The viscosity average molecular weight of PAC was calculated by Equation (2) [33]:

$$[\eta] = 2.53 \cdot 10^{-4} [M_w]^{0.72} \quad (2)$$

Membrane osmometry

Osmotic pressure (Π) of polymer solution was measured in the range of polymer concentration (C) from 0.3 to 0.9 g/dL in DMSO at 60°C with Osmomat 090, Gonotec GmbH (Berlin, Germany) [34, 35]. Number average molecular weight (M_n) was obtained as Π/C extrapolated to $C = 0$ according to Equation (3):

$$\lim_{C \rightarrow 0} \Pi C^{-1} = RT(M_n^{-1}) + A_2 C \quad (3)$$

where R is gas constant.

Size exclusion chromatography –

Low angle laser light scattering (SEC-LALLS)

The SEC-LALLS instrument of Malvern Viscotek TDA 305 (Triple Detector Array, Malvern, United Kingdom) was used in this study [36]. The instru-

ment was operated at 50°C with DMSO as solvent. A flow rate of 1 mL/min and injection volume of 100 μ L was maintained. A concentration of ~ 4.0 wt% was maintained in all samples. Low angle laser light scattering (LALLS) instrument was used as a detector at a fixed wavelength of 633 nm. The molecular weight parameters were computed using SEC-LALLS data processing system. A set of polymethyl methacrylate (PMMA) standards of narrow molecular weight distribution (PolyCALTM, Viscotek, US) of molecular weight $2.0 \cdot 10^4$ – $4.51 \cdot 10^5$ was used to calibrate the SEC-LALLS instrument. The carrier solvent was DMSO containing 0.05 m lithium bromide (LiBr) with a flow rate of 1 mL/min.

3. Results and discussion

This study primarily aimed to facilitate synthesis of a well defined, linear high molecular weight, and isotactic rich stereoregular PAC by thermal solid phase polymerization technique using hexagonal crystalline metal salts (Nickel chloride or Magnesium Chloride) with AIBN as initiator. The hexagonal crystalline metal salts adopt a layer structure on the macroscopic scale. Acrylonitrile monomers and unsaturated comonomers become enclosed between the crystalline metal compound layers with the polar groups orientated in the same direction to produce a regularly ordered arrangement. When particle size of the metallic compound is fine ($< 5 \mu$ m), the PAC polymers were found to have lower molecular weight fractions. The general mechanism for the synthesis of PAC is represented in Figure 1. The Figure 2 shows the detailed representation of the various synthesis steps involved in the polymer synthesis.

The chemical composition of the respective copolymers as determined from ^1H NMR is given in Table 1. FTIR spectra of PAC are shown in Figure 3. The chemical structures of the copolymer are presented in Figure 4. The specific peak appearing at $\sim 2244 \text{ cm}^{-1}$ in all spectra is associated with $-\text{CN}$

Figure 1. General mechanism for the synthesis of PAC

Table 1. Chemical composition of PAC

Sample code	Polymer composition [mol%]		AIBN [wt%]
PAC/01	AN(98.5)	ITA(1.5)	2.5
PAC/02	AN(98.5)	ITA(1.5)	2.0
PAC/03	AN(98.5)	ACM(1.5)	2.0
PAC/04	AN(98.5)	ACM(1.5)	2.5

Figure 2. Schematic representation of the solid state polymerization process **Figure 3.** FTIR spectra of PAC/01 and PAC/03 copolymer sample

groups stretching vibration. The strong peak at $\sim 1726\text{ cm}^{-1}$ appearing in both spectrum of the copolymers is associated with carboxyl groups ($\text{C}=\text{O}$) stretching vibration. The absorption peak at $\sim 1251\text{ cm}^{-1}$ corresponds to $\text{C}-\text{O}$ or $\text{C}-\text{N}$ stretching vibration. These characteristics peaks in the spectra confirm the copolymer structures.

Figure 5. ^1H NMR spectra of (a) PAC/01 and (b) PAC/03 in $\text{DMSO}-d_6$ at 25°C **Figure 4.** Chemical structures of PAC samples: (a) PAC/01 & PAC/02, and (b) PAC/03 & PAC/04

^1H NMR spectra of PAC/01 and PAC/03 corresponding to poly[acrylonitrile-co-itaconic acid], poly[acrylonitrile-co-acrylamide] are shown in Figure 5a and 5b. It can be seen that, the spectrum was complicated due to spin-split and coupling of methylene protons from both acrylonitrile and itaconic acid monomers in Figure 5a. The signals of methylene protons ($-\text{CH}_2$) from acrylonitrile and itaconic acid monomer units appeared at 2.1–2.2, and 2.3–2.4 ppm respectively. The signals corresponding to characteristic methine proton ($-\text{CH}$) and $-\text{COOH}$ proton from itaconic acid were observed at 3.25 and 10.2 ppm respectively. The characteristic amide proton ($-\text{CONH}_2$) from acrylamide corresponding to signal at 7.9 ppm. Compositions of the PAC/01–PAC/04 were determined by measuring the integrated areas of the resolved peaks corresponding to functional groups of respective monomers in ^1H NMR spectra.

