Modification of polyisobutylene-based oil-soluble dispersants

Solmaz Pirouz, J. Duhamel, IPR Symposium,University of Waterloo, ON N2L 3G1, Canada

Dispersants, detergents, antiwear, antioxidation, and viscosity modifier components are chemical additives which are typically added to engine oils to improve their performance during the operation of gasoline and diesel engines. They are designed to improve engine efficiency and durability. Dispersants represent the most important family of chemical additives. They have been used in engine oils since the 1950s.[1] They work by dispersing the oil insoluble combustion by-products such as soot and sludge, which are generated in the engines.

Soot or ultrafine particles (UFPs) are either carbon-rich and/or metallic in nature. Typically, these particles, which are formed by the incomplete oxidation of fuel during ignition, are smaller than 100 nm in diameter.[2] Since releasing UFPs from engines into the air can cause heart and lung failure, governmental regulations were issued to reduce the emission of these UFPs. To this end, diesel and gasoline engine manufacturers circulate the exhaust gas back into the oil where UFPs remain trapped before the exhaust gas is released into the air, in turn, resulting in higher concentrations of UFPs in the oil that lead to UFP aggregation. The UFPs aggregate into large particles (LPs) with a diameter on the order of 1 µm to minimize their surface exposure to the oil.[1] Dispersants are added to the oil to reduce the aggregation of UFPs into LPs. Dispersants are typically composed of a polar head group and an oil-soluble non-polar tail.[3] The polar part of the dispersant is expected to adsorb onto the surface of the UFPs whereas the non-polar tail stabilizes the particles in the oil.

Succinimide dispersants are of the most common dispersants used in the oil industry. They were initially developed by Le Suer and Stuart in 1966.[4] The preparation of polyisobutylene succinimide dispersant (PIBSI) begins by generating a polyisobutylene chain terminated at one end with one succinic anhydride (PIBSA) mostly via an alder-ene reaction. Then, PIBSA is reacted with a polyamine to produce PIBSI dispersants. PIBSI dispersants can also be post-modified with ethylene carbonate to further improve the performance of the dispersant.[5] The aim of this project was to synthesize a series of modified PIBSI dispersants and characterize their chemical structure.

PIBSA used in this project was donated by Imperial Oil. No information was provided regarding its chemical composition. Therefore, the first step in this project was to characterize the chemical composition of PIBSA, followed by the synthesis and modification of the PIBSI dispersants.

Experimental Procedure

PIBSI Synthesis. The PIBSI dispersants were synthesized by reacting different amine derivatives with PIBSA using PIBSA-to-polyamine mole ratios of 1:1 or 2:1 in order to generate mono-PIBSI (*m*-PIBSI) and bi-PIBSI (*b*-PIBSI) dispersants, respectively. See Figure 1 for synthesis of *b*-PIBSI dispersants. In the current study, diethylenetriamine (DETA), triethylenetetramine (TETA), tetraethylenepentamine (TEPA), pentaethylenehexamine (PEHA), hexamethylenediamine (HMDA), and octylamine were used as polyamines.
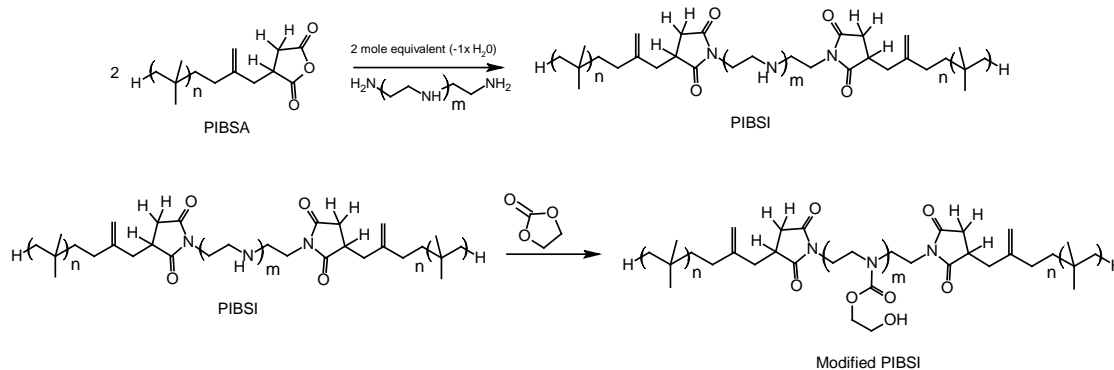
Figure 1 Synthesis and modification of succinimide dispersants.[1]

All PBSI dispersants were synthesized according to a similar procedure with different ratios of succinic anhydride of PIBSA to primary amines of the polyamine. The synthesis of *b*-PIBSI-TEPA is described in more detail as an example. PIBSA was initially precipitated from hexane into acetone to remove low molecular weight impurities that might be present in the sample. Purified PIBSA was dissolved in xylene and placed into a two-neck round-bottom flask equipped with a dean-stark apparatus to remove the water generated during the dehydration conducted at 130-140 ^{o}C. After 10 hrs, a known amount of TEPA was added to achieve a polyamine-to-PIBSA ratio of 1:2, and the reaction was left to proceed at the same temperature under nitrogen atmosphere for another 10 hours. When the reaction was complete, the product was washed three times with 30 mL of 1 M HCl, 1 M NaOH, 0.5 M NaHCO$_3$, and Milli-Q water. The product was then dried at 70 ^{o}C in a vacuum oven overnight.

PIBSI Modification: The procedure to modify the *b*-PIBSI dispersant is described in more detail for *b*-PIBSI-TEPA. *b*-PIBSI-TEPA and ethylene carbonate (EC) were mixed with a 1:5 molar ratio of secondary amine-to-EC. Xylene and triethylamine were used as solvent. The modification reaction was carried out in a sealed reaction vessel since EC is somewhat volatile at the temperature of the modification reaction. The reaction mixture was heated to 160 ^{o}C and kept at this temperature for 24 hrs. After 3, 6, and 24 hrs, a small aliquot was taken out in order to monitor the reaction progress. After completion, the reaction product was washed with 20 mL of water three times. Finally, the product was dried in a vacuum oven at 70 ^{o}C overnight.

Results and Discussion

^{1}H NMR and FTIR Peak Assignments. The ^{1}H NMR peaks for PIBSA, PIBSI, and M-PIBSI were difficult to assign, due to the much larger number of PIB protons in comparison to the protons found in the polar core of the dispersants. To facilitate the assignment, several model compounds were previously prepared by Yulin Wang to mimic the polar core, and they were used as references for the assignment of the ^{1}H NMR spectrum of the dispersants. [6]

Deuterated chloroform (CDCl$_3$) was used as a solvent in all ^{1}H NMR samples. In the ^{1}H NMR spectrum of PIBSA, the peaks at 2.6 and 3.3 ppm represent the protons in the succinic anhydride ring (Figure 2a). The peaks at 1.1 and 1.4 ppm which are out of scale in Figure 2a represent, respectively, the methylene and the methyl protons of the PIB backbone obtained in a 1:3 ratio. Finally, the peak at 5.5-5.6 ppm may be due to the presence of vinylidene groups.

