

STUDIES ON MOLECULAR WEIGHT DISTRIBUTION OF CARBON FIBER POLYMER PRECURSORS SYNTHESIZED USING MIXED SOLVENTS*

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Abstract The molecular weight distributions were estimated for carbon fiber polymer precursors such as poly(acrylonitrile-co-itaconic acid) synthesized by semi batch solution polymerization in mixed solvents media with the azonitrile compounds as initiator under the different ratios of solvent and non solvent from 0.75 to 2.5 in weight. The copolymer was characterized by using Fourier transform infrared spectroscopy (FTIR) and nuclear magnetic resonance (¹H-NMR) analyses. The molecular weight distributions were evaluated by M_v/M_n ratios estimated from viscosity and osmotic measurements, and M_w/M_n estimated from size exclusion chromatography. The molecular weight distributions of these polymers as determined from M_v/M_n and M_w/M_n are 2.9 to 3.2 and 2.0 to 2.5 respectively. The molecular distributions were close to a narrow distribution of 2.0 when the solvent/non-solvent ratio was varied between 1.4 and 2.0. Intrinsic viscosity $[\eta]$ as a function of molecular weight of poly(acrylonitrile-co-itaconic acid) was evaluated by means of low angle laser light scattering with size exclusion chromatography (SEC-LALLS) and viscometry with SEC (SEC-VISCO). The relationship between $[\eta]$ and M_w for poly(acrylonitrile-co-itaconic acid) in DMF at 50°C was $[\eta] = 1.1 \times 10^{-5} M_w^{0.79}$, where $[\eta]$ is obtained in dL/g.

Keywords: Molecular weight distribution; Size exclusion chromatography; Osmometry; Viscometry; Polyacrylonitrile copolymer.

INTRODUCTION

Polyacrylonitrile copolymers (PAC) are used in a number of industrial applications as a fiber itself including heavy duty fibers, synthetic ropes, flame resistant plastics, power transmission belts and also as a precursor for carbon fiber manufacture^[1–6]. PAC is also commonly used to produce fabric for clothing manufacture since its addition creates a material which is warming, soft and crease-resistant^[1, 7]. The physical characteristics of PAC fibers strongly dependent on molecular characteristics such as average molecular weights and molecular weight distribution of the polymer chains^[8]. When it comes to the tenacity, the selection of linear size molecules becomes indispensable^[7]. The number average molecular weights are highly representative of the linearity of the polymer molecules. Recently, carbon fibers are extensively used in many industrial fields. The physical characteristics required for fiber precursors are increasingly being raised. Under such circumstances, it is desired to develop PAC that has improved physical and mechanical properties^[9–11]. To this effect, the process of synthesizing a highly polymerized acrylonitrile is a subject of study, and research on this is scanty. The molecular parameters of PAC, such as number average molecular weight (M_n), weight average molecular weight

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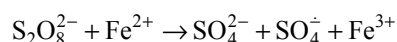
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(M_w), linearity, a narrow molecular weight distribution (M_w/M_n), molecular defect and stereo regularities of pendant functional groups, influence the physical properties of the fiber precursor^[3]. Thus polymerization conditions play a crucial role in altering the physical and mechanical properties of PAC fiber^[12]. This is due to the formation of molecular structure of polymer molecules during polymerization process. In suspension and emulsion polymerizations above 50°C, the resulting polymer might have increased degree of polymerization but tends to be a branched polymer and thus a markedly reduced solubility. The degree of branching of PAC has a marked influence on the fiber spinning process. Further, it is known that reduction of molecular and structural defects in the PAC is necessary to be used as a precursor for carbon and graphite fibers^[13, 14]. In order to meet these increasing requirements of carbon fiber precursor, it is necessary to develop a polymerization process which allows making the requisite modifications at the polymer precursor level^[9]. Various attempts have been made to obtain PAC having an increased degree of polymerization through a process which comprises reacting the mixture of acrylonitrile and comonomers in a mixed medium comprising of a solvent (S) and non solvent (NS) with different ratios^[15]. However, there is little information on the effect of S/NS ratio in obtaining the said PAC. Membrane osmometry is an excellent, simple and absolute way of determining the number average molecular weight of PAC^[16]. Gel permeation chromatography developed by Moore *et al.*^[10] is now widely used as a convenient method to determine the molecular weight distribution of linear polymers. The method is quick and has good reproducibility.