The plot of reduced viscosity as a function of concentration of all samples in DMSO is shown in Figure 6. The viscosity average molecular weight of the PAC polymers determined using Equation (2) is given in Table 2. The osmotic pressure values of samples such as PAC/01–PAC/04 are measured in DMSO at 60°C . The plot of reduced osmotic pressure, Π/C , against concentration, C , of all the polymer solutions is shown in the Figure 7. In all cases

Table 2. Viscometry, osmometry, and SEC-LALLS results for different samples

Sample code	$[\eta]^a$ [g/dL]	$M_v^a \cdot 10^{-5}$ [g/mol]	$M_n^b \cdot 10^{-4}$ [g/mol]	$M_n^c \cdot 10^{-4}$ [g/mol]	$M_w^c \cdot 10^{-5}$ [g/mol]	$M_z^c \cdot 10^{-5}$ [g/mol]	M_v^a/M_n^b	M_w/M_n^c	M_z/M_w^c
PAC/01	2.24	3.06	14.3	11.8	2.57	4.31	2.13	2.168	1.68
PAC/02	1.43	1.64	7.8	4.7	1.17	2.25	2.10	2.503	1.92
PAC/03	1.70	3.26	10.2	7.21	1.73	3.18	3.20	2.411	1.84
PAC/04	1.90	2.44	11.2	7.49	1.60	3.17	3.03	2.147	1.99

^aBy viscometry^bBy membrane osmometry^cBy SEC-LALLS **Figure 6.** The plots of reduced viscosity as a function of concentration for PAC in DMSO at 30°C **Figure 7.** The plots of reduced osmotic pressure (Π/C) against concentration C for PAC in DMSO at 60°C

linear relations are obtained when extrapolated to $C = 0$ with a linear regression coefficient of 0.9945. From the extrapolation of the Van't Hoff plots, the value of number average molecular weight (M_n) is determined. A set of four monodispersed polymethyl methacrylate (PMMA) standards corresponding to molecular weights from $2.0 \cdot 10^4$ – $4.51 \cdot 10^5$ is used to calibrate SEC-LALLS instrument. A calibration data of retention volume-detector response corresponding to four different monodisperse (PMMA) standards is given in Table 3.

The molecular weight (M_n , M_w , M_z) and the molecular weight distribution (M_w/M_n) were determined using SEC-LALLS. The values of M_n , M_w , M_z and

Table 3. Average molecular weight of PMMA calibration standards

Sample No	Molecular weight [g/mol]
PMMA1	451 000
PMMA2	139 000
PMMA3	52 600
PMMA4	20 800

Figure 8. SEC-LALLS elution curves for PAC, a) PAC/01, b) PAC/04, c) PAC/03, d) PAC/02

MWD are calculated for PAC/01–PAC/04 using SEC-LALLS data processing system which is given in Table 2. The ratio of M_w/M_n varies between 2.1 to 2.5 and also the ratio of M_z/M_w varies between 1.6 to 2.0. Figure 8a–d shows SEC-LALLS elution curves for PAC/01–PAC/04. The values of M_v , M_n (osm), M_n (SEC-LALLS), M_w , and M_z are 1.61 – $3.26 \cdot 10^4$, 7.8 – $14.3 \cdot 10^4$, 4.7 – $11.8 \cdot 10^4$, 1.1 – $2.57 \cdot 10^5$, and 2.25 – $4.31 \cdot 10^5$ g/mol respectively. It has been authors' experience that M_n values determined by SEC-LALLS are rarely in agreement with M_n values from the membrane osmometer, SEC-LALLS values generally being lower than M_n values determined from the osmometer.

The stereoregularity of PAC/01–PAC/04 are also estimated in terms of triad tacticity content using ^{13}C NMR spectra. Basically, due to higher resolu-

Figure 9. 2D-NMR – COSY-HMQC Techniques: ^{13}C – ^1H shift correlation NMR spectra

tion and more extensive sweep width, this technique is used in most studies. The bonding network between methine carbon and methine hydrogen is established using 2D-NMR – COSY-HMQC technique which is shown in Figure 9. HMQC spectrum can also be used in the assignment of the proton spectrum by dispersing the proton resonances along the ^{13}C dimension and reducing its multiplet overlaps. ^{13}C NMR spectra with wide magnetization field caused higher splitting which was observed for all carbons.

Figure 10. ^{13}C NMR spectra of isotactic PAC. Only methine carbon region is expanded (bottom).

