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Molecular weight and distribution of ultra-high molecular weight poly (p-phenyleneterephalamide)

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Abstract. The measurement of molecular weight (Mw) and distribution for ultra-high molecular weight poly (p-phenyleneterephalamide) (UHMWPPTA) is still a great challenge, because it is hardly dissolved in organic solvents normally to determine its Mw by gel permeation chromatography (GPC). In this paper, n-alkylated PPTAs with different molecular weight (including UHMWPPTA) were prepared by n-alkylation method. As the n-alkylated PPTAs with different length of alkyl chains, they can be dissolved in organic solvents such as tetrahydrofuran (THF). And the longer the alkyl side chains, the solubility is better. Molecular weight and of n-alkylated PPTAs were characterized by GPC with THF as eluent (MWGPC) and distibution was obtained by the weight molecular and number moleculr weight. The molecular weight of PPTA was measured in concentrated sulfuric acid by intrinsic viscosity measurement. The results showed a good linear relationship between them for PPTA with molecular weight from 10900 to 60800, which imply that molecular weight of UHMWPPTA could be measured by the GPC measurement of n-alkylation of PPTA.

1. Introduction

Poly (p-phenyleneterephalamide) PPTA fiber is a typical high performance fiber, with high intensity and modulus, high temperature-resistance and high chemical resistance. The molecular weight and its distribution is one of the key issues for high mechanical properties of aramid fiber. However, characterization of PPTA has been a difficult task, especially the ultra-high molecular weight of PPTA, because PPTA is hardly dissolved in the organic solvents and can only be dissolved in polar solvents, such as N,N-dimethylacetamide (often only in the presence of lithium salt), or strong acid, such as concentrated sulphuric acid or chloro-sulphonic acid[1]. Baird and Arpin et al investigated the intrinsic viscosity of dilute solutions of unfractionated PPTA in concentrated H_2SO_4 using light scattering and obtained the relationships between intrinsic viscosity and weight-average molecular weight of PPTA[2]. B. Chu et al characterized PPTA in concentrated sulphuric acid and determined the molecular weight distribution of PPTA by laser light scattering technique[3-6]. But the concentrated sulphuric acid would make the molecular weight of PPTA reduced and whose corrosive properties require special instruments. And it is hard to obtain the molecular-weight and its distribution from the gel permeation chromatography (GPC) characterization. Ogata et al n-alkylated the PPTA to determine their molecular weight distribution by using GPC with the THF as the solvent[7]. However, the measurement of molecular weight and its distribution of ultra-high molecular weight of PPTA is

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still a great challenge. In this paper, a series of n-alkylated PPTA with different molecular weight (especially UMWPPTA) were prepared by n-alkylation method. The weight-average molecular weight and its distribution of n-alkylated PPTAs were characterized by the GPC measurement of n-alkylated PPTAs in THF (MWGPC) and intrinsic viscosity of PPTAs were measured in concentrated sulfuric acid (ηinh). The results showed a good linear relationship between MWGPC and ηinh for molecular weight from 10900 to 60800, which imply that molecular weight of SHMWPPTA could also be measured by the n-alkylation method.

2. Experimental

2.1. Materials
N-methy-2-pyrrolidone (NMP) and dimethyl sulfoxide(DMSO) were bought from Sinopharm Chemical Reagent Co. Ltd and reduced the water by reacting with calcium hydride under a nitrogen atmosphere and distilled under reduced pressure. LiCl was dried at 120 °C in vacuum. Potassium hydrogen dispersed in mineral oil from 25 to 35wt% purchased from of Acros, was used as received. Alkyl bromides were brought from Sino pharm Chemical Reagent Co. Ltd and were used as received. Ultra high molecular weight PPTA (SHMWPPTA) with intrinsic viscosity 9.0dl•g−1 was kindly produced in the production line of Hebei Silicon Valley Chemical Co, Ltd.

2.2. Preparation of PPTA
PPTA with different molecular weight was prepared by solution polycondensation of the terephthaloyl chloride with p-phenylenediamine in solvent of NMP containing 1.5wt% lithium chloride (LiCl) at -5^{o}C for 20 min, and then at room temperature for 2 hours, then precipitated in water and exhaustively washed with water and dried in vacuum oven at 120^{o}C for 6 hours[7].

