

## Discussion on the Structural Features of Asphaltene Molecules

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Asphaltenes are a class of complex mixtures in petroleum fluids, which are defined as the fraction in petroleum oils soluble in aromatic solvents, such as toluene, whereas insoluble in saturated hydrocarbons, such as *n*-heptane, and asphaltenes are prepared from crude oils by this simple principle. From this operational definition, asphaltenes are anticipated as a group of complex compounds,<sup>1,2</sup> which are highly polydispersed and cannot be absolutely prescribed by some simplex physicochemical parameters.<sup>3,4</sup> There are fewer large aggregates and narrower distributions once asphaltenes are in infinite-diluted systems of higher temperatures and better solvents; however, they still exhibit a real polydispersity.<sup>1–4</sup> The average molecular weight (MW) is not necessarily a good parameter to characterize asphaltenes, simply because asphaltenes are defined through their solubility in aliphatic hydrocarbons.<sup>1</sup>

Time-resolved fluorescence depolarization (TRFD) was applied to determine the average MW and structural features of asphaltenes by the research group of Mullins,<sup>5–12</sup> and the authors arrived at three primary conclusions: (1) petroleum asphaltenes have an average molecular mass of ~750 Da (even smaller as 500 Da for coal-derived asphaltenes), with a full width at half-maximum of 500–1000 Da; (2) asphaltenes are dominated by molecules with one polycyclic aromatic hydrocarbon (PAH) unit per molecule; and (3) the most likely asphaltene PAH has roughly 7 rings. However, this method (TRFD) has been reported as being unsuitable for the study of asphaltenes.<sup>2,13,14</sup> The fundamental properties of asphaltenes,

such as their MW are still in lively debate,<sup>15–21</sup> and the MW results obtained, even by the same method but from different laboratories, can be remarkably different from each other.<sup>22–26</sup>

The equipment from Photon Technology International (PTI) used to obtain the TRFD results of asphaltenes are undoubtedly of high quality, as shown in the Mullins' paper,<sup>12</sup> but it is still doubtful that TRFD analysis is necessarily suitable to study the fundamental properties of asphaltenes, such as their MWs and structural features, although the PTI has reported this kind of work on its website.<sup>27</sup> As anticipated, the TRFD results of asphaltenes indicated that the fluorescence emission wavelength has a broad distribution range from 380 to 650 nm and the rotational correlation time has a factor of 10 variations with the emission wavelength.<sup>27</sup> The authors further concluded that, because small asphaltene chromophores have a rotational correlation time 10 times smaller than that of the big ones, inside asphaltene molecules, the blue chromophores are not cross-linked to the red ones and then there is only one PAH unit per asphaltene molecule.<sup>12</sup>

However, inside the asphaltene molecule, the polymethylene groups have been reported to be present as the bridges between

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- (1) Sheu, E. Y. *Energy Fuels* **2002**, *16*, 74–82.
- (2) Strausz, O. P.; Peng, P.; Murgich, J. *Energy Fuels* **2002**, *16*, 809–822.
- (3) Liao, Z.; Zhou, H.; Graciaa, A.; Chrostowska, A.; Creux, P.; Geng, A. *Energy Fuels* **2005**, *19*, 180–186.
- (4) Liao, Z.; Geng, A.; Graciaa, A.; Creux, P.; Chrostowska, A.; Zhang, Y. *Energy Fuels* **2006**, *20*, 1131–1136.
- (5) Groenzin, H.; Mullins, O. C. *J. Phys. Chem. A* **1999**, *103*, 11237–11245.
- (6) Groenzin, H.; Mullins, O. C. *Energy Fuels* **2000**, *14*, 677–684.
- (7) Buenrostro-Gonzalez, E.; Groenzin, H.; Lira-Galeana, C.; Mullins, O. C. *Energy Fuels* **2001**, *15*, 972–978.
- (8) Groenzin, H.; Mullins, O. C.; Eser, S.; Mathews, J.; Yang, M.; Jones, D. *Energy Fuels* **2003**, *17*, 498–503.
- (9) Buch, L.; Groenzin, H.; Buenrostro-Gonzalez, E.; Anderson, S. I.; Lira-Galeana, C.; Mullins, O. C. *Fuel* **2003**, *82*, 1075–1084.
- (10) Badre, S.; Goncalves, C. C.; Norinaga, K.; Gustavson, G.; Mullins, O. C. *Fuel* **2006**, *85*, 1–11.
- (11) Mullins, O. C.; Martinez-Haya, B.; Marshall, A. G. *Energy Fuels* **2008**, *22*, 1765–1773.
- (12) Mullins, O. C. *Energy Fuels* **2009**, *23*, 2845–2854.
- (13) Strausz, O. P.; Safarik, I.; Lown, E. M. *Energy Fuels* **2009**, *23*, 1555–1562.
- (14) Strausz, O. P.; Safarik, I.; Lown, E. M.; Morales-Izquierdo, A. *Energy Fuels* **2008**, *22*, 1156–1166.
- (15) Boek, E. S.; Yakovlev, D. S.; Headen, T. F. *Energy Fuels* **2009**, *23*, 1209–1219.