The ^{1}H NMR spectrum of *b*-PIBSI-PEHA in Figure 2a (middle) shows peaks at 2.7 and 3.5 ppm due to the protons on the ethylene segments of the polyamine whereas the peaks at 2.5 and

3.0 ppm are due to the succinimide ring protons. Finally, the peaks at 3.8 and 4.2 ppm in Figure 2a (bottom) represent the protons of the ethylene side-chain bonded to the urethane group generated on the polar core after reaction of the secondary and/or primary amine of b-PIBSI-PEHA with EC. The peak at 4.2 ppm was relatively well-resolved and it was used to determine the level of modification.
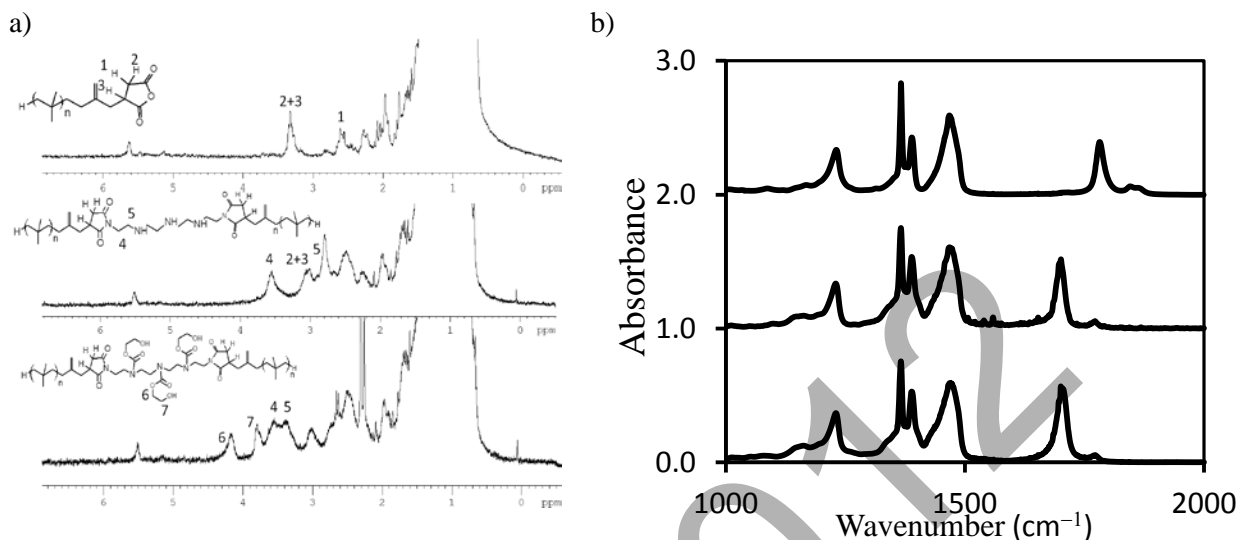

Figure 2 a)^{1}H NMR spectra of PIBSA (top), b-PIBSI-PEHA (middle) and Mb-PIBSI-PEHA (bottom), and b) FTIR spectra of PIBSA (top), PIBSI-TEPA (middle), and M-PIBSI-TEPA (bottom).

The FTIR peaks for PIBSA, PIBSI, and M-PIBSI were also assigned (Figure 2b). In the FTIR spectrum of PIBSA, the absorptions at 1785 cm^{-1} and 1390 cm^{-1} are due to the carbonyls of succinic anhydride (SA) and the methyls of the PIB backbone, respectively. Comparison of the FTIR spectrum of b-PIBSI-TEPA with PIBSA shows a new absorption peak at 1705 cm^{-1} and the disappearance of the peak at 1785 cm^{-1}, due to the carbonyl groups of the succinimide ring.

Chemical Composition Determination. Since the reactivity of primary and secondary amines toward EC might differ, we selected the b-PIBSI dispersants to conduct the modification with EC. In turn, this required that the chemical composition of PIBSA and PIBSI be carefully determined. Walch and Gaymans obtained a calibration curve that relates the ratio of the number of SA groups to isobutylene (IB) units with the ratio of the FTIR absorbance at 1785 cm^{-1} and 1390 cm^{-1}.[8] This ratio was used to calculate the average number of IB units (N_{IB}) in a PIBSA molecule per SA moiety (N_{SA}). The N_{SA}/N_{IB} ratio was found to equal 0.0204 ± 0.0004 for PIBSA, suggesting that PIBSA is constituted of 49 ± 1 IB units per SA. By assuming that each PIB chain is terminated by a single SA unit, an M_n value of $2,850\pm50$ g/mol was calculated.

Yu Shen also established a similar calibration curve to estimate the ratio of IB units per succinimide (SI) for PIBSI.[8] The N_{SI}/N_{IB} ratios of b-PIBSI-TEPA and b-PIBSI-DETA were found to equal (1:33) and (1:34), respectively. The result was different from the chemical composition of PIBSA, and could be due to a number of reasons that include hydrogen bonding of the primary and secondary amines in the polar core.

^{1}H NMR was also used to determine the chemical composition of PIBSA. The ratio of the integrals of the peaks at 3.3 and 1.4 ppm yielded a N_{SA}/N_{IB} ratio of 1:55 which is similar to the chemical composition obtained by FTIR.

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The chemical composition of PIBSI could also be determined by taking the ratio of the integrals of the peaks at 3.5 and 1.4 ppm which yielded N_{SI}/N_{IB}. In the case of *m*-PIBSI-Octylamine which can not form by hydrogen bonds, N_{SI}/N_{IB} equalled 1:47, which matches the chemical composition obtained for PIBSA. However, the N_{SI}/N_{IB} ratios for the *b*-PIBSI samples were always found to be much smaller possibly due to H-bonding of the primary and secondary amines in the polar core which might affect the peak intensities in the ^{1}H NMR spectra.

At this stage FTIR and ^{1}H NMR spectroscopy were used only to determine the chemical composition of PIBSA. Although, GPC did not yield the absolute number-average molecular weight (M_n) of PIBSA, an indirect procedure was developed. GPC was employed as a third characterization technique to determine the chemical composition of PIBSA and PIBSI. For all *b*-PIBSI samples, the main peak in the GPC trace shifted to a lower elution volume compared to PIBSA implying an increase of the molecular weight, as expected. Moreover, a shoulder appeared on the right side of the main peak, perhaps as a result of interactions between the packing material of the GPC column and the secondary amines of the PIBSI dispersants. However, it was also noted that the shoulder eluted at the same position as PIBSA and could also have been unreacted PIBSA resulting from the use of an erroneous N_{SA}/N_{IB} ratio. Therefore, PIBSA was reacted with different amounts of hexamethylenediamine (HMDA) because its full reaction with PIBSA eliminates the effect of secondary amines sticking to the GPC column. The ratio of HMDA to PIBSA, namely the [HMDA]/[PIBSA] ratio expressed in mmol/g, was changed from 0.1 to 0.4.

As the [HMDA]/[PIBSA] ratio decreased from 0.4 to 0.17 mmol/g, the shoulder intensity decreased steadily until it reached a minimum value. However, a further decrease in the [HMDA]/[PIBSA] ratio resulted in an increase of the shoulder intensity. The ratio of the shoulder intensity to the intensity of the main peak was calculated and plotted as a function of the [HMDA]/[PIBSA] ratio in Figure 3.

