

A Study on the Synthesis and Application of an Inverse Emulsion of Amphoteric Polyacrylamide as a Retention Aid in Papermaking

SHAOJIE LU,¹ RUIXIAN LIU,¹ XIMING SUN²

¹ School of Science, Tianjin University, Tianjin 300072, People's Republic of China

² School of Chemical Engineering, Tianjin University, Tianjin 300072, People's Republic of China

Received 6 April 2001; accepted 26 July 2001

ABSTRACT: A series of amphoteric polyacrylamides with different molecular weights and charges were prepared by the copolymerization of acrylamide with sodium acrylate and a subsequent Mannich reaction. The copolymerization was carried out with a redox initiation system via inverse emulsion polymerization. Reaction conditions, factors affecting emulsion stability, and applications as retention aids in papermaking were studied. Experiments showed that an ideal retention aid and a stable latex with wheat-straw pulp of a shorter fiber length could be obtained under the following conditions: the acrylamide/formaldehyde/dimethylamine ratio was 1/1/1.2, a medium of aldehyde and amine was prepared first and then was dropped into an inverse emulsion of anionic polyacrylamide, the reaction temperature was 45°C, the reaction time was 4 h, and the pH was 5.0. When the anionic degree was 5%, the cationic degree was greater than 20%, the molecular weight was between 2 and 3 million, and the filler retention was higher. © 2002 John Wiley & Sons, Inc. *J Appl Polym Sci* 84: 343–350, 2002; DOI 10.1002/app.10340

Key words: inverse emulsion polymerization; copolymerization; water-soluble polymers

INTRODUCTION

Polyampholyte is a type of high molecular weight compound that is soluble in water. In comparison with anionic and cationic polymers, it is unique. When the number of cationic groups is the same as the number of anionic groups, polyampholyte produces an apparent antipolyelectrolyte effect. The viscosity of polyampholyte increases with the increasing concentration of a salt solution.^{1,2}

Amphoteric polyacrylamide was prepared by the γ -radiation-induced template polymerization

of acrylic acid and dimethylamino ethyl methacrylate on poly(amido amines) and poly(acrylamide acrylic acid), respectively. These amphoteric polyacrylamides were used for the treatment of wastewater.^{3–6} Polyampholyte is also widely used in the petroleum and paper industries and for environmental protection.^{7–9}

A series of amphoteric polyacrylamides with different molecular weights and charges were prepared as retention aids with bleached wheat-straw pulp characterized by shorter fiber length, weak strength, and poor drainage. Better products were selected and used under different conditions. The copolymers were synthesized in inverse emulsions, which overcame such weaknesses as low solid contents, low solubility, and

Correspondence to: S. Lu.

Journal of Applied Polymer Science, Vol. 84, 343–350 (2002)
© 2002 John Wiley & Sons, Inc.

easy crosslinking in water-solution polymerizations.¹⁰ This article discusses the preparation methods and applied conditions for retention aids in papermaking.

EXPERIMENTAL

Materials

The materials used in this study were purchased as follows: acrylamide from Jiang Xi Agriculture and Science Chemical Industry, Ltd. (Nan Chang, China); acrylic acid from Beijing Oriental Chemical Industry, Ltd. (Beijing, China); white oil (liquid paraffin) from Tianjin Zhen Da Chemical Industry, Ltd. (Tianjin, China); and the rest from Tianjing Plant of Agents (Tianjin, China). The emulsifier, formaldehyde, ammonium persulfate, and urea were reagent-grade chemicals; the dimethylamine solution was at a high concentration. Acrylic acid was distilled under reduced pressure before use, and other materials were used directly.

Preparation of Anionic Polyacrylamide

The preparation was carried out in a four-necked, round-bottom flask with a stirrer, a thermometer, and a nitrogen gas inlet. About 170 mL of the white oil and the emulsifier mixed with span 80 and op-4 were added. The concentration was 0.06 (w/w) for the continuous phase. The mixture was heated in a water bath, which was stirred until the emulsifier was dissolved in the continuous phase. Acrylamide and sodium acrylate, which was prepared by the neutralization of acrylic acid with sodium hydroxide, were added. In this system, there were 24.50 g of acrylic acid, 13.80 g of NaOH, and 37.00 g of acrylamide. The acrylate acid/NaOH molar ratio was 1/1, and the acrylamide/sodium acrylate ratio depended on the needed anionic degree. The composition of the anionic polyacrylamide [poly(acrylamide sodium acrylate)] was calculated from the acrylamide/sodium acrylate molar ratio in the comonomer feed. In the reaction, ammonium persulfate and urea were used as the complex initiation system. They were used at concentrations of 0.0005 (w/w) and 0.004 (w/w) of the monomers, respectively. The reaction lasted 4 h at 60°C.

