

**SYNTHESIS AND CHARACTERIZATION OF POLY(*P*-BENZAMIDE)  
FOR ELECTORRHEOLOGICAL FLUIDS**

Ms. Sutatip Limsuwan

A Thesis Submitted in Partial Fulfillment of the Requirements  
For the Degree of Master of Science  
The Petroleum and Petrochemical College, Chulalongkorn University  
In Academic Partnership with  
The University of Michigan, The University of Oklahoma,  
and Case Western Reserve University

2001

ISBN 974-346-250-3

I 19758 273

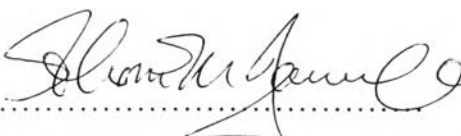
**Thesis Title** : Synthesis and Characterization of Poly(*p*-benzamide) for  
Electrorheological Fluids  
**By** : Ms. Sutatip Limsuwan  
**Program** : Polymer Science  
**Thesis Advisors** : Prof. Alexander M. Jamieson  
Assoc. Prof. Anuvat Sirivat


---

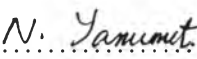
Accepted by the Petroleum and Petrochemical College, Chulalongkorn  
University, in partial fulfillment of the requirements for the Degree of Master  
of Science.

  
..... College Director  
(Prof. Somchai Osuwan)

**Thesis Committee:**

  
.....  
(Prof. Alexander M. Jamieson)

  
.....  
(Assoc. Prof. Anuvat Sirivat)

  
.....  
(Assoc. Prof. Nantaya Yanumet)

**ABSTRACT**

4172030063 : POLYMER SCIENCE PROGRAM

KEYWORD : Poly(*p*-benzamide) (PBA)/ Lyotropic Liquid Crystalline (LC) Polymers/ Electrorheological (ER) Fluids/ Suspension  
Sutatip Limsuwan: Synthesis and Characterization of poly (*p*-benzamide) for Electrorheological Fluids.

Thesis Advisors: Prof. Alexander M. Jamieson and Assoc.

Prof. Anuvat Sirivat, 153 pp. ISBN 974-346-250-3

The particle dispersion type of electrorheological (ER) fluids, typically composed of small particles dispersed in a nonconducting liquid, are fascinating materials whose structure and rheological properties can be dramatically altered by the application of an external electric field. In this study, poly(*p*-benzamide) (PBA) particles, synthesized by the direct polycondensation of *p*-aminobenzoic acid (*p*-ABA), were used as the dispersed phase and silicone oil as the medium. PBA were successfully synthesized to yield different molecular weights by changing the types of solvent and metal halide, and the amount of the phosphorus compound used. Thermal analysis indicates that the PBA are thermally stable up to around 500<sup>0</sup>C. PBA of 3,900 and 11,000 g/mol form nematic liquid crystal (LC) phases in 4%LiCl/DMAc and 4%LiCl/NMP solvents at very low concentration compared to other lyotropic LC polymers. Successful study of ER behavior of the PBA solution in the LC state was not possible due to electrolytic reaction at the electrodes. Particulate dispersion of PBA in silicone oil was found to exhibit a pronounced ER response. In the linear viscoelastic region, there is a critical electric field strength for the transition from liquid to solid state. The magnitude of the ER effect in the linear viscoelastic region is larger than that in the nonlinear due to smaller deformation of ER-induced network structures.

## บทคัดย่อ

สุทธาทิพย์ ลิ้มสุวรรณ : การสังเคราะห์และ วิเคราะห์ พอลิพาราเบนซาไมด์ สำหรับ  
ของไหลอิเล็กโตรรีโอโลจิคอล (Synthesis and Characterization of Poly(*p*-benzamide) for  
Electrorheological Fluids) อาจารย์ที่ปรึกษา : ศ. ดร. อเล็กซานเดอร์ เอ็ม จิมมีสัน (Prof.  
Alexander M. Jameison) และ รศ.ดร. อนุวัฒน์ ศรีวัฒน์ 153 หน้า ISBN 974-346-250-3