2.3. N-alkylation of PPTA
N-alkylated PPTA was synthesized by the metallation reaction of PPTA with potassium in DMSO, followed by reacting with n-alkyl bromide, as shown in the following reaction scheme. Potassium hydrogen (25% suspension in mineral oil) was dissolved in DMSO under a nitrogen atmosphere and a clear solution was obtained. PPTA resin was added into the flask stirring to dissolve. The mixture was stirred for 4~5 h at 40 ^{o}C until all the PPTA had dissolved, giving a transparent deep red coloration, then alkyl bromides was added. After stirring for another time at 40 ^{o}C, n-alkylated PPTA products were precipitated in water. The products were filtered and washed with acetone, alcohol and water several times alternately. Finally, the product was dried in a vacuum oven at 100^{o}C for 8 hours[8].

2.4. Measurements
Intrinsic viscosity of polymers in concentrated sulfuric (98 wt %) acid of concentration (Cs=0.5g/dl^{-1}) at 30 °C were measured by using a Ubbelhode viscometer. The structure of the products was characterized in KBr disks by using a FTIR spectrometer (Nicolet 8700). Element analysis instrument (ElementarVarioELIII) was used to measure the contents of elements C, H, N in different polymers to get the substitution degree of n-alkylation. The substitution degree was calculated as the equation (1) or (2)

$$DS_c = ((7C\%)/(6N\%) - 7)/n \tag{1}$$

$$DS_H = ((14H\%)/(N\%) - 4)/(2n + 1) \tag{2}$$

The molecular weight and distribution of the products were determined by Gel Permeation Chromatography (GPC) (Waters, MA). The test was carried out with a Waters e2695 pump, Waters 2414 refractive index detector and a Styragel HR5E column (5 µm). THFwas used as eluent with a flow rate of 1 ml/min. The sample was made with a concentration of 4 mg/mL, and the injection volume was 30 µl for each sample. Polystyrene (PS) standards were used to calibrate the curve[9].

3. Results and Discussion

3.1. Characterization of n-alkylated PPTA

As reported, the N-alkylation of PPTA can improve its solubility in organic solvent, such as THF. The molecular weight and distribution of PPTA can be measured by the results obtained from GPC. However, what alkyl group is more suitable? Therefore a series of n-alkylated PPTAs with different length of flexible alkyl chains were synthesized to study the effect of alkyl chains on the properties of n-alkylated PPTA. The FTIR spectra of PPTA and n-alkylated PPTA samples are shown in the Figure 1. A typical signal peak attribute to N-H in amide stretching vibration (3300 cm^{-1}) was almost absent in spectra of N-substituted polymers. Compared with curve of c, d, e, the absorption peak in the curve of b is weak, which may be caused by the degree of n-alkylation. The two strong absorption peaks at 2870 cm^{-1} and 2918 cm^{-1} were attributed to H-C- stretching vibrations bond, which demonstrated that distinctive of methylene (-CH_2-) groups in all N-substituted polymers. And the peaks at 1462 cm^{-1} and 725 cm^{-1} also indicated the presence of the alkyl group in N-alkylated polymers. The peaks at 1650 cm^{-1} (C=O stretching), 1540 cm^{-1} (CNH) and 1310 cm^{-1} (CNH) attributed to amide I, II, III bands in PPTA, respectively was reported[10] . In the cases of N-alkylated PPTAs, the amide of N-H at 3300cm^{-1} was almost absent.

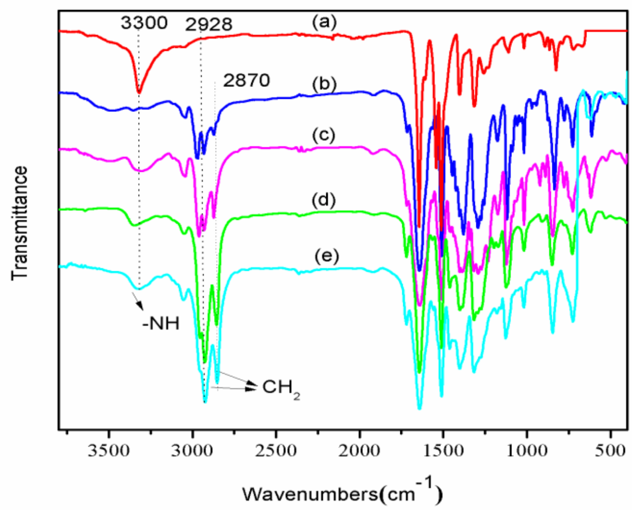

Figure 1. Spectras of PPTA and n-alkylated PPTA: (a) PPTA, (b) n-ethyl PPTA, (c) n-propyl PPTA, (d) n-butyl PPTA, (e) n-decylPPTA.