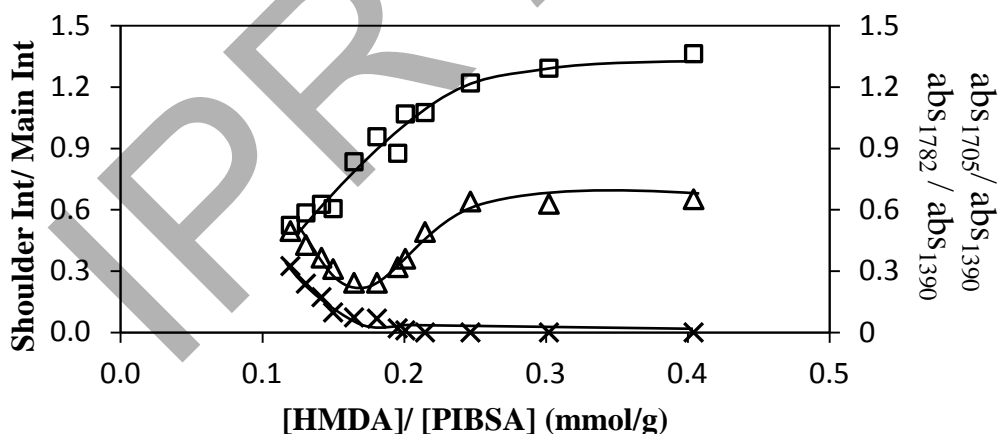**Figure 3** FTIR and GPC intensity ratios versus [HMDA]/[PIBSA] ratio; abs1705/abs1390 (□), abs1782/abs1390 (✕), shoulder to peak intensity ratio (△).

At low [HMDA]/[PIBSA] ratios, unreacted PIBSA is present as well as *b*-PIBSI-HMDA. By increasing the [HMDA]/[PIBSA] ratio, the amount of unreacted PIBSA decreases and the content of *b*-PIBSI-HMDA increases up to an optimum. Then, *m*-PIBSI-HMDA is produced and the shoulder-to-peak ratio increases until all PIBSA has reacted and a plateau appears in the plot. The [HMDA]/[PIBSA] ratio corresponding to the minimum in Figure 3 equals 0.17 mmol/g

corresponding to a chemical composition for PIBSA described by an N_{SA}/N_{IB} ratio of (1:52). This result agrees relatively well with the chemical composition of PIBSA determined by FTIR (1:49) and ^{1}H NMR (1:55). The FTIR spectra were acquired for all dispersants to confirm the analysis of the trend obtained by GPC. Whereas most of the FTIR spectrum remained unchanged, an increase of the [HMDA]/[PIBSA] ratio resulted in an increase of the absorbance at 1705 cm^{-1} indicating succinimide formation associated with a decrease of the absorbance at 1785 cm^{-1} indicating disappearance of SA. The results are summarized in Figure 3.

Modification. After the chemical composition of the *b*-PIBSI dispersants was confirmed, *b*-PIBSI-DETA, *b*-PIBSI-TETA, *b*-PIBSI-TEPA, and *b*-PIBSI-PEHA were modified by reaction with EC. The level of modification was calculated from the ratio of the number of urethane (N_{ur}) groups/104 IB units. As shown in Figure 4 the modification was nil in M*b*-PIBSI-DETA and M*b*-PIBSI-TETA and was quantitative for M*b*-PIBSI-TEPA and M*b*-PIBSI-PEHA. This result suggests that steric hindrance inhibits the approach of EC to the secondary amines of the *b*-PIBSI-DETA and *b*-PIBSI-TETA dispersants preventing modification of the dispersants.
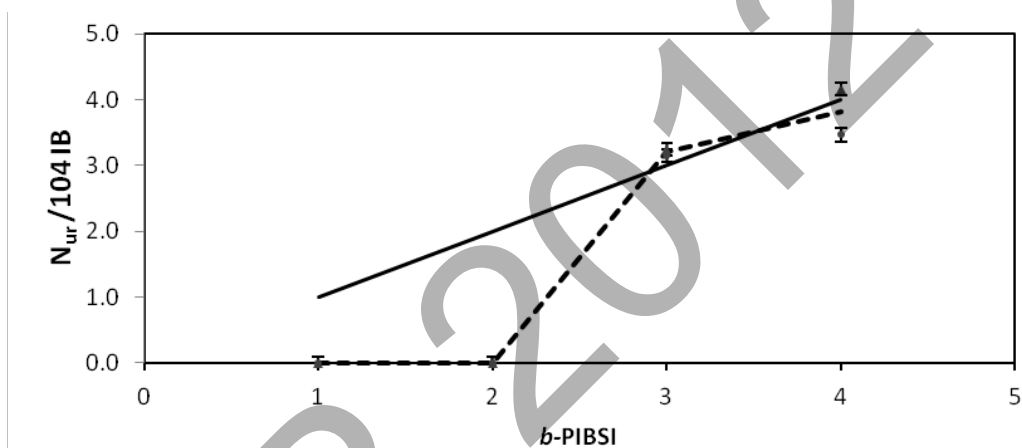
Figure 4 N_{ur}/104 IB for PIBSI-DETA, PIBSI-TETA, PIBSI-TEPA, and PIBSI-PEHA (—) expected value and (- - -) experimental value.

Conclusion

The synthesis and EC modification of PIBSI dispersants are well known procedures in the oil additive industry. However, this study represents the first example where this modification was investigated quantitatively by FTIR and ^{1}H NMR. The yield of modification was significantly improved by increasing the spacer length between the two succinimide rings. It was found to equal 0%, 0%, 107%, and 95% for *b*-PIBSI-DETA, *b*-PIBSI-TETA, *b*-PIBSI-TEPA, and *b*-PIBSI-PEHA, respectively.

References

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2. Ritter, S. *C & EN* **2005**, Sept 5, 20-22.
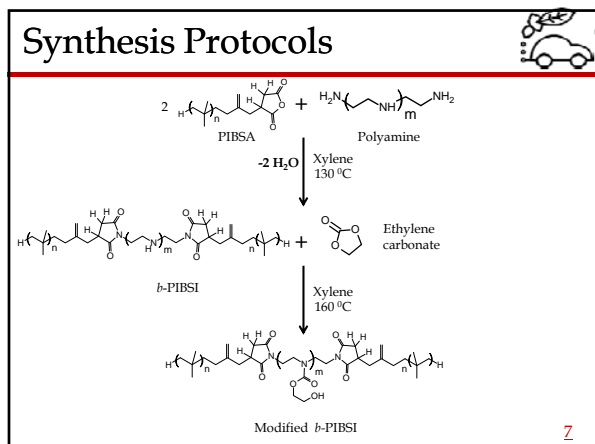3. Myers, D. *Surfactant science and Technology*, 3rd Ed., Wiley, Hoboken, 2006.
4. Le Suer, W. M.; Norman, G. R. *United States Patent* **1966**, 3 272 747.
5. Wollenberg, R. H.; Rafael, S.; Plavac, F. *United States Patent* **1989**, 4 802 893.
6. Wang, Y. Synthesis and Characterization of Ethylene Carbonate Modified Polyisobutylene Succinimide Dispersants, M. Sc. Thesis, University of Waterloo, 2010.
7. Walch, E.; Gaymans, R. J. *Polymer* **1994**, *35*, 1774-1778.
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Slide 1

University of Waterloo

IPR

Modification of polyisobutylene-based oil-soluble dispersants

Solmaz Pirouz

Supervisor: **Jean Duhamel**

Department of Chemistry
University of Waterloo
IPR 2012

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Slide 2

Outline

➢ Introduction
   • Dispersants (PIBSA and PIBSI)
➢ Background
   • Chemical composition
   • Physical characterization
➢ Experimental results
   • Determination of the chemical composition of PIBSA and PIBSI
   • Synthesis and modification of the PIBSI dispersants
➢ Future work
➢ Acknowledgements

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Slide 3

Introduction

Rudnik, L. R. in *Lubricant Additives : Chemistry and Application,* Barbadsz, E. A.; Lamb, G. D. Ed., CRC Press, Boca Raton, 2003, pp 458-490.