ของไหลอิเล็กโตรรีโอโลจิคอลชนิดสารแขวนลอย ประกอบด้วย อนุภาคขนาดเล็กกระจายตัวอยู่ในตัวกลางซึ่งไม่นำไฟฟ้า ของไหลนี้มีคุณสมบัติพิเศษ คือ เมื่อได้รับการเหนี่ยวนำจากสนามไฟฟ้า อนุภาคจะมีการเรียงตัวเป็นโครงสร้างที่มีลักษณะเป็นสายโซ่ในทิศทางขนานกับทิศทางของสนามไฟฟ้า ซึ่งอนุภาคในสายโซ่เหล่านี้ยึดติดกันด้วยแรงไฟฟ้าสถิตย์ ทำให้สมบัติทางวิทยากระแสมีการเปลี่ยนแปลง ในการทดลองนี้ใช้อนุภาคพอลิพาราเบนซาไมด์กระจายตัวอยู่ในน้ำมันซิลิโคน จากการศึกษาพบว่า พอลิพาราเบนซาไมด์สามารถสังเคราะห์ได้น้ำหนักโมเลกุลที่แตกต่างกันโดยการเปลี่ยนชนิดของตัวทำละลายและเกลือของโลหะ และปริมาณของฟอสฟอรัสที่ใช้ พอลิพาราเบนซาไมด์มีความเสถียรต่อความร้อนถึงอุณหภูมิประมาณ 500 องศาเซลเซียส และสามารถสร้างลิกวิดคริสตัลได้ที่มีความเข้มข้นต่ำมาก การศึกษาสมบัติทางวิทยากระแสของสารละลายพอลิพาราเบนซาไมด์ในสถานะลิกวิดคริสตัลไม่ประสบความสำเร็จ เนื่องจากเกิดปฏิกิริยาไฟฟ้าเคมีขึ้นที่ขั้วไฟฟ้า สมบัติทางวิทยากระแสที่ได้จากพอลิพาราเบนซาไมด์ในสถานะสารแขวนลอย พบว่า ในช่วงความเครียดต่ำมีความแรงสนามไฟฟ้าที่เป็นจุดวิกฤตในการเปลี่ยนรูปสารจากสถานะของเหลวไปเป็นของแข็ง ในช่วงความเครียดต่ำลอสสมอดูลัสมีค่ามากกว่าในช่วงความเครียดสูง เนื่องจากโครงสร้างสายโซ่ของอนุภาคถูกทำลายน้อยกว่า

## ACKNOWLEDGEMENTS

I would like to express my gratitude to the Petroleum and Petrochemical College and the Thailand Research Fund for giving a scholarship during the two academic years. I would like to give thanks to all the professors who gave me the valuable knowledge in the Polymer science Program at the Petroleum and Petrochemical College, Chulalongkorn University.

I would like to express my sincere gratitude to my advisor, Associate Professor Anuvat Sirivat, who originated this thesis work. In addition, he gave me guidance, directions, helpful suggestions of this work and proof-reading of this thesis writing. I would like to give special thanks to my co-advisor, Professor Alexander M. Jameison of Case Western University, Cleveland, Ohio, USA for his valuable suggestions. In addition, he gave me guidance, directions of this work and proof-reading of this thesis writing. I would also like to thank Assoc. Prof. Nantaya Yanumet who was a thesis committee member.

My thanks are also extended to all of the staffs of the Petroleum and Petrochemical College for giving the permission to freely use the research facilities.

Finally, I wish to express my deepest gratitude to my family and my friends for their external love, understanding and generous encouragement.