Studies on the polymerization system with water/monomer ratios have been reported elsewhere. However, studies on the effect of S/NS ratio on the polymer properties and polymerization behaviors are not widely studied. Ito *et al.*^[11] studied the properties of polymer and the structures of polymer particles of AN-vinyl acetate copolymers (93:7 in weight) which were prepared in the range of water/monomer ratio from 1.5 to 4.0 and using $S_2O_8^{2-}/Fe^{2+}$ (redox couple) initiator as represented below.



We have observed that the structure of the polymer particle became more compact with increasing S/NS ratio, resulting in reduced water contents of dewatered cakes at filtration of the polymer slurry and increased bulk densities of the polymer. The purpose of this paper is to reveal the influence of S/NS ratio on the molecular weight distributions (MWD) of PAC and also to study the effect of these parameters on the average molecular weights of PAC.

EXPERIMENTAL

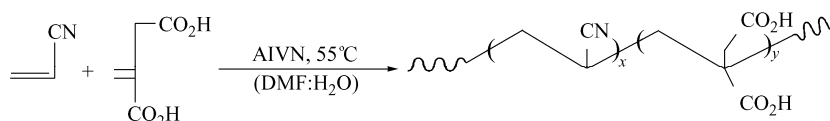
Materials

Acrylonitrile, (AN) (99%, Sigma Aldrich, Germany) was used as a monomer in the polymer synthesis. Acrylonitrile was washed with a sodium hydroxide solution of concentration 0.5 wt% and distilled at its boiling range just before polymerization to remove the inhibitor content. Itaconic acid (ITA) was used as comonomer without further purification. Commercially available 2,2'-azobis (2,4-dimethyl valeronitrile) (AIVN) (Wako Co., Japan) was used as initiator after crystallization in methanol. Analytical grade *N,N*-dimethylformamide (DMF) (Sigma Aldrich) was used for the measurements of polymer solution properties.

Polymer Synthesis

PAC/01–PAC/08 were the eight different polymer samples corresponding to various viscosity average molecular weights used in this study. The synthetic route is depicted in Scheme 1. The chemical composition of the respective copolymers is given in Table 1. These different polymer samples were prepared by varying the concentration of initiator based on azonitrile compounds in mixed solvents at 55°C. The initiator used was 2,2'-azobis (2,4-dimethyl valeronitrile) (AIVN), and the concentration was varied between 2 wt% to 2.5 wt%. The ratio of the solvents (reaction medium) and initiator quantity was varied to obtain the targeted molecular mass. The resulting polymer was filtered and washed with methanol and dried at 60°C under vacuum to constant mass. To evaluate the dewatering property of the slurry of polymers, the water content of the cake was measured by

gravimetric method. Bulk density of the PAC powder was determined according to the method as mentioned in the article^[17].



Scheme 1 General mechanism for the synthesis of PAC

Table 1. Chemical composition of AN/ITA copolymers

Sample code	Polymer composition (mol%)		AIVN (wt%)
PAC/01	AN (98.5)	ITA (1.5)	2.0
PAC/02	AN (98.5)	ITA (1.5)	2.0
PAC/03	AN (98.5)	ITA (1.5)	2.5
PAC/04	AN (98.5)	ITA (1.5)	2.5
PAC/05	AN (98.5)	ITA (1.5)	2.0
PAC/06	AN (98.5)	ITA (1.5)	2.5
PAC/07	AN (98.5)	ITA (1.5)	2.5
PAC/08	AN (98.5)	ITA (1.5)	2.0

Characterization

FTIR

FTIR spectra were measured by using a Shimadzu IR spectrophotometer. Typical conditions were as follows: wavenumber, 400–4000 cm^{-1} ; resolution, 2 cm^{-1} ; scanning, 32 counts and purging gas, N_2 (flow rate, 10 L/min).

NMR

The liquid NMR spectra were obtained on a Bruker Avance 400 MHz, Switzerland. Samples were concentrated in deuterated dimethyl sulphoxide (DMSO-d_6) about 200 g/L for ^1H -NMR spectra. ^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.