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Slide 4

Sludge Formation

UFPs

LPs

$d_{UFPs} < 100nm$

$d_{LPs} \sim 1\mu m$

Ultra fine particles (UFPs) minimize exposure of their polar surface by undergoing aggregation into large particles (LPs).

Mortier, R. M.; Malcolm, F. F.; Orszulik, S.T. *Chemistry and Technology of Lubricants,* Springer, London, 2009.

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Slide 5

Dispersants

Without dispersants

With dispersants

Polar   Nonpolar

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Slide 6

Succinimide Dispersants

Nonpolar   **Polar**

$700 < M_n < 4000 \text{ g/mol}$ $180 < M_n < 320 \text{ g/mol}$

Jao, T. C.; Passut, C. A. *Handbook of Detergents,* Showell, M. S. Ed., CRC Press, Boca Raton, 2006.

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Synthesis Protocols

PIBSA + Polyamine

-2 H₂O Xylene 130 °C

b-PIBSI + Ethylene carbonate

Xylene 160 °C

Modified b-PIBSI

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Polyamines Used to Synthesis of PIBSI

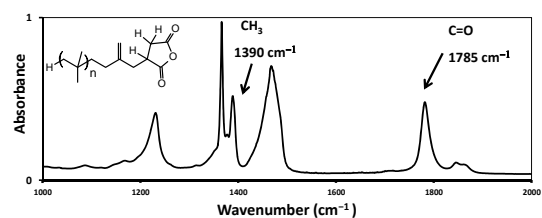|	
Octylamine	$CH_3\text{-}(CH_2)_7\text{-}NH_2$
Diethylenetriamine (DETA)	$H_2N\text{-}(CH_2CH_2\text{-}NH)_2\text{-}H$
Triethylenetetramine (TETA)	$H_2N\text{-}(CH_2CH_2\text{-}NH)_3\text{-}H$
Tetraethylenepentamine (TEPA)	$H_2N\text{-}(CH_2CH_2\text{-}NH)_4\text{-}H$
Pentaethylenehexamine (PEHA)	$H_2N\text{-}(CH_2CH_2\text{-}NH)_5\text{-}H$
Hexamethylenediamine (HMDA)	$H_2N\text{-}(CH_2)_6\text{-}NH_2$

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Research Outline

- Determination of the chemical composition of polyisobutylene succinic anhydride (PIBSA)
- Synthesis of polyisobutylene succinimide (PIBSI) dispersants
- Modification of the dispersants with ethylene carbonate (EC) and optimization of the reaction conditions.
- Determination of the chemical composition of the modified dispersants.
- Study of the effect that the modification of the dispersant has on its ability to adsorb onto carbon black particles (CBPs).

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Outline

- Introduction
  - Dispersants
- Background
  - Chemical composition
  - Physical characterization
- Experimental results
  - Determination of the chemical composition of PIBSA and PIBSI
  - Synthesis and modification of the PIBSI dispersants
- Future work
- Acknowledgements

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Nuclear Magnetic Resonance (NMR) Spectra

Wang, Y. M. Sc. Thesis, University of Waterloo, 2010

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Fourier Transform Infrared (FTIR) Spectra

CH₃ 1390 cm⁻¹   C=O 1785 cm⁻¹

C=O 1705 cm⁻¹
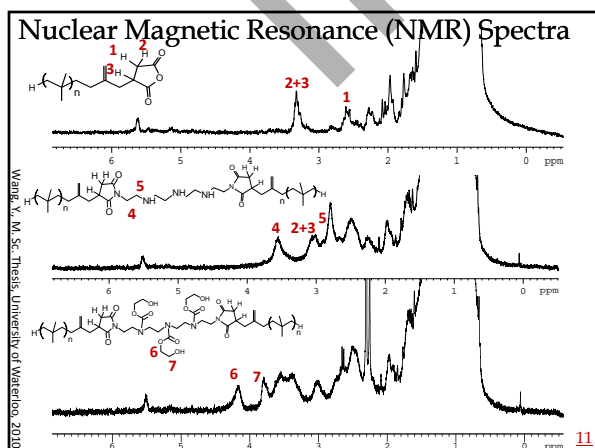
C=O 1705 cm⁻¹
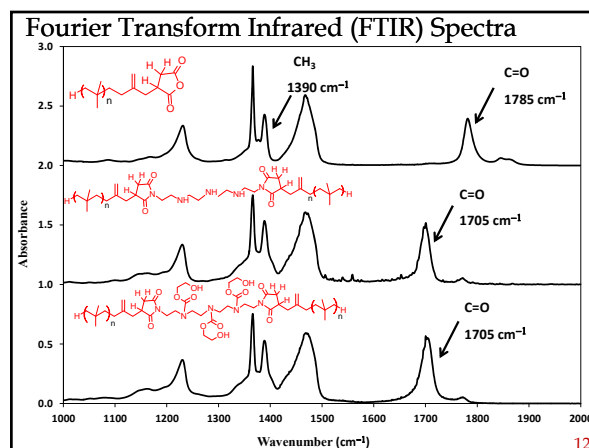
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Fourier Transform Infrared (FTIR) Spectrum

$$\frac{N_{SA}}{N_{IB}} = 0.024 \times \frac{abs(1785cm^{-1})}{abs(1390cm^{-1})} \quad \Longrightarrow \quad \frac{N_{SA}}{N_{IB}} = 0.0204 \pm 0.004 \,(\mathbf{1:49})$$

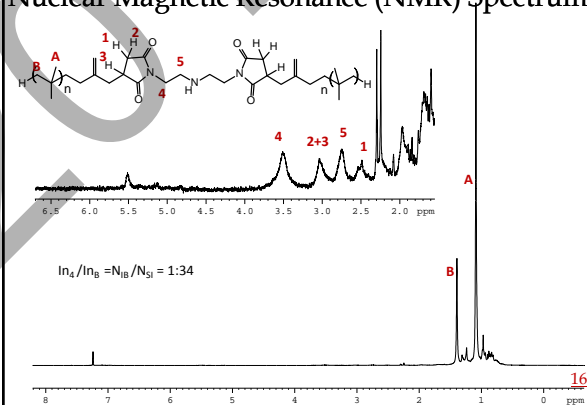Walch, E.; Gaymans, R. J. *Polymer* **1994**, *35*, 1774-1778.