The solubility of PPTA and N-alkylated PPTAs in organic solvents, such as DMSO, THF and $CHCl_3$ were tested as shown in Table 1. N-alkylated PPTAs can be dissolved in DMSO, THF and $CHCl_3$, no matter what the alkyl groups, which implies that the solubility of n-alkylated PPTA in organic solvent is not affected by length of side chain alkyl group. However, the degree of substitution is reduced with the number of carbon atoms increasing (as shown in the Table 1), when the carbon atoms is 10, the substitution degree is about 85%. But there is no difference of the solubility between n-alkylated PPTA with shorter alkyl and high substitution degree and n-alkylated PPTA with longer alkyl and rather low substitution degree. This may be due to the small molecular chains is easier to react with PPTA in DMSO than long chains, and when a longer side substitution group was introduced in the PPTA backbone chains, hydrogen bondings between backbone molecular chains would be broken. The introduction of side chains decreased the chain-to-chain interactions such as hydrogen bonding between amide groups, which discrease the close packing and regularity of polymer chains, leading to an improvement in solubility and decrease in crystallinity.

Table 1. Degree of substitution and solubility of n-alkylated PPTAs.

Sample	Alkyl chain	Degree of substitution (mole%)	Solubility		
			THF	$CHCl_3$	DMSO
1			-[b]	-	-
2	n-ethyl	98.74	+[a]	+	+
3	n-propyl	97.89	+	+	+
4	n-butyl	95.21	+	+	+
5	N-decyl	85.69	+	+	+

[a] + soluble at room temperature;
[b] - insoluble

3.2. Molecular weight and distribution of n-alkylated PPTA

The metallization reaction of PPTA did not cause any degradation of the original PPTA was reported and there was no change in molecular weight of PPTA, the molecular-weight distribution of n-alkylated PPTA would be equal to the original PPTA even after the n-alkylation reaction[7]. As we found that the n-alkylated PPTA could be dissolved in the THF and $CHCl_3$, therefore GPC measurement was taken by using THF as the solvent. To learn the effect of the length of alkyl chains on the molecular weight and distribution of n-alkylated PPTA, we obtained the molecular weigth (Mn, Mw). The results in the Table 2 showed that the alkyl length has little effect on the results of molecular weight and weight distribution.

Table 2. Results of GPC measurements for n-alkylated PPTA PPTA (η_{inh}=4.6 dl·g^{-1}).

Alkyl chain	Mn (g·mol−1)	Mw (g·mol−1)	Mz (g·mol−1)	Mw/Mn	MwGPC （g·mol−1）
n-propyl	15800	27300	41100	1.73	20100
n-butyl	16300	28500	43900	1.74	19400
n-decyl	20900	35700	66300	1.71	19500

The molecular weight of a series of n-alkylated PPTA samples with different molecular weight were measured by using the GPC measurement in THF and intrinsic viscosity in concentrated sulfuric acid to determine the relationships between intrinsic viscosity and weight molecular weight. Molecular weight of alkylated PPTAs obtained by GPC analysis are plotted in Figure 2, the weight-averaged (Mw) and number-averaged(Mn) molecular weights of these polymers obtained by the GPC and intrinsic viscosity (η_{inh})were summarized in Table 3.

$$[\eta] = \mathbf{K}M_w{}^{\alpha} \tag{3}$$

$$[\eta] = 27\mathbf{64}M_w{}^{1.386} \tag{4}$$

Table 3. Results of GPC measurements for n-alkylated PPTA.