Preparation of Amphoteric Polyacrylamide

The preparation of amphoteric polyacrylamide required the preparation of a medium of aldehyde

and amine. The process took place inside a four-necked, round-bottom flask with a mechanical stirrer. First, a dimethylamine solution was added at a low temperature, and then a formaldehyde solution was added. The reaction lasted 30 min at 15–20°C. Under the conditions of room temperature and a weak acid, a medium of aldehyde and amine was dropped into an emulsion of anionic polyacrylamide. The temperature was raised to 45°C, and the reaction lasted 4 h.

Measurements of the Degree of Amination

The amination produced a quaternary ammonium salt with chlorine through the Mannich reaction¹¹ with anionic polyacrylamide. The amination degree of the product could be calculated from chlorine analysis.

Dry amphoteric polyacrylamide (0.2 g) was dissolved in distilled water, and 1 mL of a potassium chromate solution was added. A silver nitrate solution (0.05 mol) was used for titration until the solution became brick red. The following formula was used to calculate the amination degree of the product:

Amination Degree (wt %)

$$= 128 \times 0.05 \times \frac{(V - V_0)}{1000 \times W} \times 100\%$$

where V and V_0 are the volumes of the consumed silver nitrate for the sample and blank tests, respectively, and W is the weight of the sample. The molecular weight of dimethylamino methyl acrylamide is 128.

Measurements of the Molecular Weight and Anionic Degree

The molecular weight and anionic degree were measured with reference to GB 12005.6-89 (National Standard of China).

IR Analysis of Amphoteric Polyacrylamide

The prepared polyampholyte was precipitated into ethanol, and the precipitate was washed with acetone to remove the unreacted monomer and oil phase. The product was dried at 40°C and then analyzed via an IR spectrum.

Measurements of the Filler Retention

The retention is a percentage of the weight of the remaining composition when a suspension of pulp