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Nuclear Magnetic Resonance (NMR) Spectrum

$$In_{2+3}/In_B = N_{IB}/N_{SA} = 1:55$$
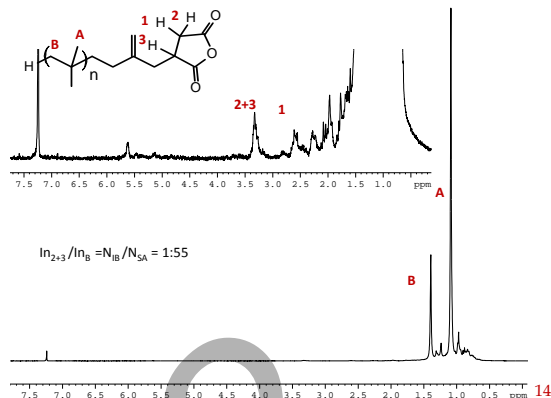
14

Fourier Transform Infrared (FTIR) Spectrum
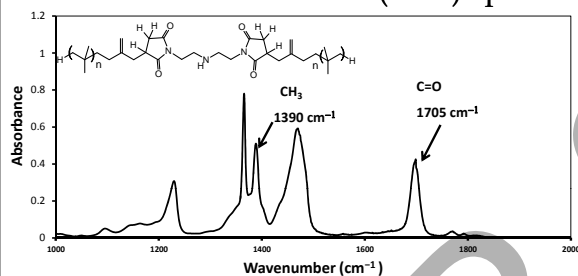
$$\frac{N_{SI}}{N_{IB}} = 0.028 \times \frac{abs\,(1705\,cm^{-1})}{abs\,(1390\,cm^{-1})} \quad \Longrightarrow \quad \frac{N_{SI}}{N_{IB}} = 0.025 \pm 0.001 (1:39 \pm 2)$$

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Nuclear Magnetic Resonance (NMR) Spectrum

$$In_4/In_B = N_{IB}/N_{SI} = 1:34$$

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Chemical Composition

Dispersants	Chemical Composition	^{1}H NMR	FT-IR (Peak Height)
PIBSA	N_{SA} / N_{IB}	1:55 (Wang, Y)	1:49 (Shen, Y)
b-PIBSI-DETA	N_{SI} / N_{IB}	1:33±1 (Wang, Y)	1:39 (this work)
b-PIBSI-TEPA	N_{SI} / N_{IB}	–	1:43 (this work)

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Outline

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Adsorption of Dispersants onto Carbon Black Particles
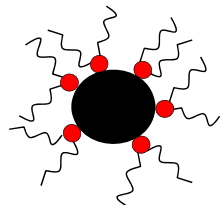

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Micelles

- ❖ PIBSI dispersants can form micelles and reverse micelles in polar and apolar solutions, respectively.
- ❖ Micellization occurs when the dispersant concentration reaches a critical value called the Critical Micelle Concentration (CMC).

Reverse Micelles   **Micelles**

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Adsorption of Dispersants onto Carbon Black Particles

C_o **Homogeneous mixture** C_{eq}
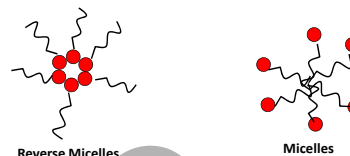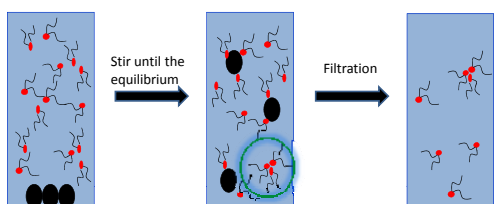
$$\Gamma = \frac{(C_0 - C_{eq}) \times V}{m \times A}$$

Γ: The amount of adsorbed dispersant at equilibrium.

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Langmuir Isotherm

$$\Gamma = \frac{\Gamma_{max} K C_{eq}}{1 + K C_{eq}}$$

$$\frac{1}{\Gamma} = \frac{1}{\Gamma_{max} K} \times \frac{1}{C_{eq}} + \frac{1}{\Gamma_{max}}$$

Γ_{max} is the maximum amount of dispersant adsorbed per unit surface, and K is the binding constant, respectively.

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$1/\Gamma$ vs. $1/C_{eq}$
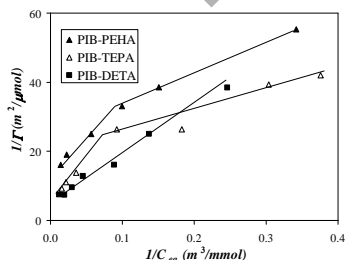
$$\frac{1}{\Gamma} = \frac{1}{\Gamma_{max} K} \times \frac{1}{C_{eq}} + \frac{1}{\Gamma_{max}}$$

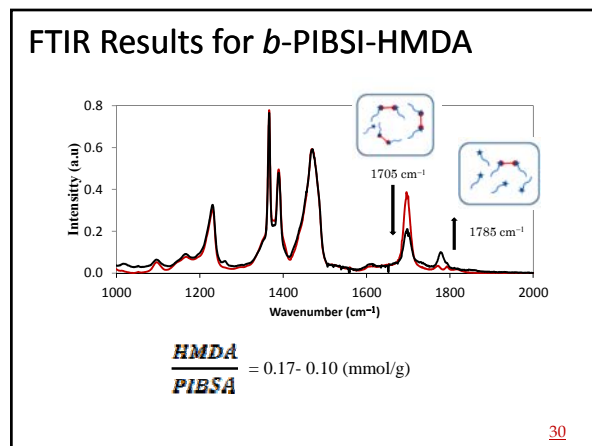Shen, Y.; Duhamel, J. *Langmuir* **2008**, *24*, 10665-10673.
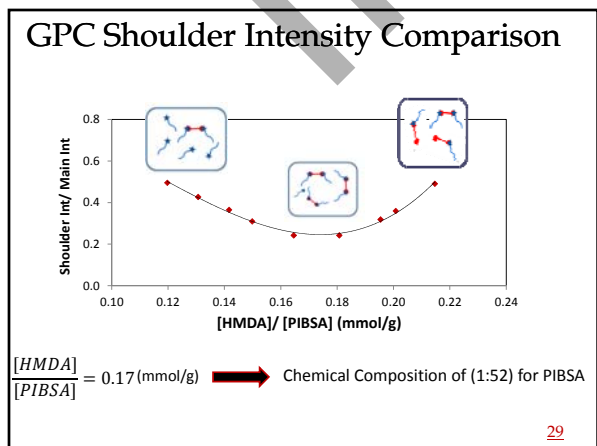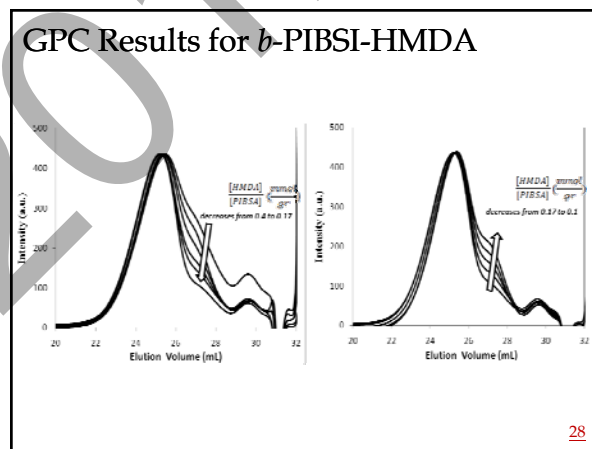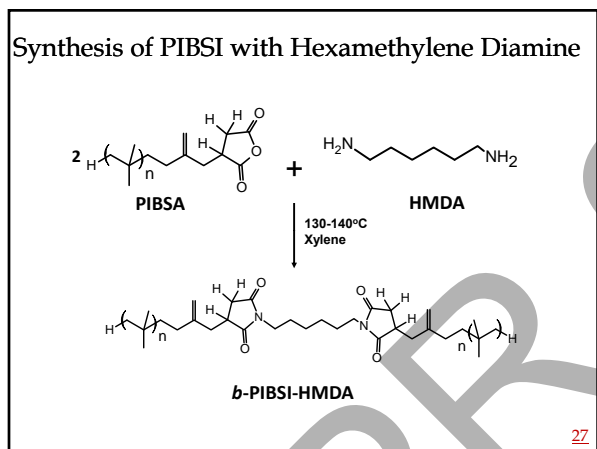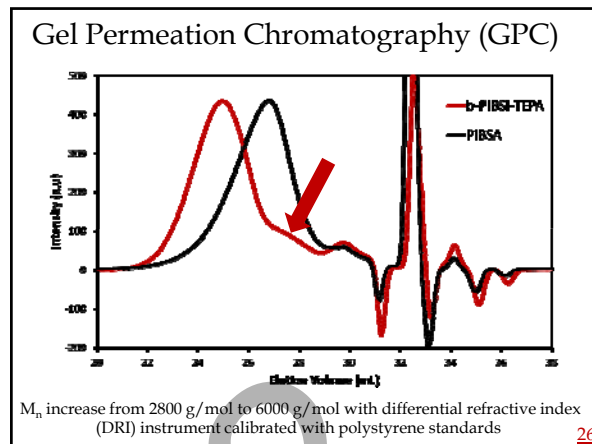
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Summary of Previous Results