Solution viscometry

Specific viscosity (η_{sp}) was measured at 30°C in DMF with an Ubbelohde capillary tube viscometer^[18, 19] maintained in a constant temperature bath. Intrinsic viscosity $[\eta]$ was obtained from η_{sp} according to the Eq. (1)

$$[\eta] = \left[(1.44 \times \eta_{\text{sp}} + 1) \right]^{1/2} - 1 / 0.36 \quad (1)$$

where η_{sp} is the specific viscosity ($\eta_{\text{sp}} = t/t_0 - 1$, where t and t_0 are the efflux time of the polymer solution and solvent respectively). The viscosity average molecular weight of PAC was calculated by Eq. (2).

$$[\eta] = 3.35 \times 10^{-4} M_v^{0.72} \quad (2)$$

Membrane osmometry

Osmotic pressure (π) of polymer solutions was measured in the range of polymer concentration (c) from 0.3 g/dL to 0.9 g/dL in DMF at 60°C with an Osmomat 090, Gonotec GmbH. Number average molecular weight (M_n) was obtained as π/c extrapolated to $c = 0$ according to Eq. (3)^[20]. The second virial coefficient (A_2) was also obtained by Eq. (3)

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

where R is the gas constant.

Bulk density measurements

The finely ground polymer powder (average particle diameter *ca.* 25 μm) was filled upto the top mark in a

measuring cylinder with a known volume (A) and weight (B). The excess material on top of the measuring cylinder was scraped off with a straight edge. The weight of the cylinder filled with polymer (C) was measured. The measurement was repeated five times using five samples of the same polymer, the average weight was taken as C . Then, the bulk density (g/cm^3) of the polymer powder was determined using the following Eq. (4).

$$\rho = (C - B)/A \quad (4)$$

Size exclusion chromatography-low angle laser light scattering (SEC-LALLS)

The SEC-LALLS instrument of Malvern Viscotek TDA 305 (Triple Detector Array) was used in this study^[21]. The instrument was operated at 50°C with DMF as solvent. A flow rate of $1 \text{ mL}/\text{min}$ and an injection volume of $100 \mu\text{L}$ were maintained. A concentration of *ca.* $4.0 \text{ wt}\%$ 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 standards of narrow molecular weight distribution (purchased from Agilent Technologies) of molecular weight 2.0×10^4 – 4.51×10^5 was used to calibrate the SEC-LALLS instrument. The carrier solvent was DMF containing 0.05 mol/L lithium bromide (LiBr) with a flow rate of $1 \text{ mL}/\text{min}$.

RESULTS AND DISCUSSION

FTIR spectrum of the PAC copolymer is shown in Fig. 1. The chemical structure of the copolymer is presented in Scheme 2. The specific peak appearing at *ca.* 2244 cm^{-1} in the spectra is associated with $-\text{CN}$ groups stretching vibration. The strong peak at *ca.* 1726 cm^{-1} appearing in spectrum of the copolymer is associated with carboxyl group's ($\text{C}=\text{O}$) stretching vibration. The absorption peak at *ca.* 1251 cm^{-1} corresponds to $\text{C}-\text{O}$ or $\text{C}-\text{N}$ stretching vibration. These characteristic peaks in the FTIR spectra confirm the copolymer structure.

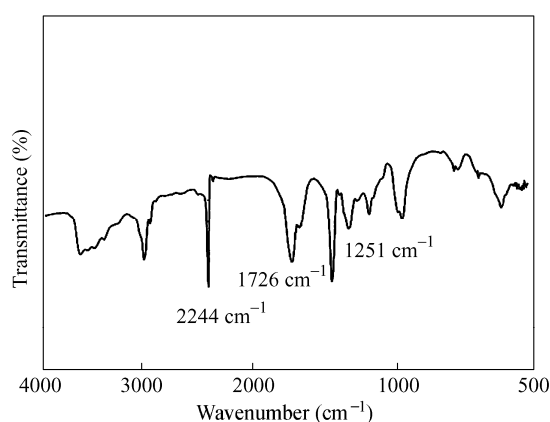
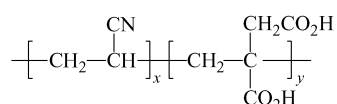