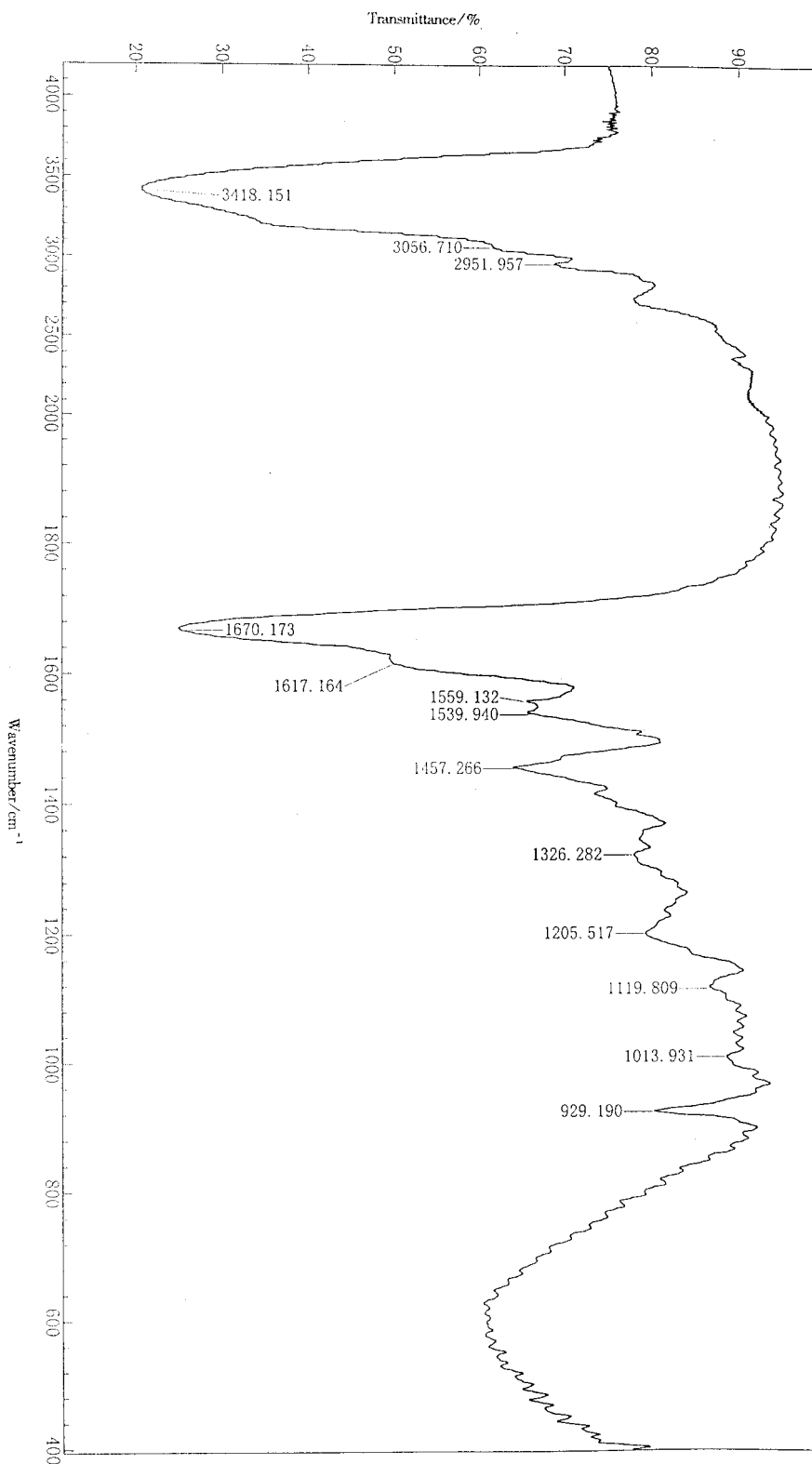


Figure 1 IR spectrum of amphoteric polyacrylamide.

Table I IR Analysis Result of Sample

Group	Type of Vibration		Wave Number (cm ⁻¹) (Analysis Value)	Wave Number (cm ⁻¹) (Value in Reference)
—CONH—	C=O	stretching	1670.2	1690–1650
—CONH—	N—H	stretching	3418.2	3500–3300
—CH ₂ N(CH ₃) ₂	N—C	stretching	1205.5	1230–1030
—COONa	C=O	stretching	1559.1	1610–1550

is filtered through a 200-mesh screen. Filler retention is expressed as¹²

$$Rt = \frac{0.94(A - C)(1 - B - D)}{(B - C)(1 - A - D)}$$

where *A* is the ash weight of the paper, *B* is the ash weight of the papermaking material, *C* is the ash weight of the fiber, and *D* is the lost weight after the sintering of talcum powder.

RESULTS AND DISCUSSION

Proof of the Amphoteric Polyacrylamide Structure

Figure 1 shows the IR spectrum of amphoteric polyacrylamide. The IR results for the sample listed in Table I show that characteristic —COONa, —CONH—, and —CH₂N(CH₃)₂ groups existed in the product.

Factors Affecting the Mannich Reaction

Effect of the Added Materials

The usual procedure for the Mannich reaction of polyacrylamide was as follows. Formaldehyde was added to the system and reacted with polyacrylamide for a period of time; a dimethylamine solution was added afterward. The conversion ratio by this method was usually low, and the reaction was incomplete. When the formaldehyde and dimethylamine ratios were high, the conversion ratio was no more than 50%. For this reason, we used a medium of aldehyde and amine instead. Its conversion ratio could reach 80% or more. The medium of aldehyde and amine was dropped into an inverse emulsion of anionic polyacrylamide. After comparing the two aforementioned ways of adding materials, we found that the amination degree of the latter was higher, that the system was more stable, and that the dissolution was quicker. The reaction mechanism is shown in