## TABLE OF CONTENTS

	<b>PAGE</b>
Title Page	ii
Abstract (in English)	iii
Abstract (in Thai)	iv
Acknowledgements	v
Table of Contents	vi
List of Tables	ix
List of Figures	x
 <b>CHAPTER</b>	
<b>I</b>	
<b>INTRODUCTION</b>	1
1.1 Background	1
1.1.1 What are Electrorheological Fluids?	1
1.1.2 Desired Properties of ER Fluids	2
1.1.3 The ER Phenomena of Particle Dispersion	4
1.1.4 Liquid crystalline (LC) Polymers	5
1.1.5 The ER Phenomena of LC Polymers	8
1.2 Applications	10
1.3 Objectives	11
 <b>II</b>	
<b>LITERATURE SURVEY</b>	12
2.1 The Particle Dispersion ER Fluids	12
2.2 The Homogeneous ER Fluids	16
 <b>III</b>	
<b>EXPERIMENTAL</b>	19
3.1 Materials	19
3.2 Methodology	19
3.2.1 Synthesis of Poly( <i>p</i> -benzamide) (PBA)	19

<b>CHAPTER</b>	<b>PAGE</b>
3.2.2 Preparation of PBA Solution for LC Formation	20
3.2.3 Preparation of PBA Dispersion System for ER Fluid	20
3.3 Characterization	21
3.3.1 Spectroscopic Characterization	21
3.3.2 Thermal Analysis	23
3.3.3 Viscosity Measurement	23
3.3.4 Formation of Liquid Crystalline (LC) Phase	25
3.3.5 Characterization for ER Fluids	26
3.4 ER Measurements	
3.4.1 Dynamic Strain Sweep Default Test	27
3.4.2 Dynamic Frequency Sweep Default Test	28
<b>IV RESULTS AND DISCUSSION</b>	<b>29</b>
4.1 Characterization of Synthesized PBA	29
4.1.1 Molecular Weight Variation	29
4.1.2 Spectroscopic Characterization	36
4.1.3 Thermal Analysis	42
4.2 The Formation of Liquid Crystalline Phase of PBA Solution	44
4.2.1 The Effect of Polymer Structure	44
4.2.2 The Effect of Molecular Weight	59
4.2.3 The Effect of Polymer-Solvent Interaction	62
4.3 ER Measurement of PBA-1 Suspension	70
4.3.1 Effect of Strain Amplitude	71
4.3.2 Transient Response	75
4.3.3 Effect of Frequency	76

<b>CHAPTER</b>		<b>PAGE</b>
<b>IV</b>	<b>CONCLUSIONS</b>	87
	<b>REFERENCES</b>	89
	<b>APPENDICES</b>	94
	Appendix A	94
	Appendix B	96
	Appendix C	116
	Appendix D	125
	Appendix E	129
	Appendix F	136
	<b>CURRICULUM VITAE</b>	138



**LIST OF TABLES**

<b>TABLE</b>		<b>PAGE</b>
1.1	Electrorheological properties and corresponding technical applications	3
3.1	Preparation of PBA solution for LC formation	21
3.2	Preparation of PBA dispersion ER fluid	21
4.1	Summary of molecular weight variation of PBA	32
4.2	Molecular weight of PBA in dilute systems	33
4.3	Remarks and assignments of peaks from FTIR spectra for PBA	38
4.4	Remarks and assignments of peaks from the solution state $^{13}\text{C}$ -NMR spectrum for PBA-1	39

## LIST OF FIGURES

FIGURE	PAGE
1.1 (a) In the presence of an electric field, the particles in an electrorheological (ER) fluid form chains or fibrillated structures (b) Mechanism of fibrillation and alignment of dielectric particles. The interaction of these dipoles cause attraction, repulsion, rotation, and alignment of particles, creating chains that align with the applied electric field	4
1.2 Schematic representation of the domain theory	6
1.3 The graph showing the viscosity-concentration relationship of a solution of poly( <i>p</i> -phenylene terephthalamide) (PPTA) with a moderate molecular weight in sulfuric acid	6
1.4 Repeating unit of poly( <i>p</i> -benzamide)	8
1.5 Presumed orientation of conventional liquid crystals and LC polymers under applied electric field: (a) low molecular weight liquid crystal; (b) liquid crystalline polymer	9
1.6 Miesowicz viscosities: (a) director perpendicular to flow direction and velocity gradient; (b) director parallel to flow direction; (c) director parallel to velocity gradient ( $\eta_a, \eta_b < \eta_c$ )	10