Figure 10 shows the typical ^{13}C NMR spectra of stereoregular isotactic PAC in which three types of carbon are observed: methine (CH), methylene (CH_2), and cyano-carbon (CN). Assignments of methine carbon peaks were adopted as Minagawa *et al.* [37] which used NMR-400 MHz spectrometer with similar splitting for carbons. The triad tacticities of the polymers prepared were analyzed using methine carbon (CH) signals in the region 26.7–27.9 ppm. They consisted of three main peaks, corresponding to three possible steric triad configurations. The peaks at 26.75, 27.3, and 27.86 ppm correspond to isotactic (mm), atactic (mr), and syndiotactic (rr) respectively. The relative intensities of the peaks corresponding to methine carbon were used for determining the triad tacticity of PAC. The extent of isotacticity (mm) of these samples was found to be in the range of 47.6–51.4% (Table 4). The Bernoulli statistics is held satisfactorily for the PAC samples as listed in Table 4.

Two of the essential requirements that, polymer precursors for high performance carbon fiber materials must possess are high molecular weight and well controlled architecture [6, 7]. The molecular and structural characteristics of carbon fiber precursor polymers synthesized through conventional polymerization processes such as aqueous slurry, and solution techniques are presented in Table 5. Typically the molecular characteristics of PAC are M_n ($4.25 \cdot 10^4$), M_v ($2.09 \cdot 10^5$), M_w ($1.82 \cdot 10^5$) (suspension process) and M_n ($4.28 \cdot 10^4$), M_v ($1.61 \cdot 10^5$), M_w ($1.43 \cdot 10^5$) (solution process). In the present solid phase polymerization technique, the molecular weight increased with conversion and molecular weight distribution around 2.1–2.5 throughout the polymer synthesis. There was also a strong dependence of the initiator concentration on the molecular weight of the polymer. Then, the molecular weights increased in a linear fashion with increasing conversion and that the absolute molecular weights (M_n (osmometry) (7.8 – $14.3 \cdot 10^4$)) were close to the

Table 4. Characterization of stereoregular PAC samples

Sample code	Chemical shift [ppm]			Triad tacticity [%]			
	mm	mr	rr	I ^a	A ^b	S ^c	4IS/A ²
PAC/01	26.77	27.39	27.86	47.8	37.4	14.8	2.023
PAC/02	26.76	27.39	27.85	47.6	36.9	15.5	2.167
PAC/03	26.76	27.36	27.86	51.4	33.9	14.7	2.629
PAC/04	26.76	27.37	27.84	50.1	35.6	14.3	2.261

^aIsotactic

^bAtactic

^cSyndiotactic

Table 5. Molecular characteristics of PAC through different polymerization techniques

Entry	Polymer	Process	Solvent	Molecular parameters				Structural parameters Triad tacticity [%]		
				$M_v \cdot 10^{-5}$ [g/mol]	$M_n \cdot 10^{-4}$ [g/mol]	$M_w \cdot 10^{-5}$ [g/mol]	M_w/M_n	I	A	S
1	AN/ITA copolymer 98.5/1.5; wt/wt AIBN, 50°C	Aqueous slurry polymerization	DMSO/H ₂ O	2.09	4.25	1.82	4.28	28.1	47	24.9
2	AN/ITA copolymer 98.5/1.5; wt/wt AIBN, 55°C	Solution polymerization	DMSO	1.61	4.28	1.43	3.34	26.4	48.5	25.1
3	AN/ITA copolymer 98.5/1.5; wt/wt AIBN, 70°C	Solid phase polymerization	No solvent used	1.64	4.70	1.17	2.503	50.1	35.6	14.3

theoretical values determined by the ratio of the initial monomer and initiator concentration (i.e., $M_{n,theo} = 53[AN]_0/[AIBN]_0$). This means that the initiator efficiency of the polymerization was close to unity. The molecular weight characteristics of PAC obtained through solid phase polymerization are M_n ($4.7 \cdot 10^4$), M_v ($1.64 \cdot 10^5$), M_w ($1.17 \cdot 10^5$). This compares well with the other conventional polymerization processes.

4. Conclusions

Isotactic rich stereoregular PAC was synthesized by solid phase polymerization using hexagonal crystalline metal salts (Nickel chloride or Magnesium chloride) with AIBN as initiator. The bonding network between methine carbon and methine hydrogen is established using 2D-NMR – COSY-HMQC technique. ¹H NMR via HMQC triad sequence was also performed for methine protons. Assignment of stereosequences was performed on methine carbon at triad sequences level using ¹³C spectroscopy. Bernoullian statistics is fitted well by the experimental results. The molecular weight distributions and various average molecular weights of PAC were estimated. Structure-property relationship, such as the intrinsic viscosity (η) versus the number average molecular weight (M_n) found in DMSO is $\eta = 2.53 \cdot 10^{-4} \cdot M_n^{0.72}$. The molecular weight distributions of these polymers as determined from M_v/M_n and M_w/M_n were 2.1 to 3.2 and 2.1 to 2.5 respectively. It is concluded that PAC with isotactic content over 50% can be prepared successfully by solid phase polymerization.

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