Fig. 1 FTIR spectrum of the AN/ITA copolymer sample



Scheme 2 Chemical structure of AN_x/ITA_y copolymer

Compositions of the PAC are determined by measuring the intensity of the signals in ^1H -NMR spectra (Fig. 2). The signal at $\delta = 2.0$ due to $-\text{CH}_2$ groups of both AN and comonomers is marked as 'A'. The signals at $\delta = 3.21$ due to $-\text{COOH}$ groups of itaconic acid (ITA) is marked as 'B'. Integral areas of the characteristic peaks were used to calculate the compositions according to the following equations:

$$S_2 = S_B \quad (5)$$

$$C_M = \frac{S_2}{S_A} \times 100\% \quad (6)$$

where S_2 is the integral area of $-\text{CH}_2-$ in comonomer, S_A is the integral area of $-\text{CH}_2-$ in the copolymer, S_B is the integral area of $-\text{COOH}$ group in the copolymer and C_M is the molar composition of the comonomer in copolymer. The composition of AN/ITA is obtained according to Eqs. (5) and (6) due to the different structures of monomers.

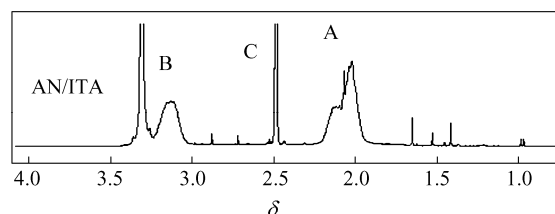


Fig. 2 ^1H -NMR spectrum of AN/ITA in DMSO-d_6 at 25°C

Polymerization conditions under different S/NS ratios and the properties of the resulting polymers are summarized in Table 2. As the S/NS ratio increases, the bulk density of the polymer also increases significantly. When the ratio S/NS is varied from 1.4–2.91, the range of bulk density of the polymer varies from 0.31–0.49 g/mL. With decreasing water/monomer ratios in polymerization, polymer particles become more compact, so that bulk densities of polymers increase and water contents of dewatered cakes decrease.

Table 2. Polymerization conditions with various solvent/monomer ratio and some properties of polymers

Sample ID	Solvent/monomer (wt. ratio)	S/NS (wt. ratio)	Temperature ($^\circ\text{C}$)	Dwell time (min)	Agitation speed (r/min)	Bulk density of polymer (g/mL)	Water content of the cake (wt% dry basis)
PAC/01	1.2	1.46	50	110	210	0.31	170
PAC/02	1.1	1.50	50	110	210	0.36	182
PAC/03	1.2	1.51	50	110	210	0.39	107
PAC/04	1.4	1.48	50	110	210	0.31	125
PAC/05	1.2	2.63	50	120	240	0.47	172
PAC/06	1.1	2.71	50	120	240	0.45	153
PAC/07	1.2	2.98	50	120	240	0.42	137
PAC/08	1.2	2.81	50	120	240	0.49	102

The plots of reduced viscosity as a function of concentration of all samples in DMF (Fig. 3) show a linear relationship which confirms the Newtonian behavior of dilute solutions of PAC in the solvent. The osmotic pressure values of samples such as PAC/01, PAC/02, PAC/03, PAC/04, PAC/05, PAC/06, and PAC/07 are measured in DMF at 60°C . The plots of reduced osmotic pressure, π/c ($\text{cm}\cdot\text{g}^{-1}\cdot\text{dL}$), against concentration, c , of all the polymer solutions are shown in the Fig. 4. In all cases 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 values of number average molecular weight (M_n), second virial coefficient (A_2) and polymer solute-solvent interaction parameter (χ) are determined. The same polymer samples with different molecular weights in a particular solvent show similar slopes with an average deviation of -0.001 but different intercepts. The plot of intrinsic viscosity against number average molecular weight in DMF is shown in Fig. 5, which is apparently linear. However it is known that the degree of homogeneity with respect to molecular weight has a much greater effect on the relation between $[\eta]$ and M_n . Intrinsic viscosity, Huggins constant, M_n and the second virial coefficient are shown in Table 3. M_v in Table 3 was obtained by the above Eq. (2).