FIGURE	PAGE
4.1 The relationship between molecular weight (MW), degree of polymerization ( $X_n$ ), and reaction time (t) of condensation polymerization when $X_n$ is equal to number average molecular weight ( $M_n$ ) over molecular weight of repeating unit	31
4.2 $\eta_{sp}/C$ and $(\ln \eta_r)/C$ versus PBA concentration of PBA-1 at 25 <sup>0</sup> C	34
4.3 $\eta_{sp}/C$ and $(\ln \eta_r)/C$ versus PBA concentration of PBA-9 at 25 <sup>0</sup> C	34
4.4 $\eta_{sp}/C$ and $(\ln \eta_r)/C$ versus PBA concentration of PBA-2 at 25 <sup>0</sup> C	35
4.5 The FTIR spectra of PBA: (a) PBA-1, (b) PBA-2, and (c) PBA-9	36
4.6 The UV-VIS spectra of PBA in 96% H <sub>2</sub> SO <sub>4</sub> : (a) PBA-1 (10 ppm), (b) PBA-2 (15 ppm), and (c) PBA-9 (18 ppm)	37
4.7 The UV-VIS spectra of PBA in 3%LiCl/DMAc: (a) PBA-1 (16 ppm), (b) PBA-2 (10 ppm), and (c) PBA-9 (18 ppm)	37
4.8 The <sup>13</sup> C-NMR spectrum of PBA-1 in 98% D <sub>2</sub> SO <sub>4</sub>	39
4.9 The solid state <sup>13</sup> C CP/MAS NMR spectrum of PBA-1	40
4.10 The solid state <sup>13</sup> C CP/MAS NMR spectrum of PBA-2	40
4.11 The solid state <sup>13</sup> C CP/MAS NMR spectrum of PBA-9	41
4.12 The DSC thermograms of PBA	42
4.13 The TGA thermograms of PBA	43
4.14 The zero-shear rate viscosity of PBA-2 in 4%LiCl/DMAc at 25 <sup>0</sup> C	47

<b>FIGURE</b>	<b>PAGE</b>
4.15 The zero-shear rate viscosity of PBA-2 in 4%LiCl/NMP at 25 <sup>0</sup> C	47
4.16 The zero-shear rate viscosity of PBA-1 in 4%LiCl/DMAc at 25 <sup>0</sup> C	48
4.17 The zero-shear rate viscosity of PBA-1 in 4%LiCl/NMP at 25 <sup>0</sup> C	48
4.18 Structure of (a) nematic , (b) cholesteric , and (c) smectic C phase	50
4.19 A polarized light micrograph of a sectioned nematic thermotropic LC polymer reveals a schlieren texture	50
4.20 Polarized optical micrographs of PBA-2 in 4%LiCl/DMAc at 25 <sup>0</sup> C with different concentrations: (a) Isotropic phase, C = 1.01-4.00 wt%; (b) Biphasic phase, C = 4.26-5.15 wt%; (c) Biphasic phase, C = 5.55 wt%; and (d) Fully LC phase, C = 6.10-8.10 wt%	53
4.21 Polarized optical micrographs of PBA-2 in 4%LiCl/NMP at 25 <sup>0</sup> C with different concentrations: (a) Isotropic phase, C = 1.01-4.02 wt%; (b) Biphasic phase, C = 4.25-5.12 wt%; (c) Biphasic phase, C = 5.34 wt%; and (d) Fully LC phase, C = 5.61-8.06 wt%	56