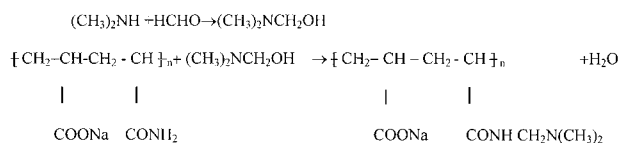
Scheme 1. Formaldehyde and dimethylamine reacted quickly and produced hydroxyl methyl dimethylamine in the reaction system. The conversion ratio of formaldehyde was relatively high, so the content of free formaldehyde in the system was low. Even if hydroxyl methyl polyacrylamide was produced from the reaction, its concentration was low. As a result, the possibility of crosslinking between molecules was small.

However, formaldehyde and polyacrylamide could produce hydroxyl methyl polyacrylamide, the system more easily resulted in crosslinking, and the product became difficult to dissolve. The reaction mechanism is shown in Scheme 2.

Effect of the Reaction Temperature and Time

Temperature control of the reaction of aldehyde and amine was important. If the temperature was too high, amine was oxygenated and turned yellow, and the recovery rate of dimethylamino methanol was low. If the temperature was too low, it took too much time. The appropriate temperature was 15–20°C. The reaction speed of aldehyde and amine was fast. It usually took 20 min for a balance to be reached (see Fig. 2). Therefore, it was meaningless to prolong the reaction time. Usually, the reaction time was within 30 min.

The Mannich reaction of polyacrylamide was also affected by the reaction temperature. At different temperatures, the amination degree versus time is shown in Figure 3. The reaction speed and amination degree increased along with the temperature in the initial stages. When the reaction

**Scheme 1**

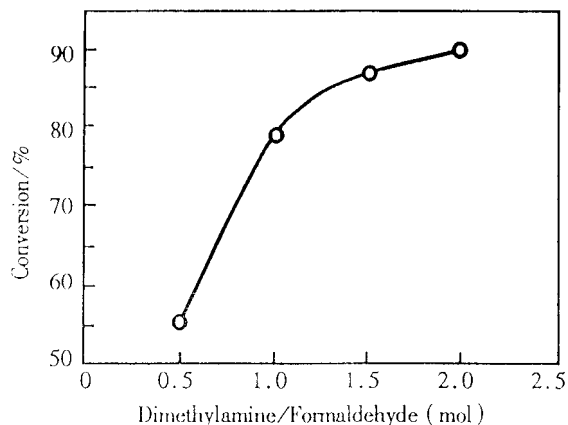


Figure 4 Effect of the dimethylamine/formaldehyde ratio on conversion. The reaction time was 20 min, and the reaction temperature was 20°C.

formaldehyde, the amination degree increased. However, when the molar ratio of formaldehyde to acrylamide was greater than 1, the amination degree was difficult to increase further. Therefore, the appropriate molar ratio of acrylamide to formaldehyde was 1/1.

Effect of pH

The effect of the pH value on acrylamide/formaldehyde crosslinking has been reported.¹³ In brief, hydroxyl methylation between amide and formaldehyde can produce *N*-hydroxyl methyl ($-\text{NHCH}_2\text{OH}$). This reaction easily occurs in neutral and basic environments. When the *N*-hydroxyl methyl activation group is introduced into a macromolecular chain, a macromolecular network structure forms with a bridge based on $-\text{CH}_2-\text{O}-\text{CH}_2-$. Therefore, the correct choice of the aldehyde/amine ratio and control of the pH value could prevent the occurrence of crosslinking. The reaction was chosen under a weak acidic

Table II Effect of Aldehyde/Amine Ratio on the Stability of the Product

Amine/Aldehyde (mol)	Stability
1.0	Gel occurred after 24 h
1.1	Gel occurred after 1 week
1.2	Stable
1.3	Gel occurred after 1 week

Oil/water (v/v) = 1.1; emulsifier = 6 wt %; temperature = 45°C; pH = 5.0.