- (16) Schneider, M. H.; Andrews, A. B.; Mitra-Kirtley, S.; Mullins, O. C. *Energy Fuels* **2007**, *21*, 2875–2882.
- (17) Qian, K.; Edwards, K. E.; Siskin, M.; Olmstead, W. N.; Mennito, A. S.; Dechert, G. J.; Hoosain, N. E. *Energy Fuels* **2007**, *21*, 1042–1047.
- (18) Kang, N.; Hua, I.; Xiao, C. *Ind. Eng. Chem. Res.* **2006**, *45*, 5239–5245.
- (19) Ali, F. A.; Ghaloum, N.; Hauser, A. *Energy Fuels* **2006**, *20*, 231–238.
- (20) Sato, S.; Takanohashi, T.; Tanaka, R. *Energy Fuels* **2005**, *19*, 1991–1994.
- (21) Peramanu, S.; Pruden, B. B. *Ind. Eng. Chem. Res.* **1999**, *38*, 3121–3130.
- (22) Becker, C.; Qian, K.; Russell, D. H. *Anal. Chem.* **2008**, *80*, 8592–8597.
- (23) Pomerantz, A. E.; Hammond, M.; Morrow, A. L.; Mullins, O. C.; Zare, R. N. *J. Am. Chem. Soc.* **2008**, *130*, 7216–7217.
- (24) Hortal, A. R.; Hurtado, P.; Martinez-Haya, B.; Mullins, O. C. *Energy Fuels* **2007**, *21*, 2863–2868.
- (25) Acevedo, S.; Gutierrez, L. B.; Negrin, J. G.; Pereira, J. C.; Mendez, B.; Delolme, F.; Dessalces, V.; Broseta, D. *Energy Fuels* **2005**, *19*, 1548–1560.
- (26) Tanaka, R.; Sato, S.; Takanohashi, T.; Hunt, J.; Winans, R. *Energy Fuels* **2004**, *18*, 1405–1413.
- (27) Photon Technology International (PTI). The measurement asphaltene molecular weight using time-resolved fluorescence depolarization spectroscopy ([http://www.pti-nj.com/LaserStrobe/TechNotes/Asphaltenes\\_ApplicationNote.pdf](http://www.pti-nj.com/LaserStrobe/TechNotes/Asphaltenes_ApplicationNote.pdf)).
- (28) Mojelsky, T. W.; Ignasiak, T. M.; Frakman, Z.; McIntyre, D. D.; Lown, E. M.; Montgomery, D. S.; Strausz, O. P. *Energy Fuels* **1992**, *6*, 83–96.
- (29) Peng, P.; Morales-Izquierdo, A.; Hogg, A.; Strausz, O. P. *Energy Fuels* **1997**, *11*, 1171–1187.
- (30) Strausz, O. P.; Mojelsky, T. W.; Faraji, F.; Lown, E. M.; Peng, P. *Energy Fuels* **1999**, *13*, 207–227.