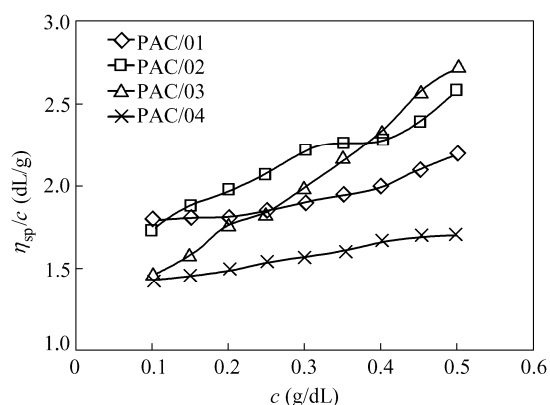


Fig. 3 The plots of reduced viscosity as a function of concentration for PAC in DMF at 30°C

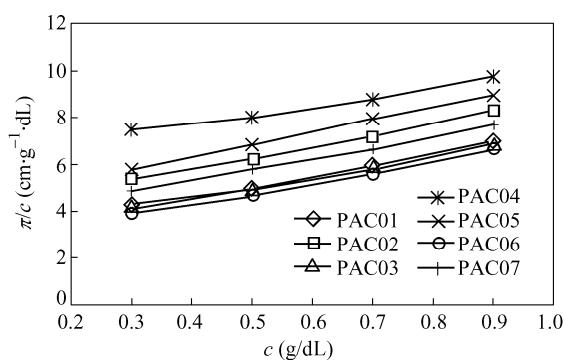


Fig. 4 The plots of reduced osmotic pressure (π/c) against concentration c for PAC in DMF at 60°C

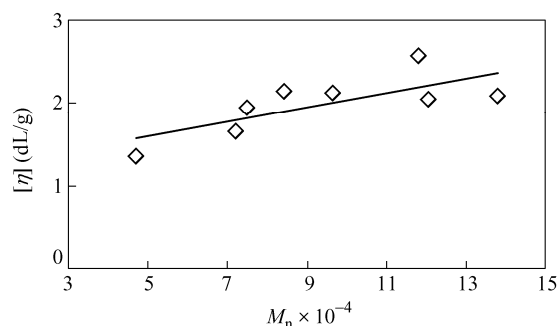


Fig. 5 Relationship between $[\eta]$ and M_n for PAC in DMF

Table 3. Molecular weight and related data of polymer samples

Sample No.	$[\eta]$ (dL/g)	k'	$M_n \times 10^{-4}$	P_n^a	$A_2 \times 10^3$ (mol·cm ³ ·g ⁻¹)	$M_v \times 10^{-5}$	M_v/M_n
PAC/01	2.54	0.3726	11.1	2226	1.69	3.51	3.17
PAC/02	1.36	0.3256	7.80	886	1.77	2.31	2.96
PAC/03	1.70	0.3549	10.2	1360	1.54	3.26	3.20
PAC/04	1.90	0.3576	7.07	1413	1.90	2.14	3.03

^a Number average degree of polymerization

Heterogeneity index, M_v/M_n ratio, is used in place of M_w/M_n , since M_w is not obtained by direct measurement. M_v/M_n ratios for samples PAC/01–PAC/04 are *ca.* 3 and no marked difference is observed in M_v/M_n ratio of polymers prepared under the condition of S/NS ratio varied from 1.2 to 1.6. A set of four monodispersed polymethyl methacrylate (PMMA) standards corresponding to molecular weights from 2.08×10^4 – 4.51×10^5 is used to calibrate the SEC-LALLS instrument. The retention time-detector response corresponding to the four different monodisperse (PMMA) standards (Table 4) is shown in Fig. 6.

Table 4. Average molecular weight and retention time of PMMA calibration standards

Sample No.	t_R^a (min)	Molecular weight
PMMA1	41.95	451000
PMMA2	44.783	139000
PMMA3	47.567	52600
PMMA4	50.4	20800