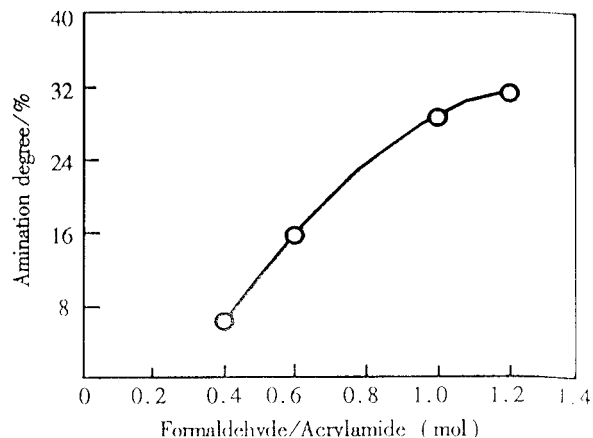


Figure 5 Effect of the formaldehyde/acrylamide ratio on the degree of amination. The acrylamide concentration was 0.52 mol L⁻¹, the reaction temperature was 45°C, the reaction time was 4 h, and the formaldehyde/dimethylamine molar ratio was 1/1.2.

medium. The product was more stable when the pH was 5.0 (see Table III).

Effect of the Properties of Amphoteric Polyacrylamide on Filler Retention in Papermaking

Effect of Different Molecular Weights

The effect of different molecular weights of amphoteric polyacrylamide on filler retention in papermaking is shown in Table IV. The higher the molecular weight of amphoteric polyacrylamide was, the greater its ability was for forming bridged groups between particles and for forming floc and the higher the filler retention was when the molecular weight of amphoteric polyacrylamide was lower than 4 million. However, if the molecular weight of amphoteric polyacrylamide was too high or its amount was too great, flocculation was strong,¹⁴ and the evenness of the paper became bad, so the strength of the paper was

Table III Effect of pH on the Stability of the Product

pH	Stability
3.0	Gel occurred after a few days
5.0	Stable
7.0	Gel occurred after 24 h
9.0	Emulsion was destroyed after 30 min

Oil/water (v/v) = 1.1; emulsifier = 6 wt %; temperature = 45°C; amine/aldehyde (mol) = 1.2.

Table IV Effect of Amphoteric Polyacrylamide (APAM) with Different Molecular Weights on Filler Retention from Wheat-Straw Pulp

Agent	Molecular Weight ($\times 10^6$)	Dosage (%)	Filler Retention (%)	Rupture Resistance Strength kg/cm^2	Breaking Length (m)
APAM	0.5	0.02	53.4	1.78	4197
		0.05	57.3	2.01	4285
APAM	1	0.02	56.5	1.80	3769
		0.05	63.7	1.70	3840
APAM	2	0.02	64.8	1.68	3677
		0.05	73.7	1.52	3561
APAM	3	0.02	72.5	1.71	3472
		0.05	82.4	1.45	3364
APAM	4	0.02	76.1	1.68	3430
		0.05	78.3	1.40	3290
APAM	5	0.02	77.8	1.47	3253
		0.05	75.2	1.34	3175
Blank		0.0	47.5	1.75	4180

Anionic degree = 4%; cationic degree = 24.5%.

reduced, and the filler retention decreased. Experiments showed that the appropriate range of molecular weights when amphoteric polyacrylamide was used as a retention aid in bleached wheat-straw pulp was between 2 and 3 million.

Effect of Different Degrees of Ionization

The density of electricity for ionic polymers is an important parameter in flocculation, so the degree of ionization of amphoteric polyacrylamide had a great influence on filler retention.

The effect of different anionic degrees of amphoteric polyacrylamide on filler retention is shown in Table V. The higher the anionic degree of amphoteric polyacrylamide was, the lower the filler retention was when the anionic degree was greater than 5%. However, when the anionic degree of amphoteric polyacrylamide with a cationic

degree greater than 20% was about 5%, the filler retention was higher.

The dewatering of pulp with a high anionic degree of polyacrylamide turns bad, as is well known, so we can understand why the filler retention declined when the anionic degree of amphoteric polyacrylamide increased (>5%). When amphoteric polyacrylamide with a lower anionic degree was used as a retention aid in pulp, a little cation in pulp was caught, so retention was efficiently improved by the addition of amphoteric polyacrylamide characterized by a lower anionic degree and a higher cationic degree.

