

CHAPTER III

EXPERIMENTAL

3.1 Materials

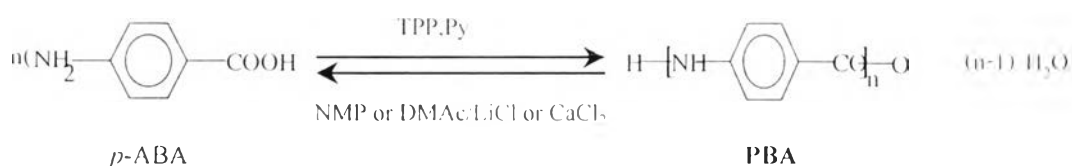
p-Aminobenzoic acid (*p*-ABA) (Fluka) was used as the monomer. It was dried for 1 h at 110°C under vacuum. 1-Methyl-2-pyrrolidone (NMP) (Lab-Scan) and dimethylacetamide (DMAc) (Lab-Scan) were used as the solvent. Anhydrous lithium chloride (LiCl) (AnalaR) and calcium chloride (CaCl₂) (Scharlau) were used to improve the dissolution power of the solvent. They were dried at 325°C for 12 h. Triphenyl phosphite (TPP) (Fluka) was used as the phosphorous compound. Pyridine (Py) (CarLo Erba Reagent) was used as the acid acceptor and reaction acceptor. Methanol (CarLo Erba Reagent) was used to precipitate and clean the synthesized PBA. Concentrated sulfuric acid (96% H₂SO₄) (Merck) was used as the solvent for UV-VIS characterization and weight average molecular weight (M_w) determination. Silicone oil, used as a medium for preparing ER fluid samples, was supplied by Dow Corning (Thailand) Ltd. and used as received. The kinematic viscosity is 100 cSt and the specific gravity is 0.960 at 25°C.

3.2 Methodology

3.2.1 Synthesis of Poly(*p*-benzamide) (PBA)

PBA was synthesized by the direct polycondensation of *p*-aminobenzoic acid (*p*-ABA) (Rivas *et al.*, 1996 and Yamazaki *et al.*, 1975). A three-neck conical flask was used to contain 1-methyl-2-pyrrolidone (NMP) or

dimethyl acetamide(DMAc), pyridine (Py), LiCl or CaCl₂, and *p*-aminobenzoic acid (*p*-ABA). The mixture was stirred until complete dissolution of the solids occurred, and triphenyl phosphite (TPP) was then added into the flask. The resulting solution was stirred at 100°C under nitrogen. The reaction mixture was poured into methanol. The product was filtered under vacuum and then washed with methanol to obtain purified PBA. The synthesis procedure of poly(*p*-benzamide) (PBA) is shown in Scheme 1. The molecular weight was varied by changing the type of solvent and metal halide; the amount of solvent; the reaction time; and the amount of phosphorus compound. The synthesized PBA was characterized by FTIR, UV-VIS and ¹³C-NMR. Weight average molecular weight (M_w) was determined by viscometry at 25°C in 96% H₂SO₄. Thermal behavior was determined by DSC and TGA.



Scheme 1. Synthesis procedure of poly(*p*-benzamide) (PBA).

3.3.2 Preparation of PBA Solution for LC Formation

PBA solution was prepared by directly mixing a weighted amount of dried PBA in suitable solvent as shown in Table 3.1, then by stirring the mixture overnight at room temperature.

3.3.3 Preparation of PBA Dispersion System for ER Fluid

ER fluid based on PBA particles was prepared by dispersing PBA particles in silicone oil by 10 wt% as shown in Table 3.2. The sample was prepared by a dispersion with an ultrasonicator for 30 minutes at 25°C. The

prepared ER fluid was kept in a desiccator prior to use, and redispersed before each experiment.

Table 3.1 Preparation of PBA solution for LC formation

Molecular weight (g/mol)	Solvent	Concentration (wt%)
3,900	4% LiCl in DMAc	4-15
	4% LiCl in NMP	
11,000	4% LiCl in DMAc	1-8
	4% LiCl in NMP	

Table 3.2 Preparation of PBA dispersion ER fluid

Particle type	Concentration (wt%)	Medium
PBA-1	10	Silicone oil

3.3 Characterization

3.3.1 Spectroscopic Characterization

3.3.1.1 Fourier Transform Infrared Spectrometer (FTIR)

FTIR spectra were obtained from a FT-IR spectrometer (Bruker, model Equinox 55/FRA 1065), in order to identify important functional groups of the synthesized PBA. The FTIR experiments were done in a transmission mode with 32 scans at a resolution of $\pm 4 \text{ cm}^{-1}$. The wave number range was $4000\text{-}400 \text{ cm}^{-1}$, using a deuterated triglycine sulfate detector (DTGS)

with a specific detectivity (D^*) of $1 \times 10^4 \text{ cmHz}^{1/2} \text{W}^{-1}$. Optical grade KBr (Carlo Erba Reagent) was used as the background material. The dried KBr was pressed hydraulically into a pellet and quickly taken to the FTIR chamber. The KBr spectra background was collected with 32 scans and a resolution of $\pm 4 \text{ cm}^{-1}$. After obtaining the background spectra, the synthesized PBA was then mixed with dried KBr at an approximate ratio of the synthesized PBA:KBr = 1:20, then ground and transferred to a sample holder using the same procedure as mentioned above.