- ➢ The chemical composition of PIBSA and PIBSI was determined by FTIR and ^{1}H NMR.
- ➢ *b*-PIBSI-TEPA and *b*-PIBSI-PEHA form reverse micelles at concentration larger than CMC, which in turn decreases their ability to adsorb on to CRPs.
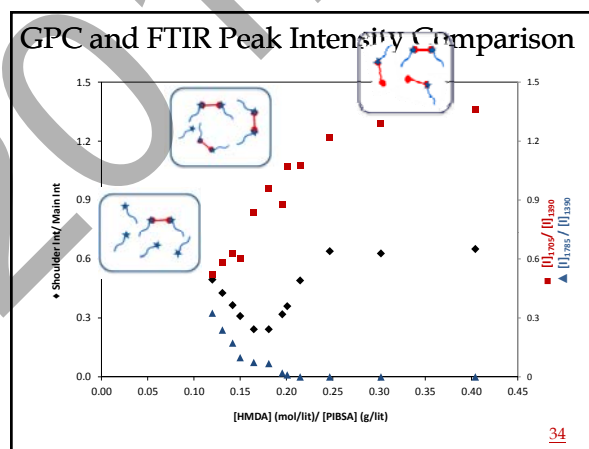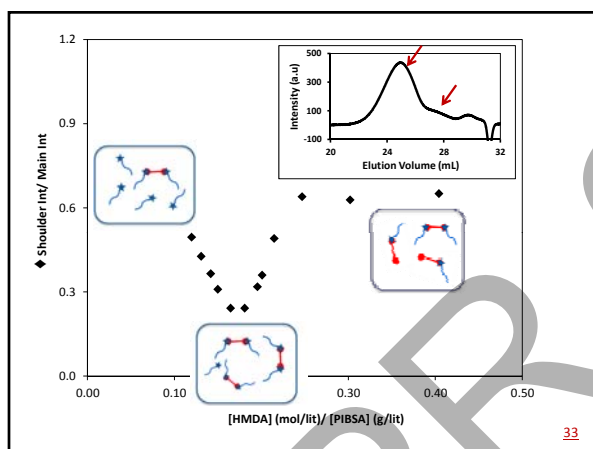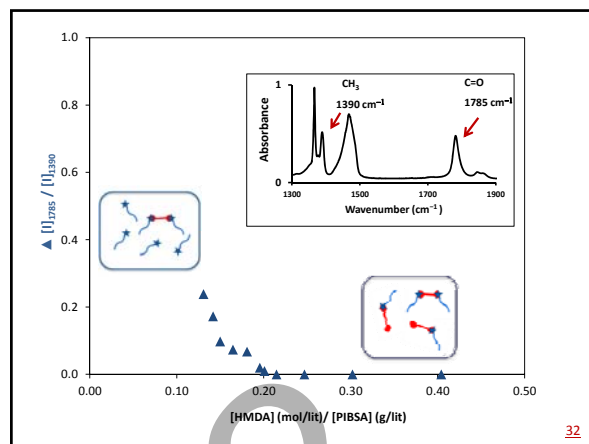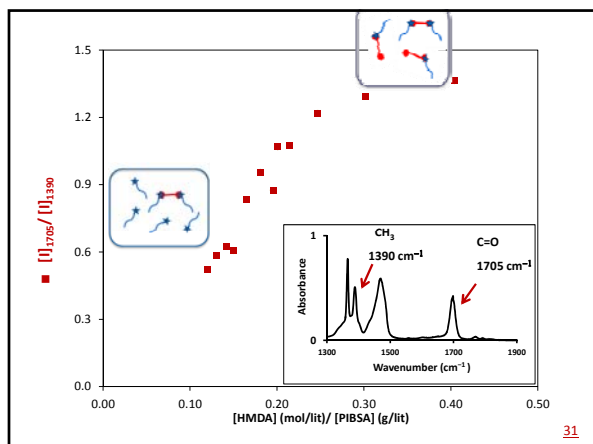
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Outline

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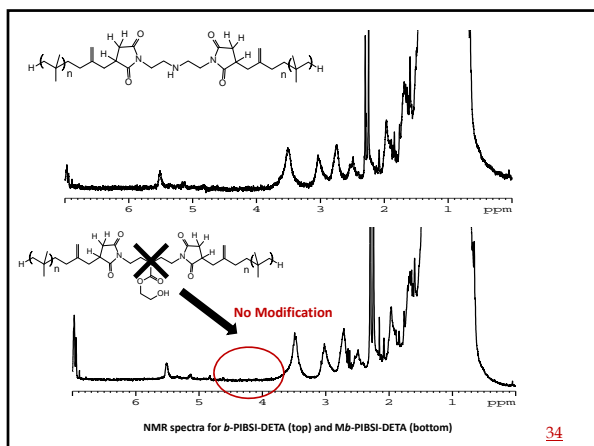- Future work
- Acknowledgements

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Gel Permeation Chromatography (GPC)

M_n increase from 2800 g/mol to 6000 g/mol with differential refractive index (DRI) instrument calibrated with polystyrene standards

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Synthesis of PIBSI with Hexamethylene Diamine

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GPC Results for *b*-PIBSI-HMDA

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GPC Shoulder Intensity Comparison

$$\frac{[HMDA]}{[PIBSA]} = 0.17 \,(mmol/g) \quad \Longrightarrow \quad \text{Chemical Composition of (1:52) for PIBSA}$$

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FTIR Results for *b*-PIBSI-HMDA

$$\frac{HMDA}{PIBSA} = 0.17 - 0.10 \,(mmol/g)$$

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10/05/2012

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GPC and FTIR Peak Intensity Comparison

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Summary

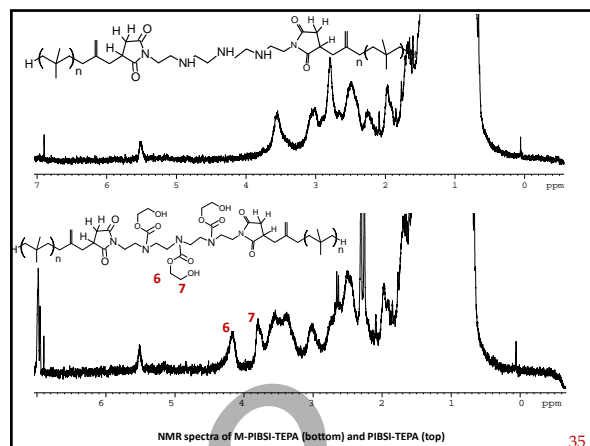| Dispersants	Chemical Composition	^{1}H NMR	FT-IR (Peak Height)	GPC
PIBSA	N_{SA} / N_{IB}	1:55 (Wang, Y)	1:49 (Walch, E)	1:52
b-PIBSI-DETA	N_{SI} / N_{IB}	1:33±1 (Wang, Y)	1:39±2 (this work)	-
b-PIBSI-TEPA	N_{SI} / N_{IB}	1:32±1	1:43±2 (this work)	-