^a Retention time in minutes

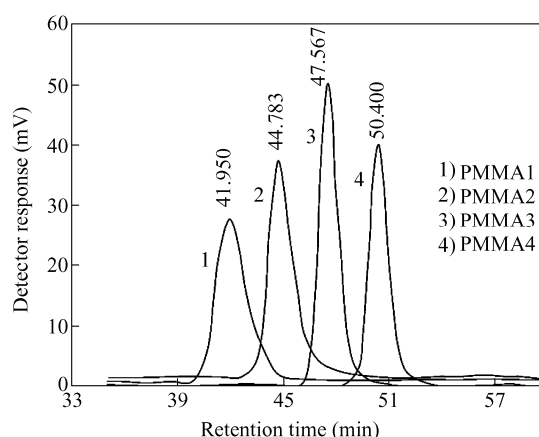


Fig. 6 The SEC-LALLS elution curves for polymethylmethacrylate standards

Evaluation of MWD from SEC-LALLS and SEC-VISCO

Masuzawa *et al.*^[22–24] have studied molecular weight distribution (MWD) of polyacrylonitrile by gel permeation chromatography (GPC). They have shown that MWD of PAN prepared by redox system could not be properly evaluated by GPC measurements in DMF, because the MWD shows unusual curves owing to the strong acid groups of the polymers originated from initiators. This is considered to be due to the unusual expansion of polymer chains caused by electrostatic interactions of the strong acid groups. Imaizumi *et al.*^[21] have shown that satisfactory molecular characteristics data of polymeric materials can be obtained using SEC-LALLS and SEC-VISCO. Hence, in this study the experiments using SEC-LALLS and SEC-VISCO were performed with 0.05 mol/L LiBr in DMF. To compare the results obtained from SEC-LALLS and SEC-VISCO, the PAC prepared under the condition corresponding to PAC/01 in Table 2, was fractionated by the successive precipitation fractionation. Dimethylformamide was used as solvent and methanol as precipitant in the fractionation. Intrinsic viscosity, M_n and related data of fractionated polymers are shown in Table 5. M_v is calculated from $[\eta]$ by Eq. (2).

Table 5. Intrinsic viscosity and molecular weight of fractions of the PAC/01 sample

Fr. No.	$[\eta]$ (dL/g)	$M_n \times 10^{-4}$	$M_v \times 10^{-4}$	$(M_v \times M_n)^{1/2} \times 10^{-4}$	M_v/M_n
1	2.89	12.72	22.5	16.9	1.77
2	2.54	11.34	21.7	15.7	1.91
3	2.28	9.32	19.9	13.6	2.14
4	1.87	8.91	18.1	12.7	2.03
5	1.42	8.52	17.4	12.2	2.04
6	1.29	7.26	15.4	10.6	2.12

From Table 5, M_v/M_n ratios of fractionated polymers are *ca.* 2, revealing that these fractions are not monodisperse. However, the distributions of average molecular weights of the fractions are not broad.

The following Mark-Houwink-Sakurada type relationship is established for obtained PAC polymers in DMF by the least square method.

$$[\eta] = 1.1 \times 10^{-5} M_w^{0.79}$$

If molecular weight distribution of the samples confirm to Wesslau's distribution^[25], it is shown that $(M_w \times M_n)^{1/2}$ is the average molecular weight corresponding to the peak of elution curve of SEC-LALLS. In this study, $(M_v \times M_n)^{1/2}$ is used as average molecular weight, M_w being replaced with M_v . The values of M_n , M_w , M_z and MWD are calculated for PAC/01–PAC/04 with S/NS ratio of approximately 1.2, using SEC-LALLS data processing system, and are given in Table 6. 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, no marked difference exists in MWD of PAC/01–PAC/04 samples. Figure 7

shows SEC-LALLS elution curves for PAC/01–PAC/04. $[\eta]$, M_n and M_w are calculated from these elution curves. Table 6 also represents the molecular weight and MWD data for PAC/05–PAC/08 with S/NS ratio of approximately 2.8. With the increase in the S/NS ratio, the average molecular weights and MWD also increased. The S/NS ratio varies in the range of 2.6 to 2.9, the M_w/M_n ratios are approximately 2. No marked change occurs in MWD data for PAC/05–PAC/08. Figure 8 shows SEC-LALLS elution curves for PAC/05–PAC/08. M_n and M_w are calculated from these elution curves.

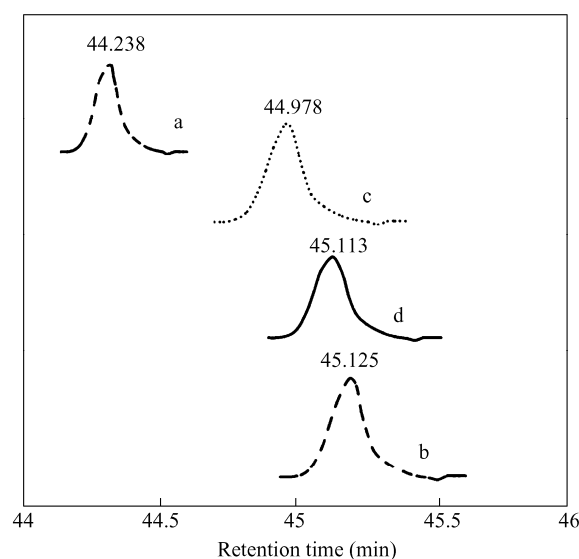


Fig. 7 SEC-LALLS elution curves for (a) PAC/01, (b) PAC/02, (c) PAC/03 and (d) PAC/04