3.3.1.2 Ultraviolet-Visible Spectrometer (UV-VIS)

UV-VIS spectra were recorded with an UV-VIS spectrometer (Perkin-Elmer, model Lambda 110), in order to observe the absorption wavelengths of the carbonyl group and benzene ring. The experiments were done with a scan speed of 240.00 nm/min and with the slit width of 2.00 nm. A deuterium lamp was used as the light source. The synthesized PBA was dissolved by 3% LiCl in DMAc and 96% H_2SO_4 . It was put into a glass cell. The PBA solution was viewed microscopically for centering and aperturing to a chamber; the transmission light was passed through the sample to record the light transmission as a function of wavelength in the range between 190-500 nm.

3.3.1.3 ^{13}C -Nuclear Magnetic Resonance (^{13}C -NMR)

^{13}C -NMR spectra were used to identify carbon of carbonyl group and benzene ring. ^{13}C -NMR spectra in solution state were recorded at room temperature using a 500 MHz JEOL spectrometer at the Scientific and Instrumental Research Equipment Center, Chulalongkorn University. The experiment was done at 9065 Hz using 4,000 scans, a pulse width of 4.75 sec, a pulse delay of 2.5 sec and a sweep width of 20,000 Hz. Deutero sulfuric acid (98 wt% D_2SO_4 in D_2O) (Aldrich Chemical Company, Inc.) and tetramethylsilane (TMS) were used as standard solvent and standard internal reference.

respectively. ^{13}C -NMR spectra in solid state were recorded at $23 \pm 1^\circ\text{C}$ with cross polarization (CP) and magic angle spinning (MAS) using an Advance 300 MHz Digital NMR spectrometer (Bruker, model DPX-300) at the National Metal and Materials Technology Center.

3.3.2 Thermal Analysis

3.3.2.1 *Differential Scanning Calorimetry (DSC)*

In order to determine the decomposition temperature of PBA, differential scanning calorimetry (Perkins Elmer, model DSC7), was carried out. PBA of 10-20 mg was packed in a aluminum pan, and heated under N_2 flowing in the DSC chamber from 25°C to 600°C at a rate of $10^\circ\text{C}/\text{min}$.

3.3.2.2 *Thermogravimetric Analyzer (TGA)*

In order to determine the thermal stability of PBA, thermogravimetric analyzer (Perkins Elmer, model TGA7), was carried out. 5-10 mg of each PBA was loaded into a Pt pan and heated from 25°C to 650°C at a heating rate of $10^\circ\text{C}/\text{min}$ under N_2 using a flow rate of 20 ml/min.

3.3.3 Viscosity Measurement

For the determination of viscosity values, three viscometers were used. The first and second are the kinematic viscometer number 46460 (C29) size 200 and number 46460 (C40) size 200, respectively. Their viscometer constants were calibrated by 80% aqueous glycerol solution at 25°C as shown in Appendix A. Their measurement range is 20-100 centiStokes. The third is the ubbelohde viscometer number B941 size 100 with the viscometer constant of 0.0163 centiStokes/sec (quoted from company). The measurement range is 3-15 centiStokes.

3.3.3.1 Definition of Terms

The kinematic viscosity is obtained from the measured flow time multiplied by the viscometer constant (K):

$$\nu = Kt \quad (3.1)$$

where ν is kinematic viscosity (centiStoke or mm^2/sec), K is viscometer constant (centiStoke/sec) and t is flow time (sec).

The dynamic viscosity is calculated from the kinematic viscosity and the density of the solvent:

$$\eta = \nu\rho \quad (3.2)$$

where η is dynamic viscosity (centiPoise or $\text{mPa}\cdot\text{sec}$) and ρ is the density of the solvent (g/cm^3).

The dynamic viscosity of the polymer solution and the solvent are η_p and η_0 , respectively. The relative viscosity (η_r) is the ratio of the two and the quantity is larger than unity.

$$\eta_r = \eta_p/\eta_s \quad (3.3)$$

The specific viscosity (η_{sp}) is the relative increment in viscosity of the solution over that of the solvent:

$$\eta_{sp} = (\eta_p - \eta_s) / \eta_s = \eta_r - 1 \quad (3.4)$$

The intrinsic viscosity ($[\eta]$) of a neutral polymer can be determined by extrapolation of Huggins and the Kraemer equations to zero concentration (Campbell *et al.*, 1989).

$$\text{Huggins equation : } \quad \eta_{sp}/C = \eta_R = [\eta] + k'[\eta]^2C \quad (3.5)$$

$$\text{Kraemer equation : } \quad (\ln \eta_r)/C = [\eta] + k''[\eta]^2C \quad (3.6)$$

where η_R is the reduced viscosity, C is the polymer concentration, k' is Huggin's coefficient, and k'' is Kraemer's coefficient.