PPTA			N-alkylated PPTA				
No	η_{inh} (dl·g^{-1})	Mw_{GPC} （g·mol^{-1}）	Alkyl chain	Mn （g·mol^{-1}）	Mw （g·mol^{-1}）	Mz （g·mol^{-1}）	Mw/ Mn
1	2.6	10900	n-ethyl	8700	13500	19400	1.56
2	4.6	21100	n-propy 1	16600	31000	49100	1.87

3	5.4	28500	n-butyl	21100	42000	67800	1.99
4	6.8	39100	n-hexyl	32000	64000	100700	2.00
5	9.0	60800	n-hexyl	50400	99600	158500	1.97

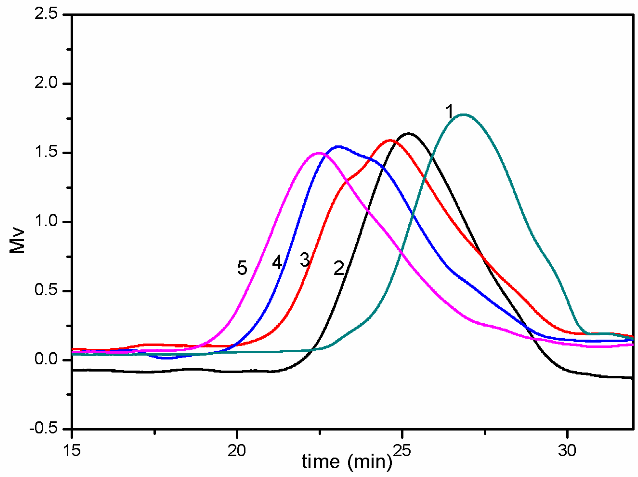

Figure 2. GPC results of n-alkylated PPTA samples with different molecular weight (η_{inh}dl·g^{-1}): 1--2.6, 2--4.6, 3--5.4, 4--6.8, and 5-9.0.

The intrinsic viscosity relates to the viscosity average molecular weight (M_w) according to the Mark-Houwink equation (3).The power exponent (α) and the K are estimated by using the method of least squares linear fit from the log-log plot of M_W and η_{inh}. According to the Figure 3 and we get the slope of the line, and the relationship of intrinsic viscosity of the PPTA and the molecular weight is to the power 1.386, and the constant K is 2764. We obtained the equation (4) which applies to the PPTA with the intrinsic viscosity from 2.6 dl·g^{-1} to 9.0 dl·g^{-1}. Figure 3 showed a good linear relationship between M_{WGPC} and η_{inh} for PPTA between 10900≤ M_W ≤60800. Also ratios of Mw/Mn seemed to increase with increasing viscosities of the PPTA from 2.6 to 6.8 as shown in Table 3, and when the viscosity increase , the ratio is closer to 2.0 , which conforms to Flory's most probable distribution[11], which imply that molecular weight of UHMWPPTA can be measured by the GPC of n-alkylation PPTA.

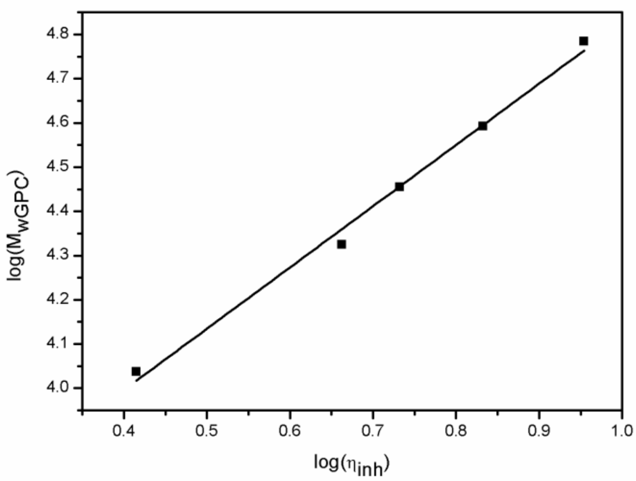

Figure 3. Molecular weight relationship of (M_{wGPC}) characterized by the GPC measurement with n-alkylated PPTAs in THF and (ηinh) intrinsic viscosity measurement of PPTA in concentrated sulfuric acid.

4. Conclusion

N-alkylated PPTA with various molecular weights and various alkyl groups, including ultra-high molecular weight PPTA were synthesized and characterized. The results from FTIR, The solubility characterization showed that the length of alkyl side chains has effect on molecular packing structure and substitution degree of the products. But as the substitution degree is different, there is no effect on their solubility in THF and $CHCl_3$. The weight-average molecular weight and its distribution of n-alkylated PPTA were characterized by GPC measurement in THF, and the intrinsic viscosity measurement of PPTA in concentrated sulfuric acid was measured. The results showed a good linear relationship between M_{WGPC} and ηinh of PPTA with molecular weight from 10900 to 60800, which imply that molecular weight of SHMWPPTA can be measured by the GPC measurement of n-alkylation PPTA.

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