The effects of different cationic degrees on filler retention are shown in Table VI. Because the pulp had a large negative charge, the filler retention increased as the cationic degree of amphoteric polyacrylamide increased. Experiments showed

Table V Effect of Amphoteric Polyacrylamide (APAM) with Different Anionic Degree on Filler Retention from Wheat-Straw Pulp

Agent	Dosage (%)	Anionic Degree (%)					
		1	3	5	7	9	11
APAM	0.05	73.7	76.4	80.2	72.5	64.0	60.3
Blank	0			48			

Cationic degree = 22%; molecular weight = 2,600,000.

Table VI Effect of Amphoteric Polyacrylamide (APAM) with Different Cationic Degree on Filler Retention from Wheat-Straw Pulp

Agent	Dosage (%)	Cationic Degree (%)					
		5.0	9.5	14.6	20.2	26.0	30.3
Blank	0			47.5			
APAM	0.05	54.0	58.0	62.1	77.0	83.4	88.2
Cationic polyacrylamide (PAM)	0.05			66.4			
Cationic starch	2			67.6			

APAM: anionic degree = 5%; molecular weight = 3,200,000; cationic PAM: molecular weight = 3,000,000; cationic degree = 21%; cationic starch: degree of substitution, 0.035.

that the filler retention was higher when the cationic degree of amphoteric polyacrylamide was greater than 20%.

In addition, experiments showed that a dual-component retention system for filler retention was better than a single retention aid. For example, the filler retention was improved by the addition of 0.2% poly(diallyl dimethyl ammonium chloride) or 5% $Al_2(SO_4)_3$ when 0.05% amphoteric polyacrylamide was added.

Generally, in an acidic papermaking system, a series of tertiary amine amphoteric polyacrylamides are used as retention aids. However, in neutral and alkaline papermaking systems, quaternary ammonium amphoteric polyacrylamide is a good filler retention aid. It is based on tertiary amine amphoteric polyacrylamide, and dimethyl sulfate is synthesized by quaternary ammoniation, or CH_3Cl is introduced into the emulsion. These questions are not discussed in detail here.

CONCLUSIONS

Amphoteric polyacrylamide was obtained by the copolymerization of acrylamide with sodium acrylate and a subsequent Mannich reaction via inverse emulsion polymerization. A stable latex with a higher molecular weight and a higher cationic degree was made through control of the material addition method and the reaction conditions. It was used as a retention aid for wheat-straw pulp characterized by shorter fiber length, weak strength, and poor drainage. The filler retention was higher than that of cationic polyacryl-

amide and cationic starch when a 0.05% sample was added to the papermaking system. Therefore, it was a satisfactory retention aid in papermaking.

REFERENCES

- McCormick, C. L.; Johnson, C. B. *Macromolecules* 1988, 21, 694.
- McCormick, C. L.; Johnson, C. B. *J Macromol Sci Chem* 1990, 27, 539.
- Siyam, T.; El-Naggar, I. M.; Aly, H. F. Presented at the International Topical Meeting on Nuclear and Hazardous Waste Management Spectrum, Seattle, WA, Aug 1966; 96, 66.
- Siyam, T.; Abd-Elatif, Z. H. In *Science and Technology of Polymers and Advanced Materials, Emerging Technologies and Business Opportunities*; Pvasad, P. N.; et al., Eds.; Plenum: New York, 1998; p 165.
- Siyam, T.; Abd-Elatif, Z. H. *J Macromol Sci Pure Appl Chem* 1999, 36, 417.
- Siyam, T. Unpublished work, 2001.
- John, T. *Eur. Pat.* 0339372 (1989).
- Zang, Q.; Li, Z. *J Funct Polym* 1994, 7, 90.
- Zhang, L. *Oilfield Chem* 1997, 14, 166.
- Yen-Jer, S. *Eur. Pat.* 21069 (1987).
- Schiller, A. M.; Suen, T. J. *Ind Eng Chem* 1956, 48, 2132.
- Long, Y. Q. *Principles of Papermaking and Engineering* (in Chinese); Tianjin Light Industry Institute: 1995.
- Yun, L. *Polym Emuls Commun* 1992, 1, 38.
- Siyam, T. In *Handbook of Engineering Polymeric Materials*; Cheremisinoff, Ed.; Marcel Dekker: New York, 1997; Chapter 9, p 119.