the aromatic units or between the aromatic and some other pendant structures<sup>28–35</sup> and the length of the polymethylenes can be from C<sub>6</sub> to C<sub>30</sub>. When two aromatic units (for example, the blue chromophore and the red one) in one asphaltene molecule were bridged by one long polymethylene chain, e.g., > C<sub>25</sub> (this was proven true for the asphaltene molecular structure by selective oxidation studies<sup>30–33</sup>), then this molecule can produce two TRFD signals with both very different fluorescence emission wavelengths and very different rotational correlation times. Furthermore, inside the polymethylene groups (even shorter below C<sub>10</sub>), the carbon–carbon bonds are liable to rotate around themselves under the TRFD analysis conditions. The remarkably different PAH units in one asphaltene molecule should produce different signals with both different emission wavelengths and different rotational correlation times and not like those with different emission wavelengths and almost the same rotational correlation time, as illustrated in the document from the PTI website.<sup>27</sup> Therefore, this possibility cannot be precluded by the work from the groups of Mullins, and in fact, these kinds of multiple PAH units present in asphaltene molecules have been proven by some other kinds of work too (see the following discussion).

Recently, Pinkston et al.<sup>36</sup> reported the results from analysis of asphaltenes and asphaltene model compounds by laser-induced acoustic desorption/Fourier transform ion cyclotron resonance mass spectrometry. The authors measured the asphaltenes isolated from a North American crude oil and obtained a MW distribution in the range of 350–1050 Da. However, the authors also stated that the model compounds used in their work fall outside the typical range of asphaltenes, with respect to the comparison of the aromaticity ratio between the model compounds and the petroleum asphaltenes. Moreover, the polymethylene chains as well as ether and sulfide bridges present in asphaltene molecules will badly degrade their analysis results. Then, the authors concluded that additional studies of alkylated model compounds with bridges are required to define their behavior during the analysis procedures from their instrumentation.<sup>36</sup> Therefore, their analysis results concerning the fundamental properties of asphaltenes are still doubtful.

Different kinds of pyrolysis techniques have been extensively applied to study the asphaltenes to obtain the important geochemical information from and to acquire more insights

about the macromolecular structures of asphaltenes.<sup>37–49</sup> The pyrolysis products of asphaltenes can be separated into saturated and aromatic fractions, and typically from the saturated fraction the alkanes, alkylated and cyclic hydrocarbons, such as the biomarkers of steranes and hopanes, can be detected.<sup>46,48</sup> From the aromatic fraction of asphaltene pyrolysates, a whole series of multiple PAH compounds (from 1 to 5 or more rings) are typically detected and some other heteroatom-containing aromatic compounds, such as dibenzothiophene, are readily detected too. Among the multiple PAH compounds from asphaltene pyrolysates, the smaller ones cannot be derived from the bigger ones because under the pyrolysis conditions the carbon–carbon bond inside the aromatic rings cannot be broken up. Because more rigorous conditions than pyrolysis are needed to split the aromatic rings, these different PAH molecules should be derived from the different aromatic units inside asphaltene molecules. Therefore, the asphaltene molecule should be characterized by containing multiple aromatic cores.

Figure 1 shows the distribution of aromatic compounds from the asphaltene pyrolysates of a Venezuelan crude oil. Prior to pyrolysis, the asphaltenes prepared from the crude oil by *n*-heptane precipitation were Soxhlet-extracted by acetone for 240 h to rule out the interferences from the adsorbed or co-precipitated compounds. Thus, ~60 mg of acetone-extracted asphaltenes were put into a glass tube (about 20 mm in diameter and 100 mm in height, with a narrower neck). This tube was then sealed under a flame, and air was extracted from the tube under a vacuum and then put into an oven for pyrolysis at 350 °C for 72 h. More details of the pyrolysis experiment have been reported in one earlier work.<sup>41</sup> The pyrolysis results of asphaltenes clearly indicated that multiple PAH units were produced from asphaltene macromolecular structures (Figure 1), and some bigger PAH compounds of more than 5 rings may have been produced from asphaltene pyrolysis too but which cannot be properly detected by gas chromatography–mass spectrometry (GC–MS) analysis. Once again, the smaller PAH compounds in Figure 1 cannot be produced from the bigger ones. With respect to the fact that all of these aromatic molecules can be readily detected directly from the crude oil maltenes, these kinds of pyrolysates have been extensively applied to obtain the geochemical information of the corresponding crude oils, which can be considered as the simulated petroleum fluids derived from oil reservoirs. Therefore, the pyrolysis results suggested that multiple PAH units are not the only ones present inside the macromolecular structures of asphaltenes.