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Outline

➢ Introduction
 • Dispersants
➢ Background
 • Chemical composition
 • Physical characterization
➢ Experimental results
 • Determination of the chemical composition of PIBSA and PIBSI
 • Synthesis and modification of the PIBSI dispersants
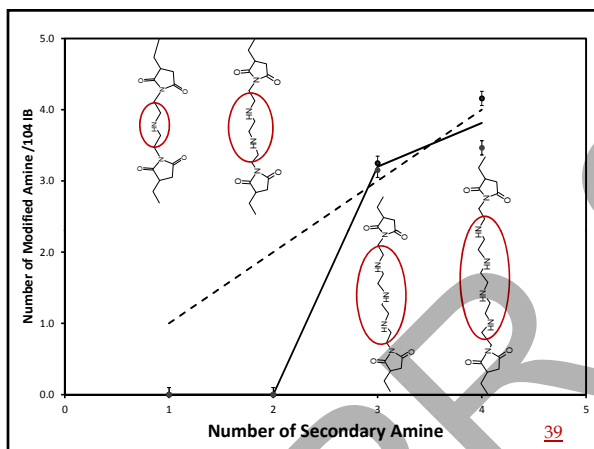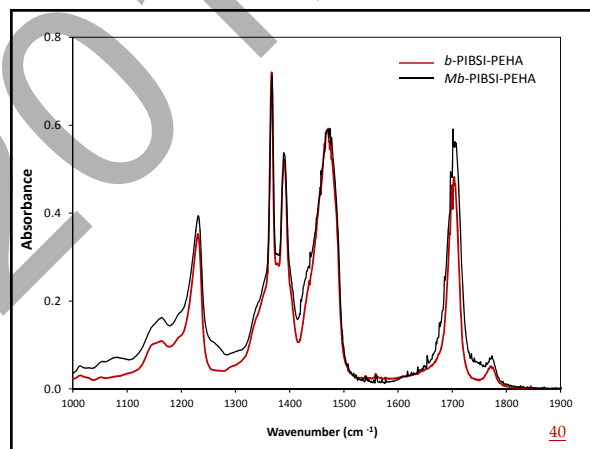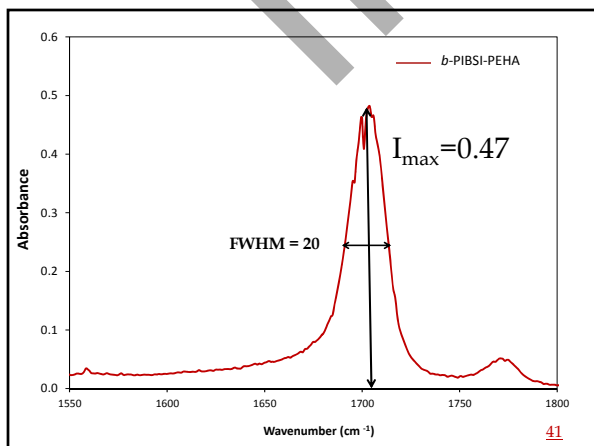➢ Future work
➢ Acknowledgements

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NMR spectra for *b*-PIBSI-DETA (top) and M*b*-PIBSI-DETA (bottom)

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NMR spectra of M-PIBSI-TEPA (bottom) and PIBSI-TEPA (top)

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$I_{max}=0.47$

FWHM = 20

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Maximum peak intensity (H_{max}) and full width half max (FWHM) at 1705 cm^{-1}.

	Unmodified PIBSI				Modified PIBSI		
	I_{max}	FWHM	Int		I_{max}	FWHM	Int
b-PIBSI-HMDA	0.35	13	13				
b-PIBSI-DETA	0.54	14	15	M*b*-PIBSI-DETA	0.49	15	15
b-PIBSI-TETA	0.53	16	15	M*b*-PIBSI-TETA	0.51	16	15
b-PIBSI-TEPA	0.49	16	14	M*b*-PIBSI-TEPA	0.64	26	22
b-PIBSI-PEHA	0.52	20	16	M*b*-PIBSI-PEHA	0.65	35	25

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Summary

- The chemical composition of PIBSA and PIBSI was determined by GPC and it was found to match well that obtained earlier by FTIR and ^{1}H NMR.
- The EC modification was successful for *b*-PIBSI-TEPA and *b*-PIBSI-PEHA, but unsuccessful *b*-PIBSI-DETA and *b*-PIBSI-TETA, certainly due to steric hindrance.
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Future Work

- Investigate the effect that the modification of the PIBSI dispersants can have on their ability to form micelles, and in turn, how it affects their ability to adsorb onto CRPs.

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Acknowledgments

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THANK YOU !

QUESTION ?

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Adsorption Isotherm

Γ: The amount of adsorbed dispersant at equilibrium.

$$\Gamma = \frac{(C_0 - C_{eq}) \times V}{m \times A}$$

C_0 and C_{eq} are the initial concentration of dispersant and the concentration at equilibrium concentration, respectively.
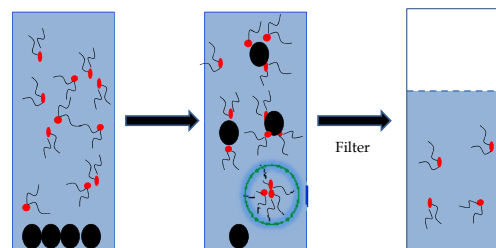
m is the total mass of CBPs.

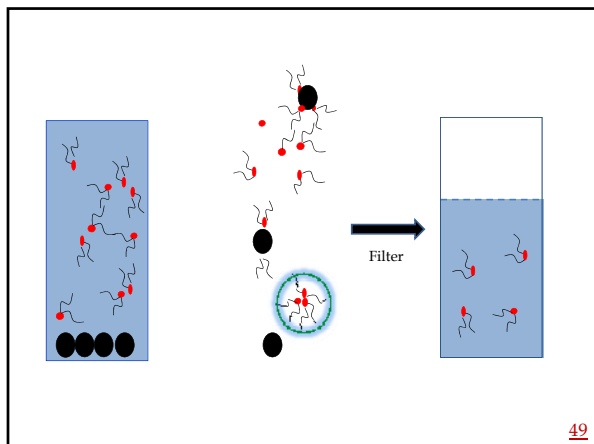A is the surface area accessible to the dispersant, (A=764m^2/g)