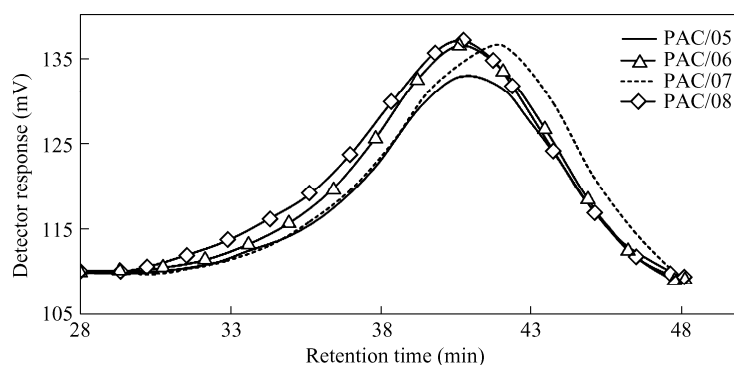


Fig. 8 SEC-LALLS elution curves for PAC/05–PAC/08

Table 6. Molecular weight and related data of polymers prepared under the condition of Table 2 calculated from SEC-LALLS results

Sample No.	$[\eta]$ (dL/g)	$M_n \times 10^{-4}$	$M_w \times 10^{-5}$	$M_z \times 10^{-5}$	M_w/M_n	M_z/M_w	t_R (min)
PAC/01	2.54	11.80	2.57	4.31	2.16	1.68	44.238
PAC/02	1.36	4.70	1.17	2.25	2.50	1.92	44.545
PAC/03	1.70	7.21	1.73	3.18	2.41	1.84	45.278
PAC/04	1.90	7.49	1.60	3.19	2.14	1.99	45.491
PAC/05	2.09	13.80	3.09	4.77	2.24	1.54	41.012
PAC/06	2.04	12.05	2.59	4.21	2.15	1.62	41.125
PAC/07	2.12	8.42	1.69	3.53	2.01	2.10	41.276
PAC/08	2.06	9.65	2.15	4.14	2.23	1.92	41.435

Initially we maintained the S/NS ratio of the reaction medium in the range of 1.4 to 1.5. Under these conditions the MWD is varied from 2.1 to 2.5 which are close to narrow molecular weight distribution. The result described above is industrially significant, because MWD directly influences the mechanical properties of fibers^[26, 27]. As a result, it is understood that using best reaction conditions of polymerization, including dewatering property, bulk density of polymer, conversion rate and solvent/monomer ratio, it is possible to produce a PAC polymer for the manufacture of high performance acrylic fibers.

In general, the chain transfer to monomer is negligible in free radical polymerizations; however, the chain transfer to the growing polymer is significant^[28]. With a marginal increase of S/NS in the mixed solvents, there is a significant improvement in the distribution ratio (2.1–2.5). This may be attributed to the action of mixed solvents themselves acting as a chain transfer agent, favoring the formation of uniform size of the polymeric molecules.

CONCLUSIONS

The molecular weight distributions and various average molecular weights of PAC synthesized under the polymerization conditions of different S/NS ratios were estimated. The molecular weight distributions of these polymers as determined from M_v/M_n and M_w/M_n were 2.9 to 3.2 and 2.0 to 2.5 respectively. The results suggest the different ways of obtaining the required distribution of different molecular weight averages in PAC syntheses. Effect of solvent/non solvent ratio on MWD was reported. With increase in the S/NS ratio, the polymer content in the polymerization system was increased and consequently the bulk density of the resulting polymer was also increased. Hence, it is suggested that polymerization in the polymer phase would produce more comparatively high molecular weight polymer, which would enlarge MWD to some degree. As a result, MWD from SEC-LALLS suggests that the mechanism of the polymerization in this system change largely in the range of solvent/ non solvent ratio from 2.6–2.9.

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