With respect to the geochemical origin of petroleum fluids, asphaltenes can be considered as the soluble fraction of kerogens in crude oils, and then the molecular structures of asphaltenes are comparable to their precursor, the kerogens.<sup>50</sup>

(31) Strausz, O. P.; Mojelsky, T. W.; Lown, E. M.; Kowalewski, I.; Behar, F. *Energy Fuels* **1999**, *13*, 228–247.

(32) Peng, P.; Morales-Izquierdo, A.; Lown, E. M.; Strausz, O. P. *Energy Fuels* **1999**, *13*, 248–265.

(33) Peng, P.; Fu, J.; Sheng, G.; Morales-Izquierdo, A.; Lown, E. M.; Strausz, O. P. *Energy Fuels* **1999**, *13*, 266–277.

(34) Murgich, J.; Abanero, J. A.; Strausz, O. P. *Energy Fuels* **1999**, *13*, 278–286.

(35) Artok, L.; Su, Y.; Hirose, Y.; Hosokawa, M.; Murata, S.; Nomura, M. *Energy Fuels* **1999**, *13*, 287–296.

(36) Pinkston, D. S.; Duan, P.; Gallardo, V. A.; Habicht, S. C.; Tan, X.; Qian, K.; Gray, M.; Müllen, K.; Kenttämä, H. *Energy Fuels* **2009**, *23*, 5564–5570.

(37) Myhr, M.; Schou, L.; Skjetne, T.; Krane, J. *Org. Geochem.* **1990**, *16*, 931–941.

(38) Eglinton, T. I.; Larter, S. R.; Boon, J. J. *J. Anal. Appl. Pyrolysis* **1991**, *20*, 25–45.

(39) Calemme, V.; Rausa, R. *J. Anal. Appl. Pyrolysis* **1997**, *40–41*, 569–584.

(40) Geng, A.; Liao, Z. *Appl. Geochem.* **2002**, *17*, 1529–1541.

(41) Liao, Z.; Geng, A.; Gracia, A.; Creux, P.; Chrostowska, A.; Zhang, Y. *Org. Geochem.* **2006**, *37*, 291–303.

(42) Lehne, E.; Dieckmann, V. *Org. Geochem.* **2007**, *38*, 1657–1679.

(43) Galarraga, F.; Marquez, G.; Reategui, K.; Martinez, A. *J. Anal. Appl. Pyrolysis* **2007**, *80*, 289–296.

(44) Behar, F.; Lorant, F.; Lewan, M. *Org. Geochem.* **2008**, *39*, 1–22.

(45) Saydut, A.; Duz, M.; Tonbul, Y.; Baysal, A.; Hamamci, C. *J. Anal. Appl. Pyrolysis* **2008**, *81*, 95–99.

(46) Meredith, W.; Snape, C. E.; Carr, A. D.; Hans, P.; Nytoft, H. P.; Love, G. D. *Org. Geochem.* **2008**, *39*, 1243–1248.

(47) Liao, Y.; Geng, A.; Huang, H. *Org. Geochem.* **2009**, *40*, 312–320.