V is the volume of the solution.
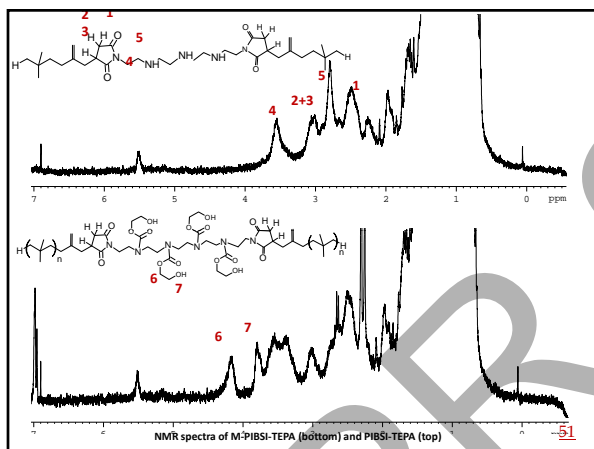
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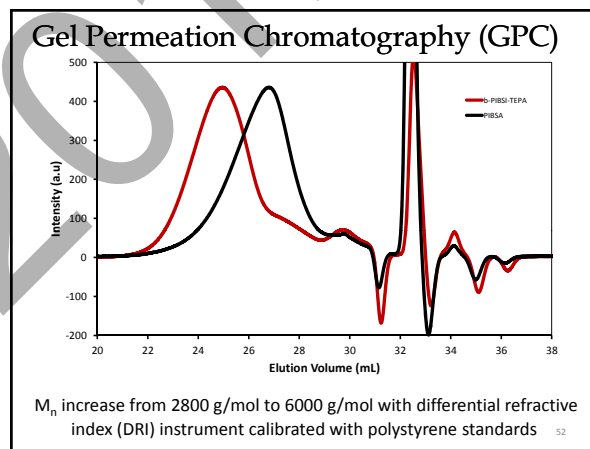## Adsorption of Dispersants vs Micelle Formation

Filter

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$$Yield = \frac{\frac{Integ\,(4.2\,ppm)}{Integ\,(1.4\,ppm)}}{\frac{N_{amine}}{N_{IB}}}$$

	$\frac{Int\,(4.2\,ppm)}{Int\,(1.4\,ppm)}$	$\frac{N_{SA}}{N_{IB}}$	Yield
Mb-PIBSI-DETA	0	1/52	0
Mb-PIBSI-TETA	0	1/52	0
Mb-PIBSI-TEPA	1/32	1/52	1.08
Mb-PIBSI-PEHA	1/27	1/52	0.96

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NMR spectra of M-PIBSI-TEPA (bottom) and PIBSI-TEPA (top)

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Gel Permeation Chromatography (GPC)

M_n increase from 2800 g/mol to 6000 g/mol with differential refractive index (DRI) instrument calibrated with polystyrene standards

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b-PIBSI

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$$\frac{N_{SI}}{N_{IB}} = 0.035 \times \frac{abs(1705cm^{-1})}{abs(1390cm^{-1})}$$

$$\frac{N_{SA}}{N_{IB}} = 0.024 \times \frac{abs(1785cm^{-1})}{abs(1390cm^{-1})}$$

(y-axis: $\times$ N_{SA}/N_{IB}, $\bullet$ N_{SI}/N_{IB}; x-axis: [HMDA]/[PIBSA] (mmol/g))

$$\frac{[HMDA]}{[PIBSA]} = 0.17 \,(mmol/g) \longrightarrow \text{Chemical Composition of (1:32) for PIBSI}$$

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GPC Trace for *b*-PIBSI-TEPA

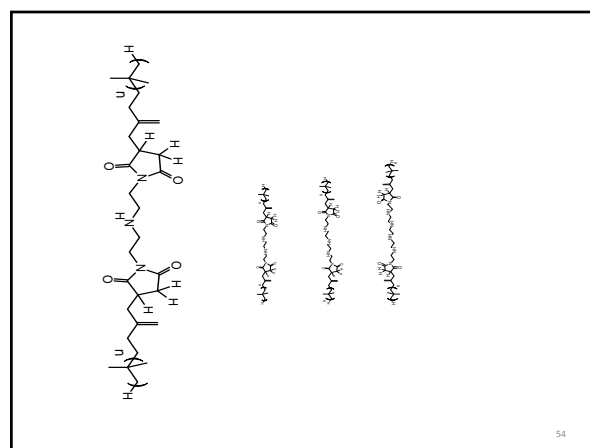(Intensity [a.u.] vs Elution Volume [mL]; $\frac{[TEPA]}{[PIBSA]} = 0.17$, $\frac{[TEPA]}{[PIBSA]} = 0.25$)

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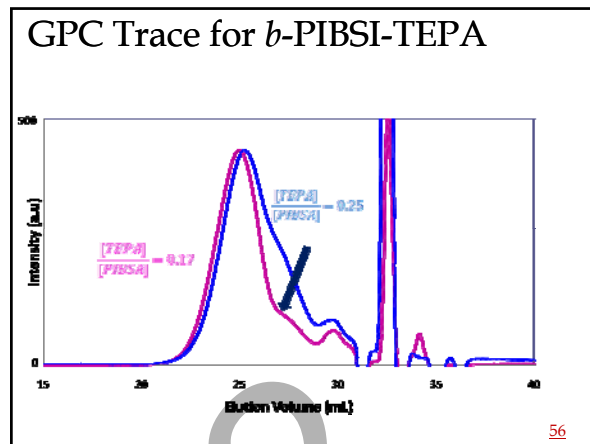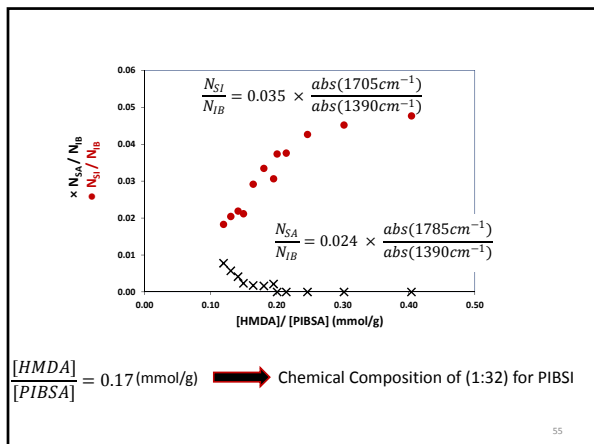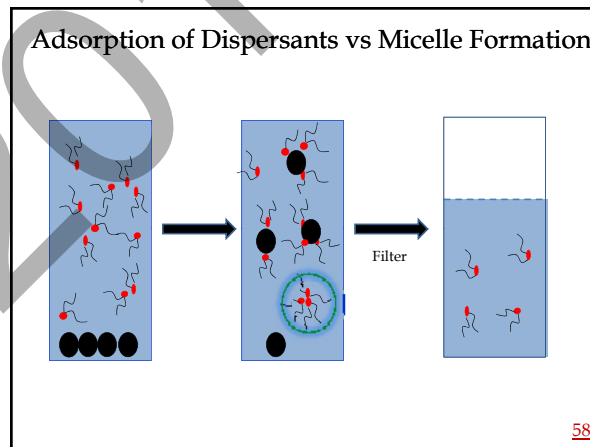
Micelles

❖ PIBSI dispersants can form micelles and reverse micelles in polar and non-polar solutions, respectively.

❖ Micellization occurs when the dispersant concentration reaches a critical value called the Critical Micelle Concentration (CMC).

Reverse Micelles   **Micelles**

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Adsorption of Dispersants vs Micelle Formation

Filter

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Summary

➢ The chemical composition of PIBSA and PIBSI was determined by FTIR and ^{1}H NMR.

➢ *b*-PIBSI-TEPA and *b*-PIBSI-PEHA form reverse micelles at concentration larger than CMC, which in turn decreases their ability to adsorb on to CRPs.

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Synthesis Protocols

2   PIBSA   2 mole equivalent (-1xH₂O)   *b*-PIBSI

b-PIBSI   Ethylene carbonate   Modified *b*-PIBSI

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