3.3.3.2 Weight Average Molecular Weight (M_w) Determination

Weight Average Molecular weight (M_w) of PBA were estimated from intrinsic viscosity determinations in 96% H_2SO_4 at 25°C using the Mark-Houwink relation (Zhou *et al.*, 1997):

$$[\eta] = (1.9 \times 10^{-7} \text{ dl/g}) M_w^{1.7} \quad (3.7)$$

3.3.4 Formation of Liquid Crystalline (LC) Phase

The formation of liquid crystalline (LC) phase of PBA solution was determined by measuring the zero-shear rate solution viscosity, η_0 , (poise) versus PBA concentration (wt%) and visual observation through an optical polarizing microscope.

Optical Polarizing Microscope

An optical microscope (Leica, model DMRXE, Xe 75 lamp polarizer), connecting with 12 V 100W transmitted light lamp, was used to observe the LC phase morphology of PBA solution. There are 2 movable eye

lens: 10 and 16 magnifications. It consists of 5 objective lens (10, 20, 40, 50 and 100 magnifications) in which the lens of 50 and 100 are oil objective lens. So the magnification of this microscope can vary from 100 to 1,600 times. The polarizer was set such that the plane of polarization was at 90 degrees to the vertical axis and a prominent axis of the specimen was set parallel to the vertical direction.

3.3.5 Characterization for ER Fluids

3.3.5.1 *Particle Size Analyzer*

Particle size distribution of PBA particles were determined by the particle size analyzer (Malvern, Mastersizer X). The appropriate concentration was adjusted by adding the particles slowly, little at a time, allowing time for the sample to mix to through the system, and then observing from the obscuration value (10-40 %). A suitable measurement time was between 10 to 30 seconds depending on the size distribution.

3.3.5.2 *Scanning Electron Microscope (SEM)*

Scanning electron micrographs were taken out to determine the morphology of PBA particles. SEM digitized photographs were obtained from Scanning Electron Microscope (JOEL) at the Scientific and Instrumental Research Equipment Center, Chulalongkorn University, with a magnification range of 35-100,000. Each sample was stickled on a brass-stub by using an adhesive tape and the surface of the sample was coated with a thin Au film, produced by a vacuum evaporation. The sample was placed into the specimen stage inside the microscope then the pictures were collected by using acceleration voltage 15 kV with the magnification of 15,000 times.

3.4 ER Measurements

A fluid rheometer (Rheometric Scientific Inc., model ARES), was used to measure rheological properties of the ER fluids in oscillatory modes. It is a strain controlled instrument; the base system consists of a test station, the power chassis, and the host computer. In this work, a modified cone and plate fixture (as shown in Appendix D) was designed and fabricated; it has a diameter of 50 mm, a cone angle of 0.0396° and the gap size of 0.063 ± 1 mm. This apparatus consists of 2 circular disks, a stationary upper plate and oscillating lower plate were made from copper and connected to a DC voltage generator. Each sample was plated between these 2 plates. The bottom plate was oscillated at a frequency with a specified strain while the top plate was held stationary and the torque was measured by a transducer. Torque can be converted to shear stress and other viscoelastic properties such as storage modulus, loss modulus, tangent, etc.

The electric field strengths (E) (0, 0.02, 0.25, 0.5, 1 and 2 kV/mm) were applied to the fluids for 5 minutes in order to obtain an equilibrium chain-like or columnar structure before each measurement. All measurements were performed at $25 \pm 0.1^\circ\text{C}$ and carried out at least two or three times. In order to obtain reproducible data, the ER fluid was redispersed by a dispersion with an ultrasonicator for 30 minutes at 25°C before each measurement.

3.4.1 Dynamic Strain Sweep Default Test

Usually, the rheological properties of viscoelastic material are independent of strain up to a critical strain. Beyond this critical strain level, the material behavior is nonlinear and the moduli decline. Thus, measurement of the strain amplitude dependence of the storage and loss moduli was the first step

taken in characterizing the viscoelastic behavior. A strain sweep test was used to establish the extent of the linearity of the viscoelastic response of a material.

The experiments were carried out at the frequency of 1 rad/sec. Initial strain and final strain were equal to 0.02 and 1.400 %, respectively. For this experiments, the level of strain was determined in order to ensure that all measurements were made within the linear viscoelastic regime.

3.4.2 Dynamic Frequency Sweep Default Test

After the fluid's linear viscoelastic regime has been established by a strain sweep, its structure can be further characterized using a frequency sweep at a strain below the critical strain. This provides more information about rheological properties at difference length or times scales. In the dynamic frequency sweep mode, measurements were made over a range of oscillation frequencies at a constant oscillation amplitude and temperature.

Initial frequency and final frequency were set to be equal to 0.05 and 100 rad/sec, respectively. The value of strain used was chosen be within the linear viscoelastic regime. In these measurements, G' , G'' , and η' were determine as a function of frequency.