FIGURE	PAGE
4.22 Polarized optical micrographs of PBA-1 in 4%LiCl/DMAc at 25 <sup>0</sup> C with different concentrations: (a) Isotropic phase, C = 4.01-8.05 wt%; (b) Biphasic phase, C = 9.99-13.04 wt%; (c) Biphasic phase, C = 13.50 wt%; and (d) Fully LC phase, C = 14.16 and 15.06 wt%	59
4.23 Polarized optical micrographs of PBA-1 in 4%LiCl/NMP at 25 <sup>0</sup> C with different concentrations: (a) Isotropic phase, C = 4.00-8.08 wt%; (b) Biphasic phase, C = 10.13-12.89 wt%; (c) Biphasic phase, C = 13.20 wt%; and (d) Fully LC phase, C = 13.51-14.15 wt%	62
4.24 The zero-shear rate viscosity of PBA-1 and PBA-2 in 4%LiCl/DMAc at 25 <sup>0</sup> C	64
4.25 The zero-shear rate viscosity of PBA-1 and PBA-2 in 4%LiCl/NMP at 25 <sup>0</sup> C	64
4.26 Postulated structure of solvated PBA in (a) LiCl/DMAc and (b) LiCl/NMP solvents	63
4.27 The zero-shear rate viscosity of PBA-1 in 4%LiCl/DMAc and 4%LiCl/NMP solvents at 25 <sup>0</sup> C	65
4.28 The zero-shear rate viscosity of PBA-2 in 4%LiCl/DMAc and 4%LiCl/NMP solvents at 25 <sup>0</sup> C	65
4.29 Typical flow curve of LC polymer	66
4.30 Some flow curves of PBA-2 in 4%LiCl/DMAc	67
4.31 Some flow curves of PBA-2 in 4%LiCl/NMP	67
4.32 Some flow curves of PBA-1 in 4%LiCl/DMAc	68
4.33 Some flow curves of PBA-1 in 4%LiCl/NMP	68

FIGURE	PAGE
4.34 G' and G'' dependence on %strain of 10 wt% PBA-1 suspension at the electric field strength of 2 kV/mm	71
4.35 G' and G'' dependence on %strain of 10 wt% PBA-1 suspension at the electric field strength of 1 kV/mm	72
4.36 G' and G'' dependence on %strain of 10 wt% PBA-1 suspension at the electric field strength of 0.5 kV/mm	72
4.37 G' and G'' dependence on %strain of 10 wt% PBA-1 suspension at the electric field strength of 0.4 kV/mm	73
4.38 G' and G'' dependence on %strain of 10 wt% PBA-1 suspension at the electric field strength of 0.25 kV/mm	73
4.39 G' and G'' dependence on %strain of 10 wt% PBA-1 suspension at the electric field strength of 0.02 kV/mm	74
4.40 G' and G'' dependence on %strain of 10 wt% PBA-1 suspension at the electric field strength of 0 kV/mm	74
4.41 G' and G'' dependence of the 10 wt% PBA-1 suspension at the electric step field strength of 2 kV/mm and frequency of 1 rad/s	76
4.42 G' dependence on frequency of 10 wt% PBA-1 suspension at various electric field strengths in the linear viscoelastic regime	78
4.43 G'' dependence on frequency of 10 wt% PBA-1 suspension at various electric field strengths in the linear viscoelastic regime	79
4.44 G' and G'' dependence on frequency of 10 wt% PBA-1 suspension in the linear viscoelastic regime at electric field strengths of 0.4 kV/mm	80

FIGURE	PAGE
4.45 $G'$ and $G''$ dependence on frequency of 10 wt% PBA-1 suspension in the linear viscoelastic regime at electric field strengths of 0.5 kV/mm	80
4.46 $G'$ and $G''$ dependence on frequency of 10 wt% PBA-1 suspension in the linear viscoelastic regime at electric field strengths of 1 kV/mm	81
4.47 $G'$ and $G''$ dependence on frequency of 10 wt% PBA-1 suspension in the linear viscoelastic regime at electric field strengths of 2 kV/mm	81
4.48 $\tan \delta$ dependence on frequency of 10 wt% PBA-1 suspension at various electric field strengths in the linear viscoelastic regime	82
4.49 $[G']_0$ and $[G'']_0$ at various electric field strengths in the linear viscoelastic regime	83
4.50 $G''$ dependence on frequency of 10 wt% PBA-1 suspension at various electric field strengths in the nonlinear viscoelastic regime	85
4.51 $[G'']_0$ at various electric field strengths in the nonlinear viscoelastic regime	86