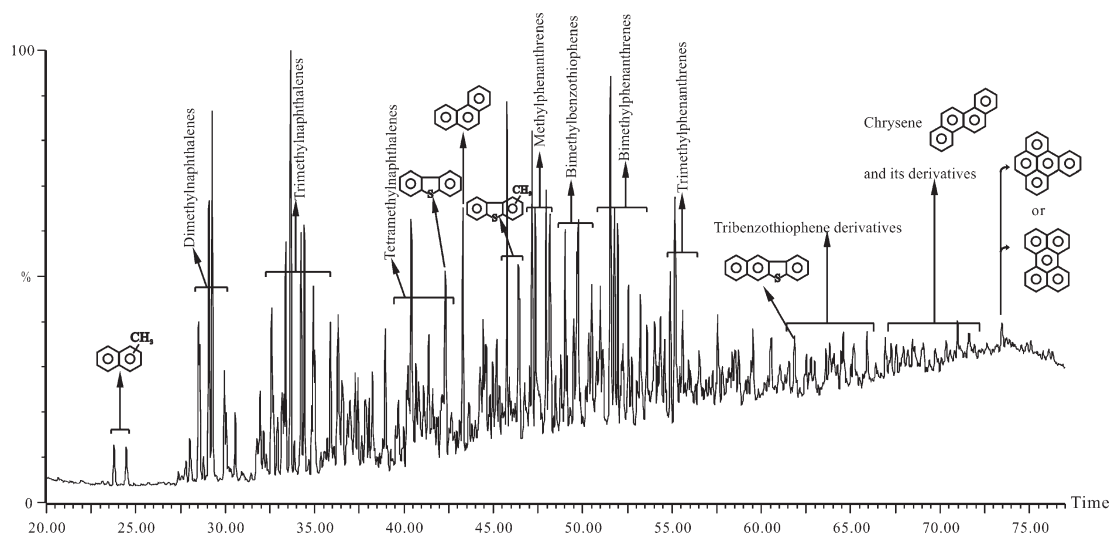
(48) Stojanovic, K.; Jovancicevic, B.; Sajnovic, A.; Sabo, T.; Vitorovic, D.; Schwarzbauer, J.; Golovko, A. *Fuel* **2009**, *88*, 287–296.

(49) Lehne, E.; Dieckmann, V.; di Primio, R.; Fuhrmann, A.; Horsfield, B. *Org. Geochem.* **2009**, *40*, 604–616.

(50) Tissot, B. P.; Welte, D. H. *Petroleum Formation and Occurrence*; Springer-Verlag: New York, 1978.

(51) Barakat, A. O. *Energy Fuels* **1993**, *7*, 988–993.

(52) Hutton, A.; Bharati, S.; Robl, T. *Energy Fuels* **1994**, *8*, 1478–1488.



**Figure 1.** Distribution of aromatic hydrocarbons from the pyrolysis products of asphaltenes isolated from a Venezuelan crude oil.

The kerogen molecules typically possess on average 2–5-ring PAH units that are highly substituted,<sup>51–53</sup> and during thermal maturation, kerogen is transformed from a macromolecule characterized by a significant aliphatic component to one containing shorter chains dominated by more condensed PAH structures.<sup>54–57</sup> From their basic geochemical origin, it can be concluded that asphaltenes should contain multiple PAH units inside their molecules, which is consistent with the PAH distribution produced from their pyrolysis.

(53) Kelemen, S. R.; Afeworki, M.; Gorbaty, M. L.; Sansone, M.; Kwiatek, P. J.; Walters, C. C.; Freund, H.; Siskin, M.; Bence, A. E.; Curry, D. J.; Solum, M.; Pugmire, R. J.; Vandenbroucke, M.; Leblond, M.; Behar, F. *Energy Fuels* **2007**, *21*, 1548–1561.

(54) Requejo, A. G.; Gray, N. R.; Freund, H.; Thomann, H.; Melchior, M. T.; Gebhard, L. A.; Bernardo, M.; Pictroski, C. F.; Hsu, C. S. *Energy Fuels* **1992**, *6*, 203–214.

According to the above discussion, asphaltenes are complex mixtures of a wide range of compounds, with an average MW that is difficult to define. There are multiple PAH units containing 2–5 or more rings inside asphaltene molecules and not only 1, as concluded by the work from the research group of Mullins.

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(55) Tang, Y.; Behar, F. *Energy Fuels* **1995**, *9*, 507–512.

(56) Larsen, J. W.; Li, S. *Energy Fuels* **1997**, *11*, 897–901.

(57) Wei, Z.; Gao, X.; Zhang, D.; Da, J. *Energy Fuels* **2005**, *19*, 240–250.